energies

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Chemical Elements Content and Distributions within Different Tissue Types of White Spruce

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Abstract: The relative proportions of different chemical components in wood tissues is one of the underlying factors that control wood properties. These proportions vary within and between woody tissues, and an accurate description of these variations is critical for parameterizing forest biogeochemical budgets and models. White spruce (*Picea glauca* (Moench) Voss) spacing intensities trials in the Petawawa Research Forest, Ontario, Canada, were sampled to evaluate variations in carbon (C), nitrogen (N), and hydrogen (H) concentrations between different tissue types, i.e., bark, cambium, knots, earlywood, latewood, and wood. Samples were freeze-dried and oven-dried to test the impact of the drying methods on these chemical elements. Freeze-dried C (51.14) and H (6.18) concentrations were significantly higher than those of oven-dried C (50.55) and H (6.06). Freeze-dried N (0.18) did not differ from oven-dried N (0.17). The spacing intensities impacted C, H, and N, with C content being higher in wider square spacings (4.3 m and 6.1 m), while the reverse was true for N and H, which exhibited higher content in smaller square spacings (1.2 m and 1.8 m). The results of this study also suggested that when it comes to the content of chemical elements, bark and knots should be treated as separate fuel types, whereas other woody tissues can be aggregated.

Keywords: carbon content; hydrogen content; nitrogen content; volatile carbon; white spruce; stand density management; wood biomass; bioenergy; wood drying methodologies; ultimate analyses

Citation: Mvolo, C.S.; Boakye, E.A.; Koubaa, A. Chemical Elements Content and Distributions within Different Tissue Types of White Spruce. *Energies* **2023**, *16*, 3257. https://doi.org/10.3390/en16073257

Academic Editors: Dimitrios Sidiras and Robert H. Beach

Received: 3 February 2023
Revised: 17 March 2023
Accepted: 1 April 2023
Published: 5 April 2023

1. Introduction

Wood biomass is one of the most important renewable sources for bioenergy production [1]. This is because all tree parts, including the canopy, branches, and bark, can be used to generate energy. Through valorization, biomass materials can be processed and used for industrial applications, forest management, and environmental resource enhancements [2]. Tree growth benefits bioenergy production, as trees convert solar energy and atmospheric carbon dioxide into biomass.

The cambium cell layer is the growing part of the tree's trunk. It annually produces new bark and wood in response to hormones that pass down through the phloem with nutrients from the leaves. These hormones stimulate cell growth, especially indole-3-acetic acid (IAA, auxin). Responsible for most of the diametral (additive or periclinal division) and circumferential (multiplicative or anticlinal division) growth of trees, the vascular cambium is a functionally uniseriate layer [3] located between the xylem and the phloem of stems, branches, and roots. Together with the xylem and phloem mother cells, it produces xylem inwardly and phloem outwardly [4]. Growth properties of spruces in the boreal forest change within a single tree ring, from earlywood to latewood [5]. The earlywood zone is produced under the strong influence of growth hormones, especially auxins, at the beginning of the growing season when newly formed buds are actively elongating. Earlywood production proceeds downward towards the tree [6,7]. Latewood production, which coincides with the cessation of shoot elongation, proceeds upward toward the crown and has thicker cell walls due to greater photosynthate availability [6,7]. Knots are the bases of tree branches embedded into the trunk. Because branches are abundant, knots are the most commonly encountered defects, affecting mostly mechanical properties but also wood machining, finishing, and gluing [8]. Due to the high percentage of reaction wood, knotwood is chemically and anatomically different from normal wood [9]. The bark is a much more complex tissue system than the wood and includes all the tissues outside the vascular cambium [4]. The bark's phloem plays an essential role in nutrient translocation. At the same time, its periderm, composed of three layers (i.e., phellem, phellogen, and phelloderm), reduces water loss and protects from mechanical injuries [4].

The underlying factors controlling wood properties are essentially the results of its chemical composition at three levels: 1—features of the structural components of the cell wall (cellulose, hemicelluloses, and lignins) and the molecules contained within the cellular structure (extractives); 2—distribution of the structural component; and 3—relative proportions of the different chemical components in the wood tissues [9]. As for the third factor, normal wood is simplified as having an elemental composition of 50% carbon (C), 44% oxygen (O), and 6% hydrogen (H) [10]. The ultimate analysis of spruce wood was found to be 51.9% carbon, 40.9% oxygen, 6.1% hydrogen, and 0.3% nitrogen (N) [11]. Focusing on spruces, in addition to these elements, Young et al. [12] found that red spruce (*Picea rubens* Sarg.) also have Ca, K, Mn, Mg, and P (in parts per thousand) and Fe, Zn, and Cu (in parts per million).

Forest carbon accounting is now a global priority as countries work to tackle climate change [13]. With the implementation of carbon taxes and credits, concerns about the accuracy of data regarding carbon content (or concentration, or fraction) are increasing [14]. A significant contributor to inaccuracy is the assumption that carbon makes up 50% of the above-ground biomass of a tree (AGB). Therefore, the accurate description of variations in carbon content (CC) should be considered, given the fact that the chemical element content differs by tree species [15–22], tree tissues [15,16,20,22–27], trees age [28], sampling height [28], and growing condition (including sylvicultural management) [24,28–30], to refine forests' carbon stocks estimation. N concentration was found to vary from bark to pith of a tree species [31] and more among woody tissues than C concentration [20,27]. Therefore, these concerns hold for all wood chemical elements, including N and H, as quantifying their variation is critical for parameterizing forest biogeochemical budgets and models [20].

