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Concentration of chemical elements in Carpathian snowbell (*Soldanella carpatica*), Javorová Valley, the Tatra Mountains

G. ZATKALÍKOVÁ and M. JANIGA

Institute of High Mountain Biology, Žilina University, Tatranská Javorina 7, SK-059 56, Slovak Republic; e-mail: janiga@uniza.sk

Abstract. This study deals with the investigation of concentrations of biogenic and potentially toxic chemical elements in a Western Carpathian, alpine endemic species - the Carpathian snowbell (*Soldanella carpatica*) - which was collected for two years in the Javorová Valley in the High Tatras. High mountain plants can be an indicator of environmental pollution and the distribution of pollutants in the atmosphere, as high mountain ranges are often a confluence for pollutants accumulated and transported in the atmosphere. To understand the functioning of pollutant uptake and distribution in the selected species, *S. carpatica*, an understanding of nutrient uptake and accumulation is also necessary, as both types of chemical elements usually interact with each other, either in their distribution in the environment or directly in their uptake by plants. We found that biogenic elements in *S. carpatica* are distributed and accumulated fairly evenly in all plant organs, whereas potential pollutants are accumulated mainly in the root and sometimes to a lesser extent in the stem. Changes in the concentrations of chemical elements in *S. carpatica* were heavily influenced by changes in location and altitude as well as by seasonal changes, contrarily to biogenic elements and potential pollutants.

Key words: Carpathian snowbell, uptake of chemical elements, accumulation, potential pollutants

Introduction

The acquisition and use of mineral elements by plants are fundamental processes necessary for their growth, development, and overall physiological functioning. Plants obtain these mineral elements primarily in the form of inorganic ions, which they extract from the soil through a complex root system. Liebig's 'law of the minimum' in the late 19th century laid the foundations for understanding the importance of mineral nutrients in plant growth, arguing that the rate of plant growth is determined by the availability of the most limiting nutrient. However, subsequent advances in research have elucidated the complex interactions and interdependencies between different nutrients, highlighting the inherent diversity of plant nutrition (Rao 2009).

Although most mineral elements are taken up by plants through the root system, it should be noted that some nutrients and potential pollutants can also be taken up directly through the leaves of plants from the surrounding atmosphere (Rao 2009).

The continuous cycling of these mineral elements through organisms and their environment underscores their fundamental importance in maintaining life processes and ecosystem functioning. Indeed, without these essential mineral elements, plants would not be able to complete their life cycle, as each element plays a specific and irreplaceable role in different physiological functions (Mayer and Ulrich 1974).

The focus of this research is to analyse the concentration of chemical elements in the Carpathian snowbell (*Soldanella carpatica*), a member of the Primulaceae family. *S. carpatica* is widely distributed in extensive European mountain systems, especially in the Carpathians and the eastern Balkans, occupying diverse habitats, with a particular preference for the understorey of mixed or coniferous forests in the montane zone (Valachovič *et al.* 2019). Investigation of chemical element concentrations in *S. carpatica* provides valuable insights into its ecological importance and potential utility as a bioindicator species for monitoring environmental health and integrity. Furthermore, insights into the physiology of different plant species are essential for understanding the movement of potentially toxic trace elements (PTEs) in the environment (Muszyńska and Labudda 2019).

In addition to essential mineral elements, the presence, and dynamics of PTEs in plants are also extremely important. While essential mineral elements play a key role in promoting plant growth and development (Rao 2009), the accumulation of potentially toxic trace elements can pose a significant risk to both plant health and ecosystem stability. Although plants have a natural tendency to absorb trace elements through root or leaf penetration, this mechanism exacerbates the persistence of PTEs in the environment (Muszyńska and Labudda 2019). As a result, excess PTEs in plant tissues can lead to contamination of the food chain, posing a serious health risk to both humans and animals (Rinklebe *et al.* 2019). Furthermore, exposure of plants to metal-contaminated environments

has a significant impact on their reproductive and vegetative growth (Yadav *et al.* 2023).

The release of heavy metals and other pollutants into the environment is mainly prompted by anthropogenic activities, including industrialisation, urbanisation, intensive agricultural practices, and mining activities. The accumulation of these substances in the environment can lead to toxicity (Yadav *et al.* 2023).

Mountainous areas, characterised by rich biodiversity and increased rainfall, are particularly vulnerable to heavy metal contamination due to their ability to accumulate aerosols and water droplets (Reiners *et al.* 1975; Viviroli *et al.* 2003). Despite potentially lower concentrations of heavy metals in precipitation at higher elevations, factors such as wind flow and cloud cover increase contaminant deposition (Natusch *et al.* 1974; Lee 2007). Consequently, understanding the pathways and ecological dynamics of PTEs in these ecosystems is essential for developing effective environmental management and conservation strategies. By unravelling the complex relationships between plants and chemical elements, this research aims to contribute to our understanding of ecosystem processes and the sustainable management of natural resources.

Material and Methods

Sampling

Emphasis was placed on the field phase of the research, where it was important to sample the plant and surrounding soil regularly and to collect sufficient samples to ensure reliable data for subsequent analysis and interpretation. Field sampling was conducted at two-year intervals (2022-2023), beginning in the fall of 2021.

