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Elemental Relationships in the Wood of Four Siberian Conifers: Whether Elements Are an Occasional Mixture

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Abstract: In the abundant literature on plant chemistry, little attention is paid to correlations among chemical elements in tissues. The goal of the research is to establish consistent correlations among elements in the xylem of four widespread Siberian conifers. X-ray fluorescent analysis has been applied to find out the elements contained in the xylem. The method allowed finding the mean count rates of Al, P, S, K, Ca, Ti, Mn, Fe, Cu, Zn, and Sr in trunks of trees. Moreover, the xylem samples were chemically treated twice, first in alcohol and then in HCl. It was found that species factor exerts a significant influence on the elemental content of a few elements, but not on all of them. The chemical treatment decreases the impact of the species factor. The treatment increases the number of significant correlations and strength of them. In some cases (especially with Al), the correlations may change the sign of the relationship. The consistent correlations may help arrange more profound chemical research revealing the forms in which the elements exist in xylem.

Keywords: plant chemistry; conifer xylem; chemical elements; X-ray fluorescent analysis; chemical treatment; correlation; afforestation experiment

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1. Introduction

As the historical background shows [1], studies on wood chemistry go back for around two hundred years. In recent decades, the priority focus in the field has been mostly on the organic compounds as the practical use of cellulose, lignin, and a range of extractives has been of great importance. However, some researchers have admitted that inorganics, though making up only 0.1–1.0% of dry wood, are essential for tree growth [2]. But not only for growth; the presence of inorganics in wood fibers may bring about depolymerization of wood polymers, consequently causing cellulose decomposition and loss of wood strength. This is true for many metals such as Fe, Cu, Cr, Sn, Zn, and others [3].

The development of methods such as EDXA and X-ray FA provided the opportunity to receive a massive amount of data on the content and distribution of inorganics in wood. Studies have recorded tens of elements in various species' wood and have revealed some details of their distribution. For example, Saka and Goring [4] found that the inorganic content is higher in earlywood compared to latewood in black spruce. According to another finding, some elements (e.g., Mn) indicated the health condition of forest stands [5]. It has been found that metal elements differently accumulate in the wood of two poplar species [6].

Generally, the content of the ash elements varies widely within and among species [3]. Krutul et al. [7] showed that metals' accumulation in Scots pine depends substantially on pollution levels from a nitrogen industrial plant. Sometimes, elements vary because of environmental changes, as Wagner et al. [8] showed in the experiments with manipulated precipitation. The variations, however, do not exclude that the elements may correlate with each other. The study by Houle et al. [5] provided indirect evidence of such correlations showing that Ca, Mg, and Mn significantly correlate with the acid-base status of the soil.

Oxalates, carbonates, and sulphates are probable forms of the elements' existence in wood. The ions may also be bound to carboxyl groups of the organic constituents. Besides this, elements are located in specific morphological structures of wood cells like middle lamella, cell corners, and ray parenchyma walls [9]. Therefore at least some elements in wood should relate to each other because they are bound through either chemical or structural causes, though may be unknown.

In Eastern Siberia, conifers totally dominate among tree species covering ca. 73% of the forested area. The conifer species are convenient objects of research because of wide distribution and substantial ecological plasticity. They are basically split into two ecological groups, light-conifers (Siberian larch and Scots pine) and dark-conifers (Siberian spruce, Siberian pine, and Siberian fir). The opportunity of this study is to involve the data from a field experiment where different species grow under similar conditions (see Section 2).

This study strives to establish correlations among several important inorganic constituents in the wood of four Siberian conifers. The correlations were observed in intact wooden samples and samples subjected to chemical extractive treatments. Hypothetically, chemical treatments may reveal or sharpen correlations among inorganic constituents.

2. Materials and Methods

2.1. Field Data

The sampling area was located about 50 km from Krasnoyarsk city with GPS coordinates N 56°12′8.49″ E 92°20′48.97″. The site is a part of afforestation experiment set up in 1971-72 by a group of scientists from the Institute of Forest SB RAS [10–12]. The list of the species included in the study is Siberian spruce (*Picea obovata* Ledeb.), Scots pine (*Pinus sylvestris* L.), Siberian larch (*Larix sibirica* Ledeb.), and Siberian pine (*Pinus sibirica* Du Tour).