Tree carbon is predominantly made of stem wood carbon, larger than the carbon stored in roots [25,32] or foliage, branches, and bark [25,26,32]. Kraenzel, Castillo, Moore, and Potvin [25] determined that 86.9% of the carbon in *Tectona grandis* was stored in shoots, while 13.1% was in roots. Furthermore, woody tissues (trunk, branches, twigs, and coarse roots) had a significantly greater carbon concentration at 49.2%, when compared to soft tissues (leaves, flowers, and fine roots) at 46.4%. The bark is known to have higher proportions of carbon and nitrogen than the previously mentioned tissues and was even discarded from other woody tissues when compiling a general model describing the chemical content of trees [20]. Therefore, the more measurements obtained for stem wood CC in different tissues and conditions, the better the overall forest CC estimates [20].

The major elements contributing to the calorific value of wood are carbon, hydrogen, and nitrogen (along with oxygen and sulphur), which can either be determined directly through ultimate analyses or predicted from the proximate analysis [1,33]. The thermochemical conversion of wood requires knowledge of its calorific value, which is a measure of the energy chemically stored in the biomass that can be transformed into usable energy [1]. In its simplest form, burning biomass fuels can be considered as the combustion of only carbon and hydrogen [34], with the calorific value increasing with the proportion of C+H [35]. In this simplistic case, and considering a 100% efficiency, all C is oxidized into carbon dioxide, and all H is oxidized into water [34]. However, complete efficiency is only theoretical, and volatile gases, called hydrocarbons, are produced from C and H incomplete combustion [34]. The N concentration is also highly important, as it determines NOx emissions during combustion [33]. Leckner and Karlsson [36] demonstrated that nitrogen oxide emission is directly related to the nitrogen content of the wood. Therefore, biomass with a lower amount of N is better for reduced NOx emissions.

The conventional oven-drying (OD) technique usually requires two stages: transferring water from the inside (high humidity) to the exterior (low humidity) and eliminating water from the outside (evaporation) [37]. The lyophilization or freeze-drying (FD) process consists of three steps: initial freezing, which crystallizes the free water; primary drying, which eliminates solid water via sublimation; and secondary drying, which removes the majority of the remaining moisture through desorption of the adsorbed water [38]. The drying process alters CC in woody material, with oven-drying resulting in less CC than freeze-drying [24,28].

White spruce has a wide niche in pure and mixed stands in boreal forests [39]. The species' geographical range is vast, from Newfoundland in the east to northwestern Alaska and from the northern treeline to British Columbia and Alberta, following the southern boreal boundary from Minnesota to Maine [40]. Therefore, accurately estimating the chemical attributes of white spruce would be beneficial in refining the Carbon Budget Model of the Canadian Forest Sector (CBM-CFS3), aiding similar models in the United States and reducing risk for wood-based biomaterial industries on both sides of the border.

Basic characterization data are available for wood, but differences across woody tissue types have surprisingly received little attention for C and even less for N and H [20]. The influence of thinning on CC has recently been assessed [28]. However, we are unaware of any study assessing the impact of spacing intensities on the elemental composition of white spruce. Similarly, the impact of oven-drying and freeze-drying on wood chemical properties is known for CC [24,28,41,42]. Yet, it is unknown whether there has been any study assessing the impact of drying processes on other chemical elements in wood. The main objective of this study was to examine the variation of chemical elements (carbon, hydrogen, and nitrogen) in different tree tissues (bark, cambium, wood, earlywood, latewood, and knot) of white spruce, as well as the impact of stand density management (spacing intensities) on their selected chemical elements, while also comparing freeze-drying and oven-drying. The radial and longitudinal variation in woody tissue and the relation between chemical compounds were also explored.

2. Materials and Methods

2.1. Stand Description

This study used materials from an initial spacing experiment conducted in the Petawawa Research Forest, established in 1967 in Ontario, Canada. Four spacing treatments were chosen: 1.2 m, 1.8 m, 4.3 m, and 6.1 m. Four healthy trees were randomly selected from each treatment, felled, and pruned in July 2008 [43].

2.2. Sample Collection and Preparation

The collected material was stored in a warehouse at the Université du Québec en Abibiti-Témiscamingue (UQAT). In 2018, these wood disks were transferred to the Natural Resources Canada–Northern Forestry Centre (NoFC). Each disk had a bark-to-bark sample batten cut with pith at the center, with a random sampling direction. Battens were visually checked to avoid compression wood, knots, and piths. They were segmented into three-ring samples from rings 1 to 15 and five-ring samples from rings 16 to 35. Samples were labeled according to their highest ring number (oldest cambial age), with the boundary between growth rings determined by visual inspection.