Sampling of plant (*Soldanella carpatica*) was carried out in the Javorová Valley at seven different sampling sites, starting at the entrance to the valley and ending at Žabie Javorové lake. Each sampling site was at a higher elevation than the previous site. Sampling began at an elevation of 1137 m a.s.l. The second sampling site was located approximately 100 vertical metres above the first site at an elevation of 1213 m a.s.l. The location of the third site remained dynamic due to the variable occurrence of *S. carpatica* in this part of the valley and the desire to maintain approximately 100 m spacing between sampling sites. However, despite this variability, all sampling sites remained within 30 m of the original location of the third site at approximately 1270 m a.s.l. The fourth site was located at 1390 m a.s.l. and the occurrence of *S. carpatica* was the most abundant here compared to the other sampling sites. The fifth sampling site was located at 1470 m a.s.l. The sixth sampling site had a similar problem to the third site, and therefore the individual samples taken at this site had a slight variation in location due to the variable abundance of *S. carpatica* in this part of the valley. The seventh and final sampling was carried out at 1878 m a.s.l. However, the occurrence of *S. carpatica* at this altitude was limited to the summer and autumn months due to the climatic conditions (snow cover). The sampling location at this site was variable, like the third and sixth sampling sites, but occurred at approximately the same altitude.

Sampling took place throughout the growing season, particularly during the flowering period (May-August). During the spring months (March, April, May), sampling was carried out only at the lower sampling sites depending on the amount of snow, the highest being site 4. In the winter months (December, January, February) only site 1 was sampled due to the amount of snowfall.

The sampling process itself involved collecting 5 parts of the plant: leaf, stem, root, flower, and surrounding soil (to a depth of approximately 2 cm). Due to the high mountain climatic conditions in the Javorová Valley, *S. carpatica* flowers at different altitudes in different months (from spring to summer). Therefore, it was only possible to sample the flower at 2 to 3 sampling sites within a month. Even so, the number of flower samples that could be taken was very small and insufficient for analysis. It is also important to mention that the sampling of the above-ground parts of the plant (leaf and stem) during the spring months included both new shoots and leaves and stems that were preserved from autumn of the previous year beneath the snow cover.

Sample preparation

After collection, samples were dried separately in Petri dishes. Drying was performed naturally at room temperature to prevent evaporation of chemical elements from the sample. This process took at two weeks at the minimum, as samples such as stems and roots required more time to dry completely. After drying, the samples were ground into powder in a cryogenic ball mill (RETSCH Cryomill, Germany). The grinding container had to be washed with demineralised water after each sample to avoid contamination. The grinding frequency was set at 30 Hz/s for each sample. The grinding time was set from 40 s to 2 min. for plant samples. Soils required more time for complete grinding, usually 2 to 4 min.

Laboratory analyses

Samples processed this way were examined by XRF spectral analysis using an ED XRF spectrometer Delta (BAS - INNOV X, USA) to analyse the presence and concentration of chemical elements in the samples. The biogenic (essential) elements P, S, Cl, Ca, K, Ni, Mn, Fe, Cu, Zn, and Mo and the potential contaminants Cr, Ti, Rb, As, Se, Sr, Zr, Ag, Cd, Sn, Sb, Ba, and Pb were analysed using this method. The ground samples were placed in a small plastic vial with a transparent foil base. It was important that the sample covered the entire surface of the bottom. The samples should be at least one centimetre high in this vial. It was also important that the sample quantities were approximately the same. To measure the samples correctly, it was important to choose a method for measuring the plant material. The results from the spectrometer (BAS - INNOV X, USA) were then

entered into a matrix in an Excel spreadsheet, which was later used for statistical analysis. Mercury content was determined individually using a DMA-80 direct mercury analyser (Millestone, Italy), in 'standard' mode. Each sample had to be weighed on KERN 770 (Kern and Sohn, Germany) scales so that the analyser could determine the concentration of total Hg in mg/kg. The sample quantities used for mercury analysis ranged from 0.0015g to 0.0085g. The DMA-80 analyser operates on the principle of combustion of the sample at a temperature of 650° C, in which Hg evaporates from the sample and condenses by rapid cooling. The analyser then calculates the average value of the measured Hg for each sample.

For accurate measurements in both analysis methods, a certified reference material (CRM) was used, for plant samples: 'Polish Virginia Tobacco Leaves' (IC-INCT-PVTL-6), (ICHTJ, Poland) and for soil samples: 'Loam soil' (ERM-CC141), (IRMM, Belgium).

Statistical analyses

The concentrations of chemical elements analysed by XRF spectral analysis, which were high enough to be captured by the measurement, were plotted as a function of location (expressed as altitude) and season. These graphs were generated in Statistica Ver.10 (Statsoft, Inc.) following a standardised procedure. The dependent variable corresponding to the chemical element of interest was plotted on the y-axis, while the grouping variables (month and altitude) were plotted on the x-axis. Whisker tables were used to calculate the standard error (± SE) to improve the representation of variability within the dataset. Significance (p-value) was determined using the Kruskal-Wallis test to identify significant differences in the concentrations of the elements as a function of the categories.

In cases where significant differences in element concentrations were observed within individual plant organs or soil samples, separate graphs were generated to facilitate clearer visualisation. These plots showed different trends in mean concentrations and standard errors and provided an overview of the behaviour of individual elements within the plant. To improve readability, dashed lines were used to show trends in element concentrations with altitude, acting as auxiliary indicators without suggesting logical continuity due to sporadic sampling points. Due to the limited availability of data during the winter and spring months (December to April), these months have been combined into a single category called 'Dec/Apr'.