The feature of the experiment is that it runs under levelled out conditions of growth for all the species. The upper 50 cm soil layer was removed, homogenized, and dispersed over the experimental plot. Each species occupies 2400 m^2, with the initial planting density being 40,000 saplings per ha.

Altogether, 12 sample cores, each 12 mm thick, from four species, three trees per species were collected. The sampling took place in October 2017 from trees without apparent damage.

2.2. Sample Preparation

For two weeks, the cores were air-dried in a laboratory. After the drying, 2-mm thick slices were sawn from the cores with the help of a Bosh circular saw perpendicular to the wood grain (Figure 1).

Our tool is made of BK-2 (Russian classification) steel which is basically an alloy of 98% WC and 2% Co. However, the State Standard (GOST) admits the residual elements in the amount of 0.2%. Theoretically, some quantities of the metals might be transferred from the saw to the wooden slices, which would produce a systematic error. Still, the error should be rather insignificant—because the hardness difference between the wood and the steel is huge. So, the saw's wear and tear are small. On the other hand, the probability of introducing impurities from the instrument does exists and avoiding it at the present level of technology is hardly possible.

After the sawing, the slices were clean and smooth enough for the subsequent analysis, and no sandpaper was used during the preparation procedure.

Figure 1. The cores after extraction are wrapped in a piece of firm paper and marked (**a**). A view of a core in a wooden holder after sawing has been performed (**b**). The wooden slice is ready for extraction.

2.3. X-ray Fluorescent Analysis

The wood elements chosen for monitoring were: aluminum, phosphorus, sulfur, potassium, calcium, titanium, manganese, iron, copper, zinc, and strontium. The measurements of the relative content of the elements were performed with the help of Itrax Multiscanner (COX Analytical Systems) coupled with Multiscanner Navigator software (Figure 2). The multi scanner outputs are the so-called counts or count rates, relative dimensionless units. In some cases, the counts may be recalculated into absolute concentrations. However, such calibration procedures are available only for a limited number of elements (see, e.g., [13]), and the study operated only with the measured elemental count rates.

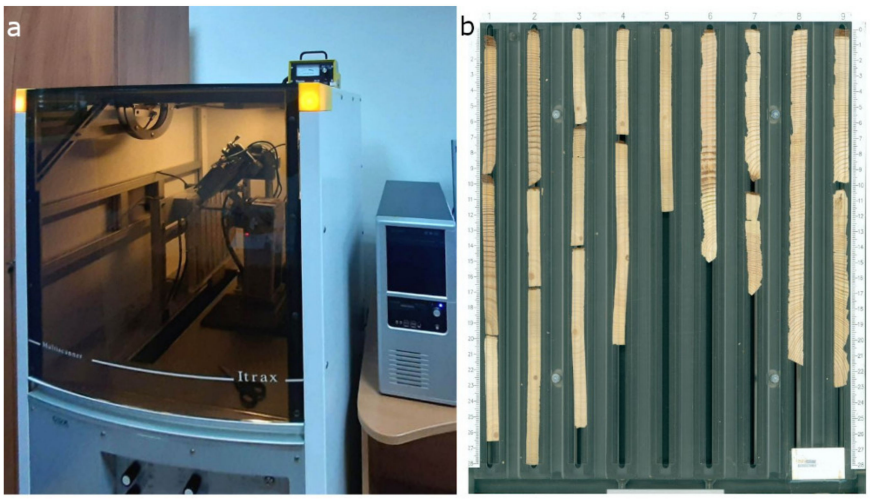

Figure 2. The Itrax Multiscanner facility (**a**) and the wooden slices in a plastic holder (**b**) ready for scanning.

The spatial scanning steps along the slices were every 100 µm, and the scanning X-ray beam was 2 mm wide.

2.4. Chemical Treatment

To test the above given hypothesis, a double chemical treatment was performed. Each element studied in each sample had three sequences of counts: original, after alcohol, and after HCl extraction.