The discs were sanded before being cut into battens to reveal a non-oxidized surface [41], minimizing air drying effects on carbon loss. Battens' sections were scraped with a surgical scalpel and reduced to half-matchstick dimensions. These wood sticks were sealed in plastic bags and stored in a freezer before being ground with a Wiley Mill (No. 20 Mesh). Each sample was split into 2 drying treatments. Half were oven-dried (Thermo

Scientific, Lindberg/Blue M, Model# MO1450A-1, Asheville, NC, USA, [44]) at 70 °C for 3 days, and the other half was freeze-dried at −50 °C for 7 days using an 8 L freeze-drying system (Labconco Co., Kansas City, MO, USA, [45]). The trees from the widest spacing, with the highest growth rate (i.e., widest ring width), were used to sample earlywood and latewood (visually determined). Knots were collected wherever available on the discs, and the cambium was shaved with a surgical scalpel on the discs after collecting the bark. A total of 292 samples (half freeze-dried and half oven-dried, i.e., 144 wood, 54 bark, 40 knots, 26 cambium, 14 earlywood, and 14 latewood) were used for the final analyses.

2.3. Chemical Analysis

Dried samples were analyzed using the LECO Truspec Micro CHNS Analyser (LECO Instruments ULC, Mississauga, ON, Canada) [46], calibrated with a certified EDTA standard. Quality assurance was achieved using certified reference materials, with checks every 20 samples. Volatile mass fraction (VMF) and volatile carbon concentration (Cvol) were computed following the equation described in Gao, Taylor, Chen, and Wang [24].

2.4. Statistical Analyses

We provide descriptive statistics on the chemical composition of white spruce and how it varies across different tissue types (i.e., bark, cambium, earlywood, knot, latewood, and wood (or ringwood, i.e., combined earlywood and latewood)) using measures of central tendency (i.e., mean) and variability (e.g., standard deviation, minimum and maximum). To ensure that the sample data came from a normally distributed population, we used the Shapiro–Wilk test to check for normality. The data were not normally distributed ($p < 0.05$) and thus did not meet the parametric test assumptions. We used the non-parametric Kruskal–Wallis test with Wilcoxon's post hoc test for pairwise comparison to ascertain if the differences in spruce chemical composition between tissue types and silvicultural treatments were significant. Spearman's rank correlation was also used to summarize the strength and direction (negative or positive) of a relationship between tree age or height and chemical content in the cambium, bark, and wood (or ringwood). For all tests, we used a significance level of $p < 0.05$. The statistical analyses were performed using R statistical software [47].

3. Results

3.1. Chemical Content of the White Spruce Tree

The chemical composition of the spruce trees has been summarized in Table 1. The freeze-dried carbon, nitrogen, and hydrogen contents were higher than the same elements' oven-dried values (Table 1). A Wilcoxon signed-ranks test (W) indicated that the difference between the freeze-dried and oven-dried carbon (W = 14,238, $p < 0.001$) and between freeze-dried and oven-dried hydrogen (W = 14,016, $p < 0.001$) was statistically significant. However, the difference between the freeze-dried and oven-dried nitrogen was not significant (W = 113,48, $p = 0.34$).

Figure 1 shows a strong correlation with different pairs of the elemental chemical composition of the tree tissues. The strongest significant positive correlation was recorded between oven-dried nitrogen (ODN) and freeze-dried nitrogen (FDN) and the least between freeze-dried carbon (FDC) and freeze-dried hydrogen (FDH). Similarly, the strongest significant negative correlation was recorded between oven-dried carbon (ODC) and volatile carbon (Cvol) and the least between FDC and FDN.

3.2. Variation of the Chemical Composition of White Spruce Trees with Tissue Types

The chemical composition of white spruce varied significantly across the trees' tissues (Figure 2, Table 2). The knot contained the most FDC, followed by the bark, and then, in decreasing order, wood (or ringwood, i.e., combined earlywood and latewood), earlywood, latewood, and cambium. A similar result was observed for the ODC, and in this case, the content was highest in the knot, followed by the bark and then by wood, cambium, earlywood, and latewood in decreasing order.

Table 1. Summary of chemical characteristics of spaced spruce trees.

	FDC	FDN	FDH	ODC	ODN	ODH	VMF	Cvol
				Part 1—overall means				
Mean	51.14	0.18	6.18	50.55	0.17	6.06	0.02	1.88
SD	1.46	0.21	0.25	1.62	0.21	0.21	0.03	1.81
Max	54.80	0.73	6.83	54.20	0.73	6.43	0.18	10.30
Min	46.10	0.01	5.58	41.10	0.01	5.04	0.00	0.01
Median	51.10	0.07	6.17	50.60	0.06	6.11	0.01	1.35
				Part 2—means by spacing				
1.2 m	50.79(1.32)	0.23(0.23)	6.16(0.30)	50.08(0.65)	0.22(0.24)	6.02(0.19)	0.03(0.04)	2.44(1.79)
1.8 m	50.40(1.20)	0.20(0.23)	6.11(0.17)	50.23(0.67)	0.22(0.23)	6.10(0.17)	0.03(0.03)	1.84(1.39)
4.3 m	51.16(1.15)	0.21(0.22)	6.11(0.18)	50.77(0.73)	0.19(0.19)	6.08(0.17)	0.02(0.02)	1.64(1.35)
6.1 m	51.15(1.35)	0.22(0.27)	6.03(0.17)	51.23(0.96)	0.19(0.23)	6.04(0.16)	0.02(0.03)	0.99(1.31)

FDC: freeze-dried carbon, FDN: freeze-dried nitrogen, FDH: freeze-dried hydrogen, ODC: oven-dried carbon, ODN: oven-dried nitrogen, ODH: oven-dried hydrogen, VMF: volatile mass fraction, Cvol: volatile carbon, SD: standard deviation, Max: maximum, and Min: minimum.