Chemical elements with insufficient data, resulting in a significant fraction below the limit of determination (LOD), were evaluated using contingency tables. These tables, compiled in Excel, allowed a comparative analysis of measured (YES) and unmeasured (NO) data in different plant organs and soil samples, with significance tests performed using the chi-square test ($\chi 2$). Flower samples are also presented in this part of the analysis to illustrate the small number of these samples. Flower samples were not used in other parts of the analyses because too little variability in these data would affect comparisons with other plant organs and the analysis would not be accurate.

Results

Concentrations of essential nutrients detected

Sulfur

The habitat of the plant - defined by altitude, influences the accumulation of S in the different organs (Fig. 1a), the level of S was also different in the soils (Fig. 1b) in the respective altitudinal gradients. The analysis shows a significant change in the amount of S in the root and in the soil depending on the altitude. These results also show a possible link between the amount of S in the soil and the amount of S in the rest of the plant - as the amount in the soil increases or decreases, the amount in the rest of the plant changes, and we can therefore assume that *S. carpatica* obtains its S mainly from the soil. At the same time, we observe a reduced amount in the plant, especially in the root, around the third, fourth and fifth sites, while the amount in the soil is more or less stable. Based on these results, we can speculate that once the amount of S in the soil is stable, the plant does not need to accumulate an additional amount, as there is probably no stress situation for this element in the

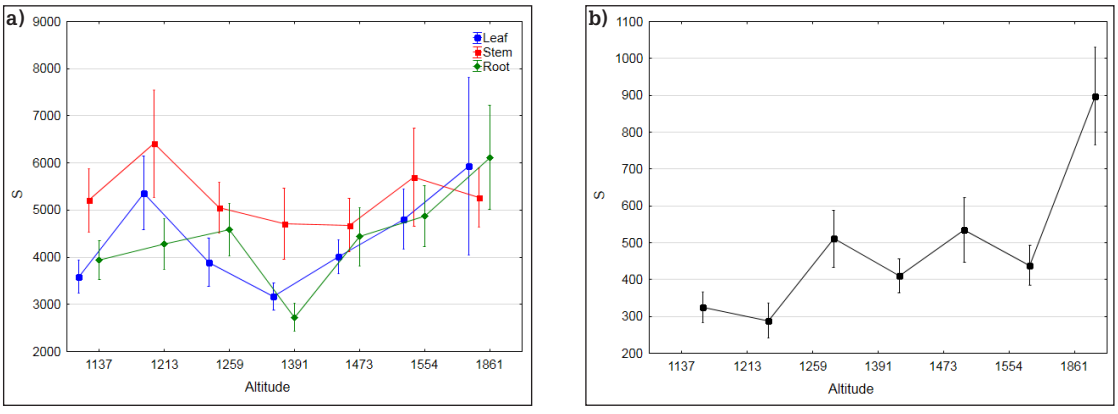

Fig. 1. Mean (± SE) levels of sulfur in a) *S. carpatica* organs (K-W H: leaf = 11.35, p = 0.08; stem = 1.47, p = 0.96; root = 15.41, p = 0.02) and soil b) (K-W H: soil = 24.39, p = 0.0004) depending on site indicated by altitude (m a.s.l.).

environment. In the second habitat, however, the amount of S in the soil is relatively low and, contrarily, the amount of S in the plant increases.

The amount of S in *S. carpatica* in plant organs (Fig. 2a) and surrounding soil (Fig. 2b) also varies with season. The analysis shows significant changes in S concentrations in leaves and stems. In addition, S concentrations vary in all parts of the plant. Increased amounts in the plant are observed at the end of summer as well as in the autumn, winter, and spring, apart from the month of October, when the amount decreases significantly in all parts of the plant.

Chlorine

Altitude also affects the amount of Cl in *S. carpatica* organs and the surrounding soil (Fig. 3a). The amounts of Cl in the stem (Fig. 3b) are shown separately because they are significantly higher. However, movement of Cl in the plant is similar - it rises and falls in equal proportion in all parts. The amount of Cl in the soil is constant throughout the study area.

Changes in Cl amount in *S. carpatica* organs and surrounding soil during the year are presented in Fig. 4a. The stem (Fig. 4b) is shown separately because it has a significantly higher Cl content

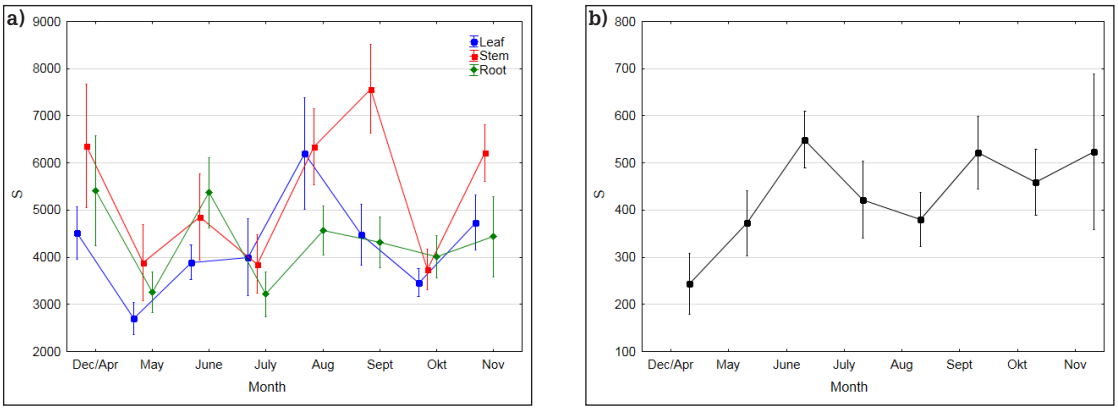

Fig. 2. Mean (± SE) levels of sulfur in a) *S. carpatica* organs (K-W H: leaf = 17.77, p = 0.01; stem = 25.52, p = 0.0006; root = 10.7, p = 0.15) and soil b) (K-W H: soil = 8.46, p = 0.29) depending on season.