First, we performed the initial scanning of the slices through the multi scanner in their original condition in 2017.

Second, in 2021, we put the wood samples in pure alcohol at the temperature of 78 °C, where they were under extraction for eight hours. Then the samples were air-dried above a silica gel layer at room temperature. The final drying went on under pressure to avoid the warpage of the samples. Then we scanned the dried samples through Itrax Multiscanner for the second time.

Third, the extraction of the wood samples took place at 0.2 M HCl. The concentration was chosen in contrast to the standard recommendations of 0.5 M concentration [14]. We had to use a lower HCl concentration to prevent the xylem's disintegration and to ensure further scanning. After the treatment and drying, we scanned the samples for the third time.

In various research, different methods for the extraction of major inorganic cations are used for elemental analysis. The chlorohydric acid has been traditionally used to extract chemical compounds from wood. It allows effective extracting of the salts of metals of the first and second groups of the Mendeleev's table.

To take Ca as an example, HCl readily extracts calcium carbonate and calcium oxalate [15]. Schilling [16] showed that 0.2 M HCl is enough to remove the Ca oxalates.

The use of HCl has an advantage because of its fugitiveness. Its traces can be easily removed from wood by drying. Moreover, its weak concentrations help to preserve the integrity of wooden specimens. According to our experience, the nitric acid would further decrease the mechanical properties of wooden specimens and often leads to their disintegration.

2.5. Statistical Analysis

As said above, the outputs after the scanning are counts received from regular points along the wood samples, in our particular case, every 100 μm. Regarding the physical dimensions, all the wood samples are slightly different because of differences in the growth of trees. Thus, the series of the counts from different trees have different lengths. To make the series comparable, we calculate the mean values for the series of counts. In other words, every wood sample is the mean values of counts of the elements falling on one scanning point.

A parametrical correlation analysis is not possible because the amount of data is low (altogether 12 trees). Instead, non-parametrical statistics should be used. In this study, the Spearman rank correlation approach has been applied.

Another statistical problem with the data available is that the trees belong to four different species, which may produce illusory correlations. For example, if an element's content in one species is regularly higher than its content in another species, combining the data in the same analysis may show a correlation that is not accurate—because it is the species factor that produced the correlation. To find out in which cases the species factor exerts a significant impact on the correlations, the non-parametrical Kruskal–Wallis ANOVA was applied. The Kruskal–Wallis test detects if the data from different groups have the same distribution. In our case, the groups are species of trees. If the p-value for the mean counts of an element was lower than 0.05, this was interpreted as the significant difference between species and, therefore, as the significant impact of the species factor on the elements' mean counts.

All the calculations have been performed with the help of Statistica 6.1 (StatSoft, Tulsa, OK, USA) software.

3. Results and Discussion

The goal of the study was to establish significant relationships between chemical elements in the xylem of four widespread conifers. The chemical forms which may include the elements are poorly known. However, methods of X-ray fluorescent analysis allow getting a massive amount of data regarding the variety of elements that researchers may find in trees' xylem. A correlation analysis may reveal the relationships sought. If one manages to establish consistent correlations among the elements, then the knowledge may serve to plan deeper research on the natural causes of the relationships. The initial data used to calculate the correlations are provided in Table S1 (see Supplementary Material).

Table 1 shows the impact of species factor on the distribution of elements among the trees. The impact of species factor implies that the elemental counts are not randomly scattered among the trees, irrespective of the species. Rather, the elemental counts in one species may be steadily larger or smaller than the counts in another species. The p-values < 0.05 shown in the table indicate that the species factor significantly influences the distribution. It means that one can hardly interpret the correlation of the particular element to any other element as an intrinsic correlation between them.

Table 1. Results of Kruskal–Wallis ANOVA: impact of species factor on variation of elemental counts.