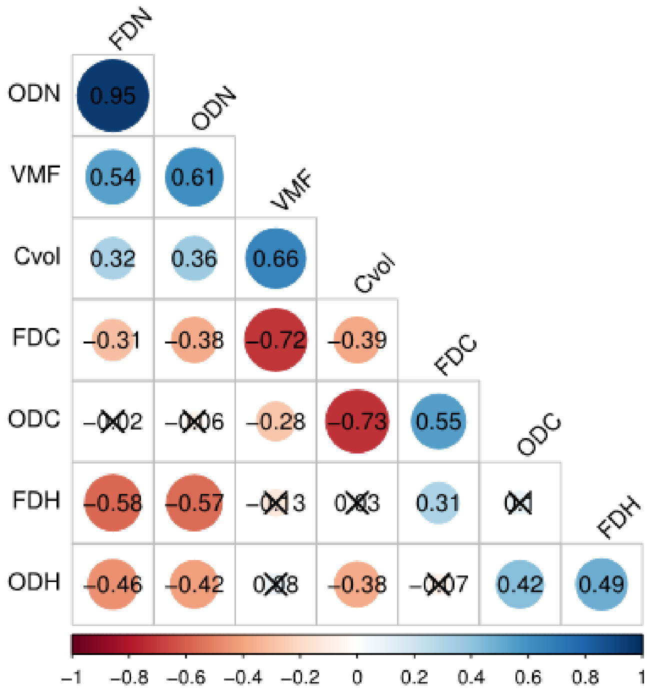

Figure 1. Correlation matrix between chemical elements in white spruce tissues. Insignificant ($p > 0.05$) correlations are marked by crosses. FDC: freeze-dried carbon, FDN: freeze-dried nitrogen, FDH: freeze-dried hydrogen, ODC: oven-dried carbon, ODN: oven-dried nitrogen, ODH: oven-dried hydrogen, VMF: volatile mass fraction, and Cvol: volatile carbon.

The content of FDN in the bark was highest, followed by the cambium and further in order of decreasing trend by earlywood, latewood, and equally by knot and wood. On the other hand, the content of ODN in the cambium was highest, followed by the bark and further in order of decreasing trend by earlywood, latewood, wood, and knot.

The content of FDH in the knot was highest, followed by the latewood and earlywood, and further in order of decreasing trend by wood, cambium, and bark. However, the content of ODH was equally higher in the cambium and knot, followed by the wood, and further in order of decreasing trend by earlywood, latewood, and bark.

The content of VMF was highest in the bark and latewood, followed equally by the cambium, earlywood, latewood, knot, and wood. On the other hand, the content of Cvol was highest in the cambium, followed by the latewood, earlywood, bark, wood, and knot.