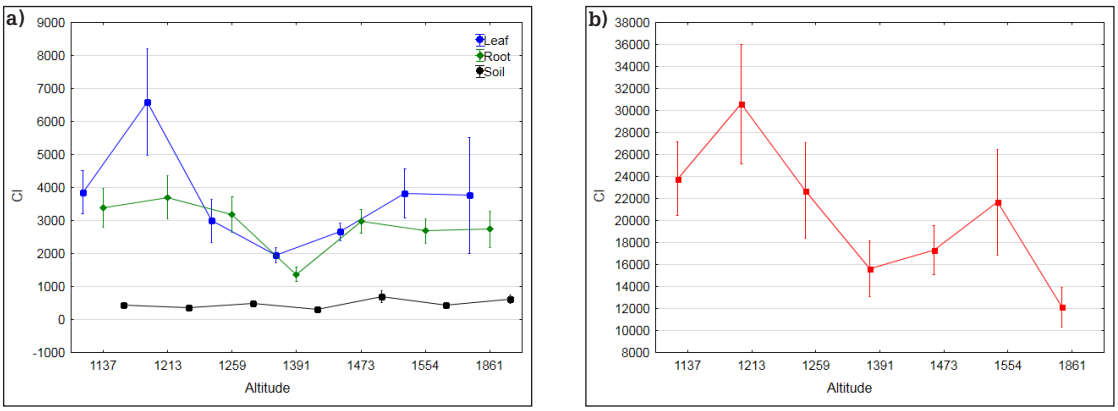

Fig. 3. Mean (± SE) levels of chlorine in a) leaf and root of *S. carpatica* and soil depending on site indicated by altitude (m a.s.l.) (K-W H: leaf = 18.99, p = 0.004; root = 16.7, p = 0.01; soil = 13.09, p = 0.04) and stem b) (K-W H: stem = 9.54, p = 0.14).

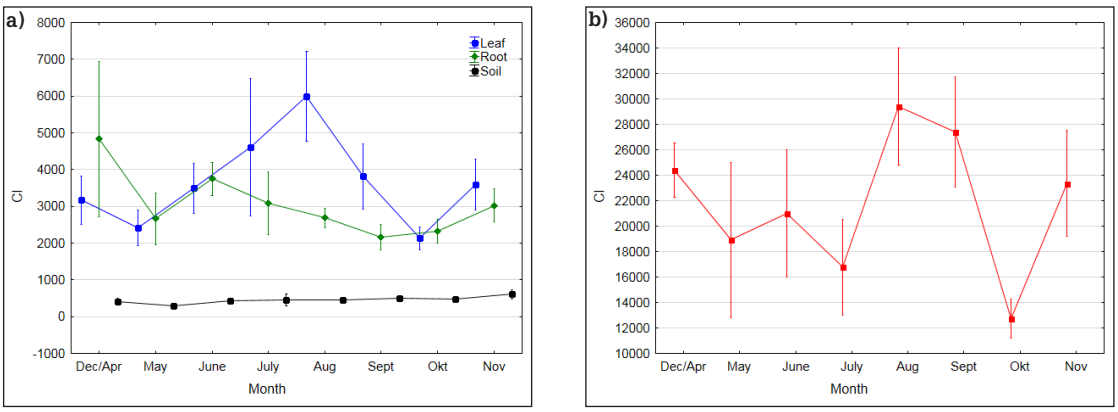

Fig. 4. Mean (± SE) levels of chlorine in a) leaf and root of *S. carpatica* and soil (K-W H: leaf = 12.55, p = 0.08; root = 10.33, p = 0.17; soil = 11.76, p = 0.1) and stem b) (K-W H: stem = 19.69, p = 0.006) depending on season.

than the other samples, while the p-value shows us the significant changes in Cl concentration in this plant organ during the year; particularly the sharp increase in Cl concentration in August followed by a sharp decrease in October. From the graph we can see that the amount of Cl in leaves and stems increases during the summer months and the plants accumulate it most in the stem and least in the root.

Calcium

Ca concentrations in *S. carpatica* and its surrounding soil as a function of site-defined elevation are presented in Fig. 5a. Ca concentrations in plant organs and soil follow a similar pattern. They begin to decrease around the fourth site. Significant changes in Ca concentrations occur in the leaf and root and change most significantly in the soil due to site and altitude changes. Ca concentrations in plant organs and their surrounding soil also change similarly based on seasonal shifts (Fig. 5b). These changes are significant in the stem. Ca concentrations increase in all parts of the plant and its soil, particularly in the winter and summer months.

Potassium

The variability of K concentrations in *S. carpatica* and its surrounding soil, due to differences in elevation, are presented in Fig. 6a. The amounts of K in the stem (Fig. 6b) are shown separately as they are significantly higher. The movement of K concentrations in leaves and roots is similar. Significant changes in concentrations occur in the root and in the soil. However, the decreasing and increasing amounts in the soil behave independently of the plant. Concurrently, we observed that the plant accumulates this element mainly in the stem.

K concentrations in *S. carpatica* organs and in the surrounding soil (Fig. 7a) also vary over the year (seasons). The stem (Fig. 7b) is again shown separately because it has a significantly higher K content. The highest concentrations and the most significant changes in the concentrations of this element are observed in the leaves and the stem, particularly during the summer months.