Element	Original	After Alcohol	After HCl
Al	0.0627	0.536	0.3761
P	**0.0307** *	0.3061	0.4329
S	**0.0307**	0.6217	0.5062
Ti	**0.0329**	**0.0405**	**0.0273**
Mn	**0.0329**	**0.03**	0.0656
Fe	0.0719	0.0656	0.0987
Cu	0.1234	0.5062	0.2181
Zn	0.8629	0.9104	0.3466
Ca	**0.0434**	0.1834	0.4415
Sr	0.0656	0.2276	0.9217
K	0.4415	0.3916	0.2276

* The p-values < 0.05 are given in the bold font.

The data from Table 1 demonstrate that the content of quite a number of elements depends significantly on species factor (P, S, Ti, Mn, Ca). However, chemical extraction decreases radically the number of such elements. After HCl extraction, the only content of Ti depends significantly on the species factor. It means that a correlation between Ti and any other element may be due to the species factor, not because of the chemical interaction between the elements.

As it is widely known, xylem of trees is a very complicated natural medium which roughly includes the primary wall, middle lamella, and secondary wall. In the cells' genesis, a remarkable transition takes place from a pectin-rich primary wall to a relatively low-pectin secondary wall. The latter, however, is known for a massive production of hemicellulose and cellulose organized in ordered layers [17].

It is unknown which of the major xylem cell structures, primary and secondary walls, is first to be washed out from inorganic elements by the applied extraction agents. However, supposedly, the absorption power of cellulose microfibrils in the secondary wall may be relatively low. Practical studies focused on sorption technologies evidence that unmodified native cellulose has a strongly limited metal-binding capacity. That is because the native cellulose has a poor chemical structure with a low amount of oxygen-based functional groups [18–20].

Based on this assumption, one could infer from Table 1 that the species-specific content of the inorganics may be in the secondary wall of the wood cells. In a sense, the secondary wall may bear the species' signal expressed in the elemental content. The removal of the signal from the wood leads to that no one can see a significant difference among species after the extraction application.

A remarkable exclusion is Ti. The studies performed decades ago have shown a species-specific pattern of Ti accumulation in terrestrial plants. Moreover, Ti fertilization acts on plants in a species-specific manner [21].

Table 2 summarizes Spearman rank correlations among the elements studied in the original state and after extractions in alcohol and HCl. As follows from the table, the number of significant correlations among the elements grows strongly from the original state of the samples to the post-extraction condition. Given the insignificant impact of the species factor, the number of correlations in the original state is two (Al-Cu and Al-K). After the alcohol extraction, the number of significant correlations amounts to 11 and after HCl extraction 29 cases. Moreover, the correlations after the extraction application become generally stronger. In the untreated condition, there are no correlations higher than 0.8–0.9. After the alcohol extraction, there are seven such correlations and, after HCl extraction, 13 cases of high correlations.

Table 2. Spearman rank correlation matrices for mean elemental contents in trunks of the four conifers.