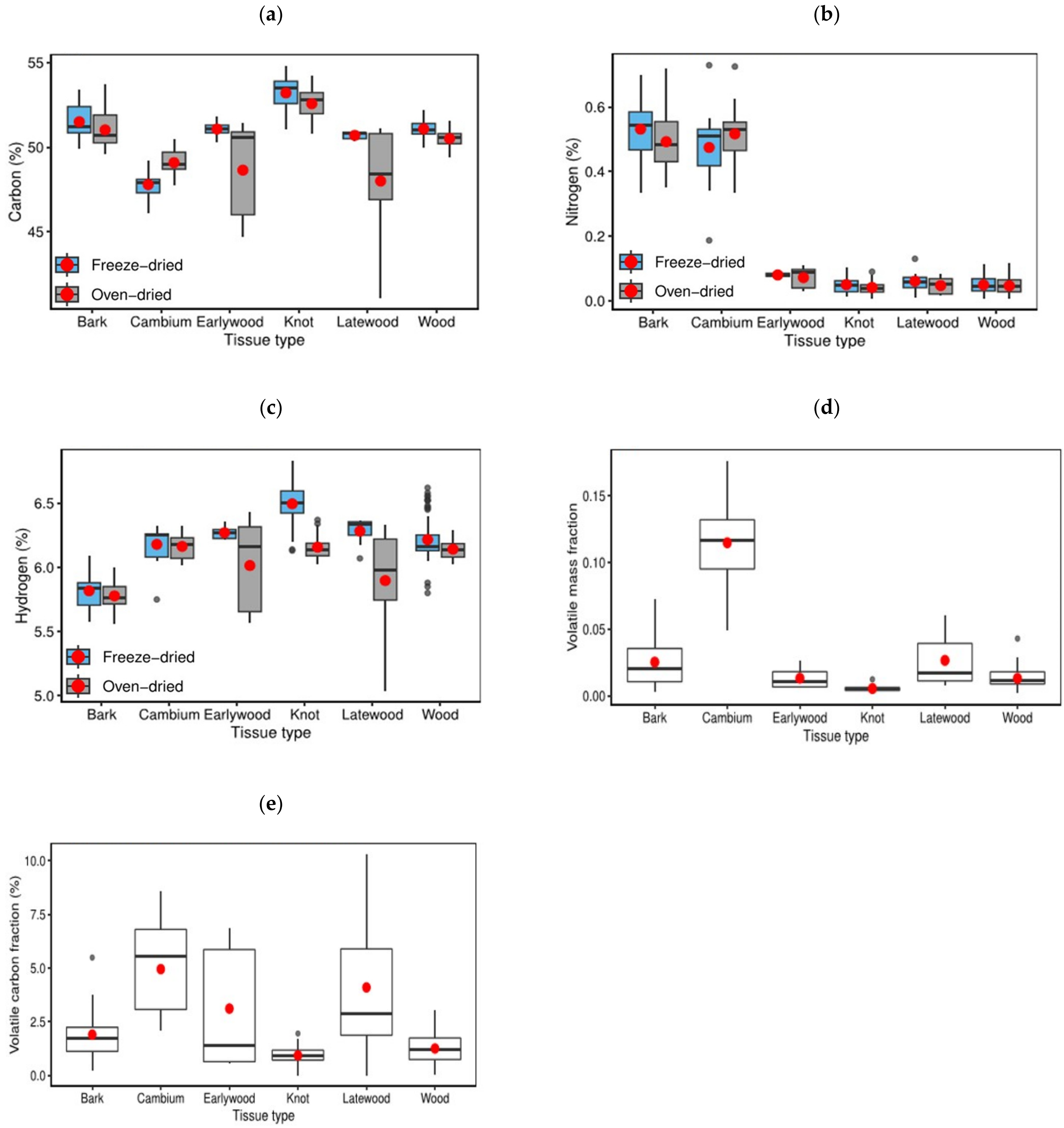

Figure 2. Box plot showing the chemical composition in different tissues of white spruce. In the plots, (**a**) denotes carbon, (**b**) nitrogen, (**c**) hydrogen, (**d**) volatile mass fraction and (**e**) volatile carbon fraction. Each plot's upper and lower parts are the maximum and minimum values, respectively. The median is represented by a horizontal black bar. The red dots indicate the mean value.

3.3. Silvicultural Treatments' Effects on Spruce Tree Chemical Composition in Different Tissues

The FDC content (all tissues pooled together) was highest in the spacing of 4.3 m and 6.1 m, followed by 1.2 m and the lowest in 1.8 m (Table 1). ODC was highest in 6.1 m spacing, then 4.3 m, 1.8 m, and lastly in 1.2 m. FDN showed its highest content in 1.2 m, then 6.1 m, 4.3 m, and lowest in 1.8 m. ODN and FDH were higher in the spacing of 1.2 m and 1.8 m, followed by 4.3 m and 6.1 m. ODH had its highest content in 1.8 m and 4.3 m, followed by 1.2 m and 6.1 m. VMF was similar in the four spacing treatments. Lastly, the highest content of Cvol was at 1.2 m, followed by 1.8 m, 4.3 m, and 6.1 m.

Table 2. Pairwise comparison of chemical content between tissues using Wilcoxon's post hoc test.

	Bark	Cambium	Earlywood	Knot	Latewood
			FDC		
Cambium	0.00 *				
Earlywood	0.42	0.00 *			
Knot	0.00 *	0.00 *	0.00 *		
Latewood	0.03 *	0.00 *	0.12	0.00 *	
Wood	0.09	0.00 *	0.89	0.00 *	0.03 *
			FDN		
Cambium	0.17				
Earlywood	0.00 *	0.00 *			
Knot	0.00 *	0.00 *	0.01 *		
Latewood	0.00 *	0.00 *	0.17	0.64	
Wood	0.00 *	0.00 *	0.00 *	0.95	0.53
			FDH		
Cambium	0.00 *				
Earlywood	0.00 *	0.27			
Knot	0.00 *	0.00 *	0.01 *		
Latewood	0.00 *	0.06	0.51	0.01 *	
Wood	0.00 *	0.76	0.06	0.00 *	0.18
			ODC		
Cambium	0.00 *				
Earlywood	0.24	0.76			
Knot	0.00 *	0.00 *	0.00 *		
Latewood	0.07	0.81	0.81	0.00 *	
Wood	0.13	0.00 *	0.76	0.00 *	0.19
			ODN		
Cambium	0.59				
Earlywood	0.00 *	0.00 *			
Knot	0.00 *	0.00 *	0.06		
Latewood	0.00 *	0.00 *	0.17	0.74	
Wood	0.00 *	0.00 *	0.08	0.59	0.91
			ODH		
Cambium	0.00 *				
Earlywood	0.65	0.97			
Knot	0.00 *	0.97	0.97		
Latewood	0.57	0.65	0.97	0.65	
Wood	0.00 *	0.88	0.97	0.97	0.65
			VMF		
Cambium	0.00 *				
Earlywood	0.14	0.00 *			
Knot	0.00 *	0.00 *	0.00 *		
Latewood	0.96	0.00 *	0.15	0.00 *	
Wood	0.00 *	0.00 *	0.84	0.00 *	0.09
			Cvol		
Cambium	0.00 *				
Earlywood	0.95	0.20			
Knot	0.00 *	0.00 *	0.34		
Latewood	0.18	0.34	0.66	0.02 *	
Wood	0.01 *	0.00 *	0.37	0.19	0.03 *

FDC: freeze-dried carbon, FDN: freeze-dried nitrogen, FDH: freeze-dried hydrogen, ODC: oven-dried carbon, ODN: oven-dried nitrogen, ODH: oven-dried hydrogen, VMF: volatile mass fraction, and Cvol: volatile carbon. The values in the table represent probability levels at 0.05 significance level (*).