Manganese

Mn concentrations in the organs of *S. carpatica* and its surrounding soil vary with location, i.e. with changing altitude (Fig. 8a). The movement of Mn concentrations in all plant organs is similar. The highest concentrations are recorded around sampling sites 4 and 7. Mn levels in the soil show similar characteristics to those in the plant, but still differ. Significant changes in Mn concentrations are recorded in all plant organs as well as in the soil (dependant on location). Mn concentrations in plant organs and their surrounding soil also vary throughout the year

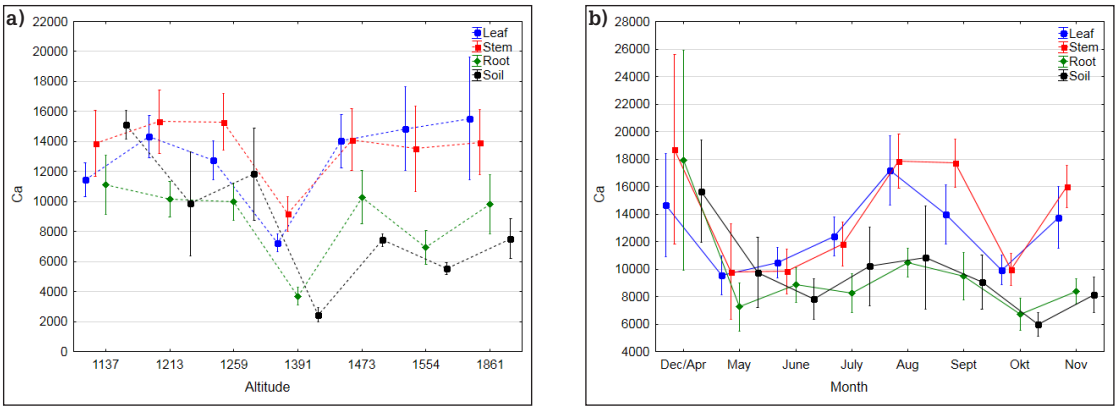

Fig. 5. Mean (± SE) levels of calcium in *S. carpatica* organs and soil depending on a) site indicated by altitude (m a.s.l.) (K-W H: leaf = 17.84, p = 0.006; stem = 8.26, p = 0.2; root = 25.8, p = 0.0002; soil = 47.05, p = 0.00) and b) season (K-W H: leaf = 12.5, p = 0.08; stem = 29.01, p = 0.0001; root = 8.96, p = 0.25; soil = 5.46, p = 0.6).

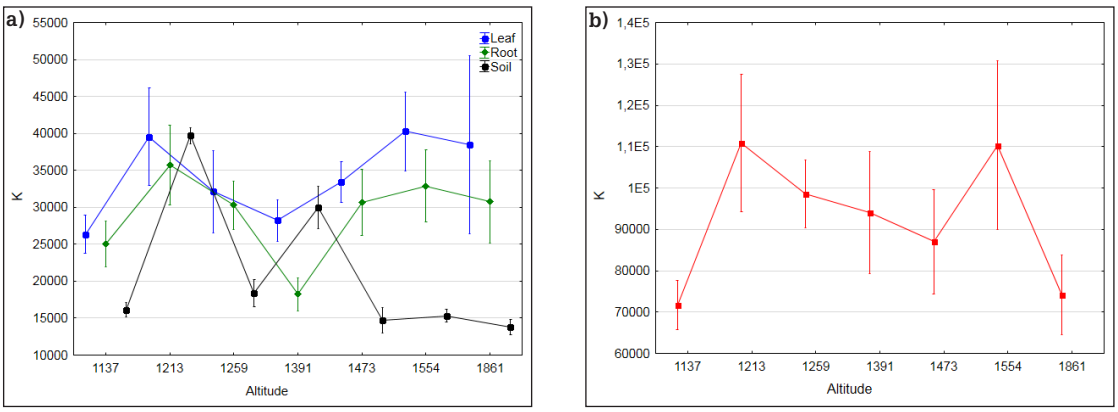

Fig. 6. Mean (± SE) levels of potassium in a) leaf and root of *S. carpatica* and soil depending on site indicated by altitude (m a.s.l.) (K-W H: leaf = 10.1, p = 0.12; root = 14.03, p = 0.03; soil = 49.9, p = 0.00) and b) stem (K-W H: stalk = 7.23, p = 0.3).

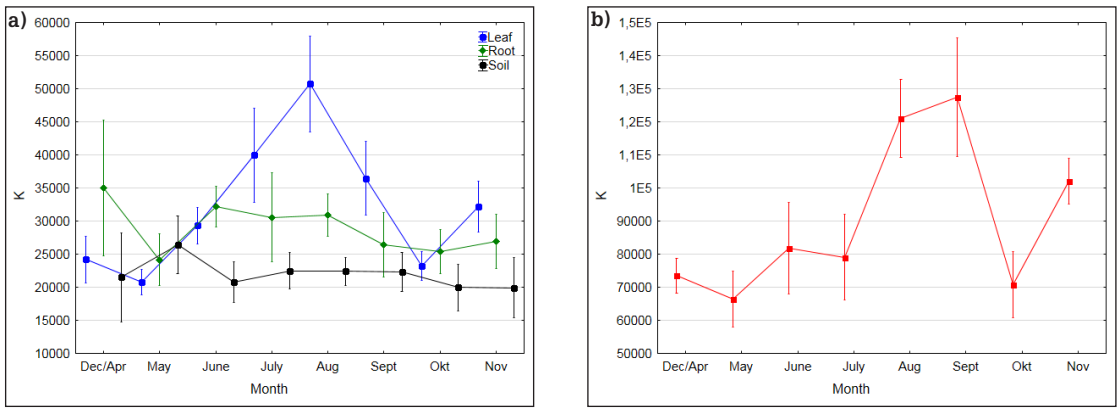

Fig. 7. Mean (± SE) levels of potassium in a) leaf and root of *S. carpatica* and soil (K-W H: leaf = 25.9, p = 0.0005; root = 5.9, p = 0.55; soil = 4.7, p = 0.7) and b) stem (K-W H: stem = 25.4, p = 0.0007) depending on season.