	OrgAl *	**OrgP**	**OrgS**	**OrgTi**	**OrgMn**	**OrgFe**	**OrgCu**	**OrgZn**	**OrgCa**	**OrgSr**
OrgAl										
OrgP	**−0.80** **									
OrgS	**−0.80**	**0.99**								
OrgTi	0.52	−0.57	**−0.59**							
OrgMn	**0.71**	**−0.69**	**−0.69**	0.32						
OrgFe	−0.41	0.51	0.53	**−0.64**	−0.02					
OrgCu	**−0.59** †,§	**0.86**	**0.87**	−0.42	**−0.62**	0.41				
OrgZn	−0.01	0.03	0.07	0.28	0.21	−0.08	0.31			
OrgCa	**0.88**	**−0.80**	**−0.79**	0.50	0.55	−0.36	−0.46	0.13		
OrgSr	0.28	−0.19	−0.23	−0.04	0.39	0.30	−0.36	−0.47	0.03	
OrgK	**0.63**	−0.36	−0.38	0.28	−0.01	−0.55	−0.15	−0.14	**0.60**	−0.02
	AlcAl *	**AlcP**	**AlcS**	**AlcTi**	**AlcMn**	**AlcFe**	**AlcCu**	**AlcZn**	**AlcCa**	**AlcSr**
AlcAl										
AlcP	**0.97**									
AlcS	**0.99**	**0.96**								
AlcTi	−0.31	−0.43	−0.28							
AlcMn	−0.28	−0.41	−0.23	0.52						
AlcFe	−0.08	−0.20	−0.01	0.41	0.21					
AlcCu	0.42	0.27	0.43	0.27	0.35	0.27				
AlcZn	0.52	0.39	0.53	0.21	0.28	0.26	**0.87**			
AlcCa	0.22	0.08	0.25	0.15	**0.62**	0.08	0.24	0.40		
AlcSr	**−0.82**	**−0.86**	**−0.83**	0.28	0.46	−0.04	0.04	−0.09	0.01	
AlcK	**0.75**	**0.68**	**0.73**	0.19	−0.10	0.13	0.43	0.56	0.38	**−0.64**
	HclAl *	**HclP**	**HclS**	**HclTi**	**HclMn**	**HclFe**	**HclCu**	**HclZn**	**HclCa**	**HclSr**
HclAl										
HclP	**0.90**									
HclS	**0.89**	**0.99**								
HclTi	**0.64**	0.52	0.43							
HclMn	0.41	0.08	0.07	0.57						
HclFe	**0.75**	**0.64**	0.55	**0.85**	**0.62**					
HclCu	**0.87**	**0.92**	**0.90**	**0.59**	0.27	**0.70**				
HclZn	**0.79**	**0.93**	**0.90**	0.55	−0.03	**0.66**	**0.80**			
HclCa	**0.63**	**0.69**	**0.68**	0.19	−0.07	0.36	**0.71**	0.52		
HclSr	**−0.65**	**−0.58**	**−0.61**	−0.13	0.07	−0.19	−0.45	−0.44	**−0.59**	
HclK	**0.64**	**0.85**	**0.80**	0.45	−0.20	0.52	**0.80**	**0.88**	**0.69**	−0.29

* Org = original elemental contents in untreated samples, Alc = elemental contents after alcohol extraction, Hcl = elemental contents after HCl extraction. ** Significant at $p < 0.05$ correlations are marked by the bold font. † Correlations in which impact of species factor is insignificant at $p > 0.05$ for both elements are marked by the grey background. § Significant correlations combined with insignificant impact of species factor are marked by red font.

It is not firmly known why the inorganics could correlate to each other in the xylem of trees. Most probable is that the extractive agents flush first out the xylem lumens and parenchyma cells. The content of lumens may be more or less "occasional", and the content of the walls is not. If so, this could explain the increase in the amount and strength of the correlations.

From a stoichiometric viewpoint, correlations between metals and non-metals may arise from binding them into salts molecules. In this study, P- and S-based acids may build salt-alike complexes with other elements. The elements are metals such as Al, Fe, Cu, Zn, Ca, and K. The existence of such complexes may also explain why metals often correlate with other metals, which could be a sort of inductive correlation—mediated by a third agent. One could pay attention that P is very strong (up to 0.99) related to S, and this relation is seen from the very beginning, in the untreated samples. The cause of such a relation is unknown, but if it is a basic independent factor, it may create correlations between other metal elements bound separately for P and S.

At first sight, the element that does not fit into the pattern is Sr. It has negative correlations with almost all other elements studied, both metals and non-metals. However, Sr is known to be a chemical analogue of Ca, and hence a competitor to the latter—because Sr can readily substitute Ca in many natural compounds. If therefore, Sr negatively correlates with Ca because of the competition, then it may negatively relate with other elements with which Ca correlates positively.

Another example of an inductive correlation is the pair Al-Cu (Figure 3). At first sight, there is a hard explainable change of the negative sign of correlation in the untreated samples to positive correlation after the HCl extraction. On the other hand, as a known biophile element, Cu always relates positively to P and S (Table 2). Phosphorus and sulfur are large participants in the biochemical machinery of the cell. Aluminum often acts as a toxic agent for the living cells, so it would negatively impact P and S in trees that absorb more Al ions. After the intensive extraction, Al may remain as a trace element bound, along with other metals, to pectin functional groups. Hypothetically, pectin may absorb P- and S-based biochemical molecules and preserve them during extraction. If this is true, then the correlation in the pair Al-Cu reflects the relations between Al and biophile P and S.