The silvicultural treatments affected the chemical compositions of white spruce (Table 3). To this end, the Kruskal–Wallis H test showed that there was a statistically significant difference in the content of FDC (Z = 20.15, p = 0.00), ODC (Z = 28.43, p = 0.00), FDH (Z = 13.95, p = 0.00), ODH (Z = 12.68, p = 0.01), ODN (Z = 16.87, p = 0.00), VMF (Z = 16.11, p = 0.00), and Cvol (Z = 37.81, p = 0.00) in white spruce trees. Nevertheless, there was no statistically significant difference (Z = 0.62, p = 0.08) in FDN content between different treatments.

Table 3. Pairwise comparison of silvicultural treatments (spacing) on the chemical composition in white spruce using Wilcoxon's post hoc test.

Spacing	1.2 m	1.8 m	4.3 m
		FDC	
1.8 m	0.00 *		
4.3 m	0.04 *	0.33	
6.1 m	0.00 *	0.39	0.50
		FDH	
1.8 m	0.09		
4.3 m	0.31	0.63	
6.1 m	0.01 *	0.02 *	0.01 *
		ODC	
1.8 m	0.17		
4.3 m	0.01 *	0.19	
6.1 m	0.00 *	0.00 *	0.01 *
		ODN	
1.8 m	0.01 *		
4.3 m	0.01 *	0.21	
6.1 m	0.02 *	0.47	0.11
		ODH	
1.8 m	0.13		
4.3 m	0.29	0.89	
6.1 m	0.06	0.01 *	0.06
		VMF	
1.8 m	0.05 *		
4.3 m	0.92	0.08	
6.1 m	0.16	0.00 *	0.42
		Cvol	
1.8 m	0.01 *		
4.3 m	0.01 *	0.19	
6.1 m	0.00 *	0.00 *	0.02 *

FDC: freeze-dried carbon, FDN: freeze-dried nitrogen, FDH: freeze-dried hydrogen, ODC: oven-dried carbon, ODN: oven-dried nitrogen, ODH: oven-dried hydrogen, VMF: volatile mass fraction, and Cvol: volatile carbon. The values in the table represent probability levels at 0.05 significance level (*).

3.4. Relationship between Tree Age and Height on the Chemical Composition of Spruce Trees in Different Tissues

We observed a considerable association between tissue chemical composition, tree height, and age. Spearman's rank correlation showed a significant correlation between tree height and FDC and ODH in the bark tissue (Table 4). The relationship between the tree height and the other variables (Table 4) in the bark tissue was not significant. In the case of the cambium, Spearman's rank correlation showed a significant correlation between tree height and ODH (Table 4) but not between the height and the other variables. In the wood tissue (Table 4), Spearman's rank correlation was significant between tree height and FDC, ODN, and Cvol. Nevertheless, the relationship between the tree height and the other variables in the wood was not significant (Table 4). We also explored the relationship between tree age and the chemical composition of wood. The Spearman's rank correlation showed a significant correlation between FDN, ODH, VMF, and Cvol and age, but not with the other variables (FDC, FDH, and ODN) (Table 4).

Table 4. Spearman-rank correlation between bark/tissue and tree height and age.

	Height							
	FDC	FDN	FDH	ODC	ODN	ODH	VMF	Cvol
	Bark							
rho	−0.41	−0.03	−0.29	−0.29	0.15	−0.38	−0.17	−0.09
p-value	0.03 *	0.88	0.14	0.14	0.46	0.05 *	0.38	0.66
S	4611.5	3375.1	4217.5	4234.3	2795.2	4527.5	3845.6	3184.6
	Cambium							
rho	0.19	0.01	0.04	−0.22	−0.25	−0.74	0.26	0.38
p-value	0.53	0.96	0.89	0.48	0.41	0.01 *	0.39	0.19
S	293.8	359.66	348.72	442.36	453.66	632.1	269.44	225.07
	Wood							
rho	0.41	−0.13	0.10	−0.19	−0.47	−0.23	−0.18	0.26
p-value	0.001 *	0.28	0.39	0.11	0.001 *	0.06	0.12	0.03 *
S	36,411	70,162	55,808	74,113	91,606	76,316	73,558	46,003
	Age							
	FDC	FDN	FDH	ODC	ODN	ODH	VMF	Cvol
	Wood							
rho	−0.07	−0.42	0.05	−0.22	0.08	−0.23	0.40	0.25
p-value	0.57	0.00 *	0.65	0.06	0.48	0.05 *	0.00 *	0.03 *
S	66,395	88,268	58,796	76,119	57,025	76,553	37,020	46,555

FDC: freeze-dried carbon, FDN: freeze-dried nitrogen, FDH: freeze-dried hydrogen, ODC: ov-en-dried carbon, ODN: oven-dried nitrogen, ODH: oven-dried hydrogen, VMF: volatile mass frac-tion, and Cvol: volatile carbon. The significance level is $p < 0.05$ (*).

4. Discussion

4.1. Content of C, H, and N in White Spruce and Impact of Drying Method

The impact of oven-drying on wood chemical properties is well known for C, with freeze-dried material having a significantly higher C fraction than oven-dried material [24,28,41,42]. The significantly higher H fraction found in this study for freeze-dried material than oven-dried material suggests that oven-drying also negatively impacted this element. Freeze-drying is known to preserve the chemical composition of wood [48] and temperature-sensitive products (such as volatile compounds). It has therefore been established as the drying method of choice for many bio-industrial applications [49,50]. The higher loss in both C and H with the oven-drying process may be attributed to the hydrolysis of the acetyl groups of hemicelluloses with increasing temperature, which causes a decrease in the degree of carbonyl [48]. Although not statistically significant, it is worth noting that oven-drying also had a negative impact on the N fraction. The lack of significant difference in the N content with the two drying processes may be attributed to wood extractives being quickly removed through evaporation (OD) and sublimation (FD).