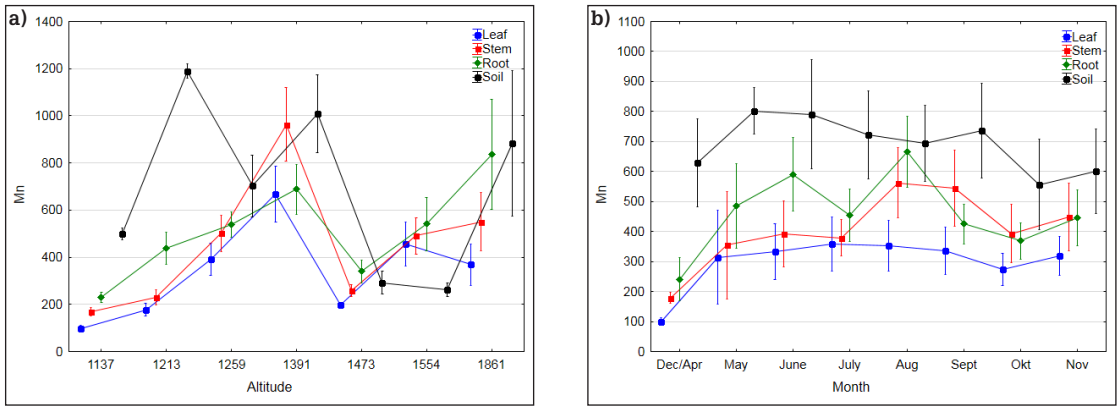

Fig. 8. Mean (± SE) levels of manganese in *S. carpatica* organs and soil depending on a) site indicated by altitude (m a.s.l.) (K-W H: leaf = 53.27, p = 0.00; stem = 43.64, p = 0.00; root = 28.49, p = 0.00008; soil = 42, p = 0.00) and b) season (K-W H: leaf = 8.97, p = 0.25; stem = 12.39, p = 0.09; root = 7.4, p = 0.38; soil = 5.64, p = 0.58).

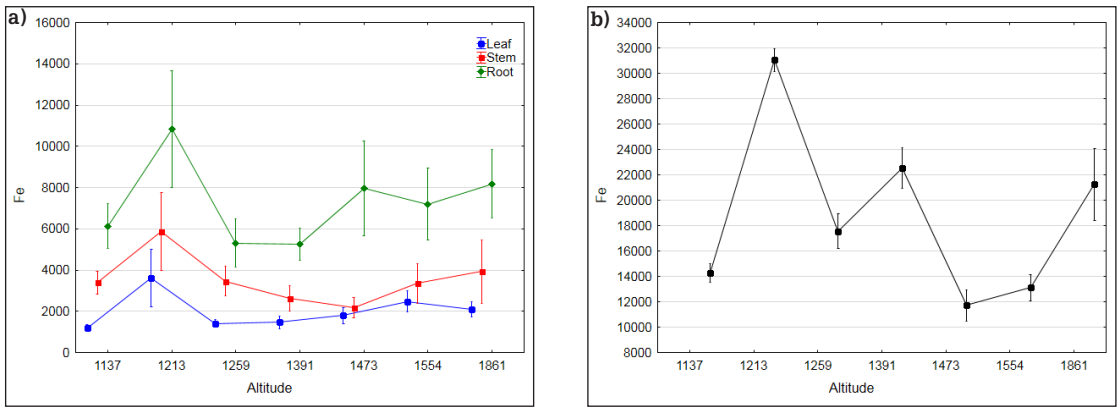

Fig. 9. Mean (± SE) levels of iron in a) *S. carpatica* organs and b) soil (K-W H: leaf = 11.008, p = 0.09; stem = 3.2, p = 0.8; root = 5.89, p = 0.43; soil = 55.45, p = 0.00) depending on site indicated by altitude (m a.s.l.).

(Fig. 8b). These amounts decrease during the winter months, though changes in Mn concentrations in both plant and soil are not considered significant.

Iron

Fe concentrations in plant organs (Fig. 9a) and in the surrounding soil (Fig. 9b) vary similarly with changing elevation and location. In all parts of the plant, the amount of Fe increases slightly around site 2, but this increase is most pronounced in the root. It also increases significantly in the soil at this site, which, together with the highest accumulation in the root, suggests that Fe uptake by the plant is related to Fe concentrations in the soil.

Changes in the amount of Fe in the organs of *S. carpatica* (Fig. 10a) and in the surrounding soil (Fig. 10b) also occur as a result of the year-season Again, the highest concentrations are confirmed in the root and soil. However, the most significant changes in Fe concentrations during the year are recorded in the leaf and stem. The Fe content in all parts of the plant increase slightly during the summer months. It is lowest in the spring and autumn months.