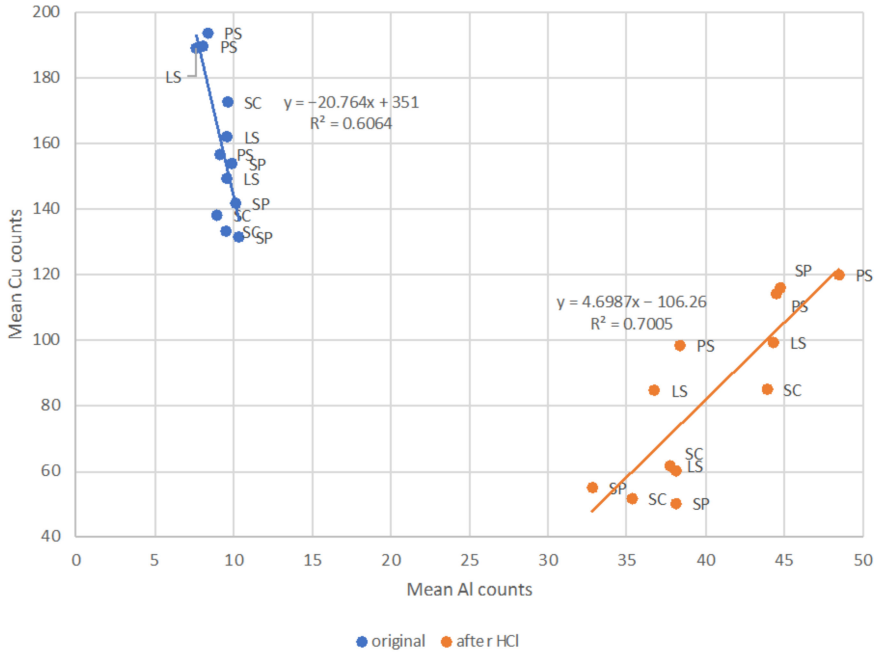

Figure 3. Relation of Al and Cu counts in untreated samples (•) and after HCl extraction (•). SP = Siberian spruce, LS = Siberian larch, PS = Siberian pine, SC = Scots pine.

However, it should be admitted that the given explanation may be insufficient. More profound research is necessary to reveal the foundations of the relationships.

Among the abundant literature dedicated to plants and trees' chemistry, relatively fewer sources provide evidence of significant relationships between elements. For example, Houle et al. [5] reported Ca, Mg, and Mn were significantly correlated to acidity status of

the soils. If the elements correlate significantly to a common factor, then they might also correlate with each other.

It is unknown if a chemical treatment can alter the existing correlations or even reveal them. As it follows from the results, the chemical treatment, in the form of extraction, can reveal but also destroy the correlations. In the Electronic Supplement, the spreadsheet is provided that contains the initial data used to estimate the correlations among the elements.

4. Conclusions

Plant chemistry generally and dendrochemistry, in particular, are very advanced areas of research. The methods applied to analyze the elements content predetermine many questions that researchers may solve in their studies. In our research, the X-ray fluorescent analysis was applied. Compared to direct chemical methods, the X-ray FA supplies relative amounts of elements' content and largely depends on the studied substance properties. However, it can rather quickly provide massive data on a wide spectrum of elements.

Because of the latter, one may consider a question of correlative relationships among the elements. If one finds consistent correlations, further, deeper research may be arranged. Probably, other methods should be in effect—because X-ray FA leaves a serious gap in the information provided. The gap is the lack of knowledge about the forms in which the elements exist in the xylem. Nevertheless, the information about consistent correlations may close in the search for profound relationships governing the elemental content and properties of xylem in trees.

To conclude, a substantial number of significant correlations among elemental count rates have been found in the study. Some of the correlations depend on species factor but many of them do not. The chemical extractive treatment, alcohol and HCl, increase both the number and the strength of the correlations. In several cases, the treatment changes the sign of the correlation, which requires a further analysis.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ijpb13020014/s1, Table S1: Mean elemental counts in cores of four studied conifers.

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