The white spruce FDC (51.14), ODC (50.55), and Cvol (1.88) of this study are close to values recently measured in a white spruce thinning experiment [28], despite C data in this study were pooled among many tissue types (including bark). In contrast, Mvolo, Stewart, Helmeste, and Koubaa [28] only measured stemwood. Although we sampled white spruce in the boreal forest, these close values confirm earlier findings by Martin, Gezahegn, and Thomas [20], suggesting that except for bark, wood chemical trait values derived from stemwood can be used to accurately represent whole-tree trait values in models of forest C and N stocks and fluxes for temperate species. The 1.88% volatile carbon fraction found in this study (pooled for all tissues) is higher than the 1.4% reported by Gao, Taylor, Chen, and Wang [24] on smaller trees and lower than the 2.7% reported by Mvolo, Stewart, Helmeste, and Koubaa [28] on bigger trees. It confirms that the volatile carbon fraction increases with the size of the tree. This may be because total carbon also increases with trees' size. Additionally, the volatile carbon is a significant part of forest tree carbon that should be included in carbon accounting [24,28,41,42].

Both the FDN (0.18) and the ODN (0.17) in this study are comparable to the 0.14 found by Merrill and Cowling [31] for Norway spruce (*Picea abies* (L.) Karst.). Although this value appears small, it is paramount for the microorganisms and insects living in the wood [31] and the amount of NOx released during combustion [33,36]. FDH (6.18) and ODH (6.06) in this study are in the range of ODH reported for Norway spruce (6.20) [51] and spruce wood (6.1) [11].

The insignificant correlation between ODC vs. ODN agrees with earlier studies [33,52], as the significant correlation between ODC vs. ODH = 0.42 [33]. However, the significant correlation between ODN vs. ODH = −0.42 contradicts Telmo, Lousada, and Moreira [33]'s results. The drying process did not significantly change the results of the correlations between C vs. H and N vs. H. However, one can see the impact of drying on the correlations between C vs. N, with FDC vs. FDN being significant, while ODC vs. ODN was not. The reason for this difference between the two drying processes is still unclear. A better understanding may be achieved if the three levels suggested by Pereira, Graça, and Rodrigues [9] and other analysis viewpoints (e.g., cell biology, wood anatomy) are contemplated together on the same samples.

4.2. Variation of the Chemical Composition of White Spruce Tissue Types with Silvicultural Treatments

Based on previously observed relationships between CC and growth rate, the increase in CC with initial spacing presented in Table 1-Part 2 was expected for both FDC [28] and ODC [26,28,30]. However, despite the increasing tendency established in these previous studies, the differences between diameter classes [25,30], social classes [28], tree volume [26], and canopy position [15] were not significant, contrary to the significant differences found in this study (Table 3). As previously stated [22,28], direct cross-study comparisons of CC are difficult because no standard protocol exists for sampling or measuring CC. Our study contrasted even-aged trees collected in the same location, at the same ages and tree heights, on the same tissue type, and using the same CC measurement processes. Despite the significant variation in CC found in this study for white spruce, one must recall the finding of Elias and Potvin [17], suggesting that the impact of social classes on CC may be species-specific and must be further studied.

We are unaware of a previous study establishing the impact of initial spacing on ODN, FDN, ODH, FDH, VMF, and Cvol. Except for the insignificant variation in FDN (and the limited impact on ODH), all these chemical properties showed a significant decrease with initial spacing. This is understandable, given that CC increased with initial spacing. Except for the oxygen content that was not analyzed in this study, C, N, and H are the main components of a tree, and an increase in one component is likely to induce a decrease in another.

4.3. Variation of the Chemical Composition of White Spruce Trees with Tissue Types

Bark represented 14% of red spruce trees growing in Maine [53], with large variations (6.9% to 14.8%) along Norway spruce stems [54], and this tissue ranked first for N content and second for C content in this study. The high amount of FDN and ODN in bark tissue in this study agrees with Merrill and Cowling [31], who found that N content in the bark was three to eight times higher than in wood. N content in the cambium was not statistically different from that in the bark. This very high N content in cambium also agrees with Merrill and Cowling [31], who found N to decrease from cambium to a minimum in heartwood and increase again near or at the pith. Merrill and Cowling [31] attributed this pattern to removing N from dying parenchyma cells (in the heartwood) and retrieving them in the cambium through the ray tissue of the sapwood. The higher proportion of N in earlywood compared to latewood in this study is in agreement with Merrill and Cowling [31]'s finding for sapwood of Eastern white pine (*Pinus strobus* L.) and white ash (*Fraxinus americana* L.). Merrill and Cowling [31] related this difference to the greater amount of parenchyma in earlywood cells compared to latewood cells. N content (ODN) is comparable in the remaining tissues except for these two tissues. One can therefore use bark N to represent both bark and cambium and wood N to represent the remaining tissues.