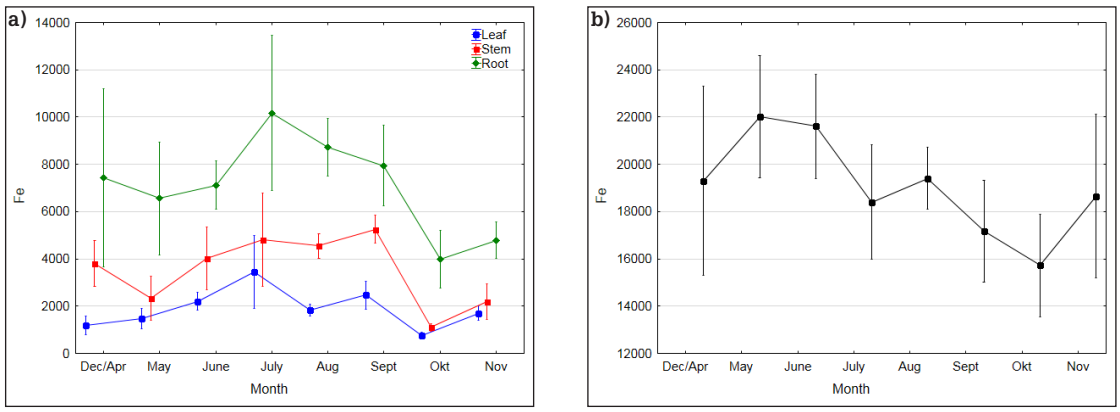

Fig. 10. Mean (± SE) levels of iron in a) *S. carpatica* organs and b) soil (K-W H: leaf = 20.25, p = 0.005; stem = 30.77, p = 0.00007; root = 12.23, p = 0.093; soil = 9.21, p = 0.24) depending on season.

Zinc

Changes in Zn concentration in leaves and stems of *S. carpatica* as a function of location (altitude) are presented in Fig. 11a. These concentrations were significantly lower than Zn concentrations in roots and soil (Fig. 11b). Significant changes in Zn concentrations under the influence of varying sites are recorded in leaf, root, and soil. In all parts of the plant, Zn concentration increased around site 4.

Phosphorus, nickel, copper and molybdenum

The presence of P, Ni, Cu and Mo in organs of *S. carpatica* and soil was not regular. Therefore, only a chi-square test was performed on the observed data in Table 1.

A high p-value > 0.05 indicates a non-significant relationship between organ type, soil, and the presence of detected elements. Therefore, we accept the null hypothesis indicating that there is no statistically significant relationship between the presence of detected element and either organ or soil type. However, based on Table 1, we can conclude that the presence of detected P in the root may be related to the presence of detected P in the soil.

Concentration levels of potential pollutants/harmful elements

Mercury

Total Hg (T-Hg) concentrations measured in *S. carpatica* organs (Fig. 12a) and in the surrounding soil (Fig. 12b) vary at sites with different elevations. Hg in the plant was most concentrated in the root and least in the stem. However, the most significant changes in Hg concentrations were recorded only in the soil. In leaves and stems, Hg concentrations did not change significantly with altitude. However, in roots, Hg concentrations increased around site 7. Hg concentrations in the surrounding soil (Fig. 12b) were significantly higher than in the plant. They were most elevated at sites 3 and 7. We also observed an increase in plant organs at the same sites. Thus, we can assume that the presence of Hg in the plant depends on the presence of Hg in the soil.

Changes in Hg concentrations in *S. carpatica* organs (Fig. 13a) and in the surrounding soil (Fig. 13b) vary throughout the year. The highest concentrations were found in soil, roots, and leaves and increased throughout the year, particularly in late autumn. However, significant changes in Hg concentrations were only recorded in the leaf. This may be related to the probable increase in precipitation during these

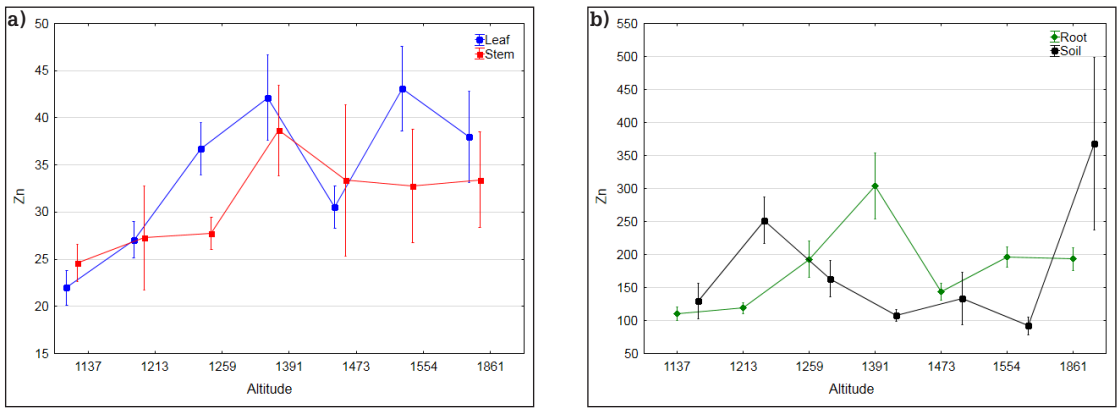

Fig. 11. Mean (± SE) levels of zinc in *S. carpatica*, in a) leaf and stem depending on site indicated by altitude (K-W H: leaf = 31.03, p = 0.00002; stem = 9.53, p = 0.15), and in b) root and soil depending on site indicated by altitude (m a.s.l.) (K-W H: root = 34.09, p = 0.00001; soil = 27.9, p = 0.00009).