Knot represented one-third of the total log volume in Norway spruce growing in southern Finland, with large variations with tree height [55], and this tissue ranked first for the carbon and hydrogen content in this study. The high amount of both C and H in knots than in other tissues is explained by the high percentage of compression wood in knots [9]. Compression wood is known to have higher lignin content [56], with a greater amount of both C and H [57] than normal wood, and thicker tracheid walls [58] than normal wood, resulting in higher CC [19,23], but also H and C. Overall, despite some discrepancies, there is a consistency in the variation between knot, cambium, and bark with other woody tissue (wood, earlywood, and latewood), i.e., if a difference is found between knot (or bark or cambium) and a woody tissue, the same difference may be expected with other woody tissues. This agrees with findings by Martin, Gezahegn, and Thomas [20] and Nordin [59], suggesting that bark should be treated as a separate fuel type. Knots should also be treated as a separate fuel type, while other woody tissues could be aggregated.

Worldwide, the amount of bark generated annually from industrial wood harvesting is many times higher than the 50 million tons reported for North America only. A significant amount is added by the many biotic infestations (e.g., spruce budworm) [60]. About half of the industrially generated bark is burned for energy production or disposed of in landfills [60]. Knots are hard to digest in paper industries and are often burned to produce heat and power [61]. Spruce bark has high concentrations of several polyphenolic compounds with promising commercial potential [62]. Spruce knots are also a rich source of bioactive polyphenols [63–66]. Therefore, using these tissues as sources of high-value extracts presents a higher value added compared to burning [62]. Dedicating each tree tissue to the best use allows for generating more industry revenue streams. It may even create a market for low-value biomass, such as small trees from early thinnings [62] or non-merchantable top bole with a high percentage of knots and bark.

4.4. Impact of Tree Age and Height on the Chemical Composition of White Spruce Tissues Type

ODN is known to vary between heartwood and sapwood [31]. ODC also varied in some species between heartwood and sapwood [16,19,23,32]. Therefore, although the lack of radial variation for FDC in this study is in agreement with our recent study on white spruce [28], we suggest that radial variations of chemical elements in wood should be evaluated as differences between the tissues (pith, heartwood, and sapwood) and not as inter-ring annual differences. We also suggest evaluating longitudinal variation in woody tissue using relative height and samples collected at fixed calendar years (and not fixed cambial age as done in this study). This may allow for discarding confounding factors such as age, climatic impacts, and the impact of the living crown [43].

5. Practical Implications and Limitations

The main achievement of this study was measuring the amount of carbon, hydrogen, and nitrogen stored in different tissues of managed white spruce trees. The chemical contents indicate that growing larger trees with wider square spacing (e.g., 4.3 m and 6.1 m) allows for more carbon storage in the forests. In a recent thinning experiment, we similarly found that trees from heavy thinning stored more carbon than trees from light and medium thinning [28]. This study also demonstrated that the increasing carbon with square spacing happens at the expense of nitrogen and hydrogen. Aside from the practical implications on forest management, the results of this study indicate that knots and bark could be used to maximize both calorific value and biochemical yield. Indeed, because it ranked first for carbon and hydrogen, the knot is expected to produce more energy than other tissues. In contrast, bark may be more concerned with NOx emissions because it has the highest nitrogen content. Both bark and knots are appealing for the extraction of polyphenolic compounds, and the valorization of these tissues in the processing of high-value chemicals should be encouraged. Although this study adds a significant piece of knowledge in this field, a larger sampling (compared to the total of 292 samples), with a greater sampling number for the tissues that are more difficult to collect (e.g., cambium, earlywood, and latewood), will add scientific value to subsequent work.

6. Conclusions

This study quantified the impact of initial spacing on wood nitrogen and hydrogen content. It also quantified the effect of drying technologies (freeze-drying vs. oven-drying) on these elements. White spruce carbon content significantly increased with initial square spacing, while the reverse, i.e., a significant decrease, was observed for nitrogen and hydrogen content. Trees in smaller initial square spacing (1.2 m and 1.8 m) also lost more volatile carbon than trees in wider initial square spacing (4.3 m and 6.1 m). Oven-drying had a negative impact on all three elements (C, H, and N), which was significant for C and H. The drying process also affected the correlations between chemical elements, with a significant correlation between freeze-dried C vs. N, while the oven-dried correlation was not. The high content of N and C in bark and C and H in knots plead for dedicating these tissues to high-value-added conversions, e.g., in the biochemical industries, where their high concentrations of several polyphenolic compounds make them more attractive.

Author Contributions: Conceptualization, C.S.M.; methodology, C.S.M.; formal analysis, E.A.B. and C.S.M.; resources, C.S.M. and A.K.; data curation, C.S.M.; writing—original draft preparation, C.S.M. and E.A.B.; writing—review and editing, C.S.M., E.A.B. and A.K.; supervision, C.S.M.; funding acquisition, C.S.M. and A.K. All authors have read and agreed to the published version of the manuscript.

Funding: Natural Resources Canada funded this research through the Forest Innovation Program (FIP).

Data Availability Statement: Contact the corresponding author for data sharing.

Acknowledgments: The authors thank Bouslimi Besma (UQAT), Jared Salvail (CWFC), Natalia Startsev (CWFC), and Mofetoluwa Akindele (CWFC) for samples preparation. The support of Joe Crumbaugh (Canadian Forest Service chemical analysis laboratory in Edmonton) was instrumental in carrying out this research. Comments on the submitted manuscript by four anonymous reviewers are greatly appreciated.

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

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