		Plant organ					
		Flower	**Leaf**	**Root**	**Soil**	**Stalk**	**Sum**
P	Measured		11	19	19	16	65
	Unmeas.	11	76	69	71	74	301
	Sum	11	87	88	90	90	366
Ni	Measured		4	5	6	3	18
	Unmeas.	11	83	83	84	87	348
	Sum	11	87	88	90	90	366
Cu	Measured	3	43	41	33	38	158
	Unmeas.	8	44	47	56	52	207
	Sum	11	87	88	89	90	365
Mo	Measured	6	51	53	44	56	210
	Unmeas.	5	36	35	45	34	155
	Sum	11	87	88	89	90	365
Ti	Measured	3	62	58	53	58	234
	Unmeas.	8	25	30	37	32	132
	Sum	11	87	88	90	90	366
As	Measured		6	14	13	16	49
	Unmeas.	11	81	74	76	74	316
	Sum	11	87	88	89	90	365
Se	Measured		1	1	3		5
	Unmeas.	11	86	87	86	90	360
	Sum	11	87	88	89	90	365
Zr	Measured		45	34	35	45	159
	Unmeas.	11	42	54	54	45	206
	Sum	11	87	88	89	90	365
Cd	Measured		3		1	1	5
	Unmeas.	11	84	88	88	89	360
	Sum	11	87	88	89	90	365
Sn	Measured	4	15	16	15	14	64
	Unmeas.	7	72	72	74	76	301
	Sum	11	87	88	89	90	365
Sb	Measured	6	37	41	30	36	150
	Unmeas.	5	50	47	59	54	215
	Sum	11	87	88	89	90	365

Table 1. The number of times that the amount of elements (P, Ni, Cu, Mo, Ti, As, Se, Zr, Cd, Sn and Sb) was above the detection limit of a spectrometer and the number of times that it was under the detection limit of a spectrometer in the different organs of *S. carpatica* and in the soil. The calculated chi-square statistic for this analysis was: P: $x^2 = 5.51$, p-value = 0.238; Ni: $x^2 = 1.77$, p-value = 0.78; Cu: 2 = 4.31, p-value = 0.36; Mo: $x^2 = 3.54$, p-value = 0.47; Ti: $x^2 = 9.59$, p-value = 0.048; As: $x^2 = 6.94$, p-value = 0.14; Se: $x^2 = 4.107$, p-value = 0.39; Zr: $x^2 = 13.88$, p-value = 0.007; Cd: $x^2 = 4.24$, p-value = 0.37; Sn: $x^2 = 3.00$, p-value = 0.56; Sb: $x^2 = 4.04$, p-value = 0.4. The df was 4.

months. This is also confirmed by the slightly higher concentrations in leaves at the same time.

Chromium

Changes in Cr concentration in the organs of *S. carpatica* and its surrounding soil as a function of location - defined by altitude - are presented in Fig. 14a. The movement of Cr concentrations in all organs of the plant is similar. The highest Cr concentrations were measured in the stem. Significantly, the concentration increases at sampling site 2 in the stem and root, and the lowest concentrations are recorded at site 4. The analysis only shows significant changes in Cr concentrations in the leaf and root. However, Cr concentrations in all plant organs and in the soil tend to increase with increasing altitude.

Changes in Cr concentration in the organs of *S. carpatica* and its surrounding soil as a function of seasonal changes are presented in Fig. 14b. The behaviour of Cr concentrations in the root and stem is similar. Significant changes in Cr concentrations

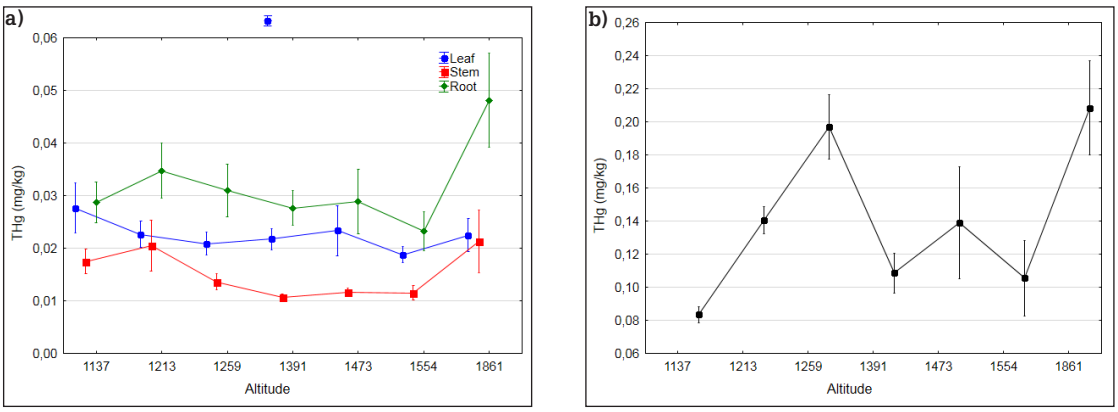

Fig. 12. Mean (± SE) levels of total Hg in a) *S. carpatica* organs and b) soil (K-W H: leaf = 2.46, p = 0.9; stem = 7.6, p = 0.3; root = 7.4, p = 0.3; soil = 31.7, p = 0.00002) depending on site indicated by altitude (m a.s.l.).

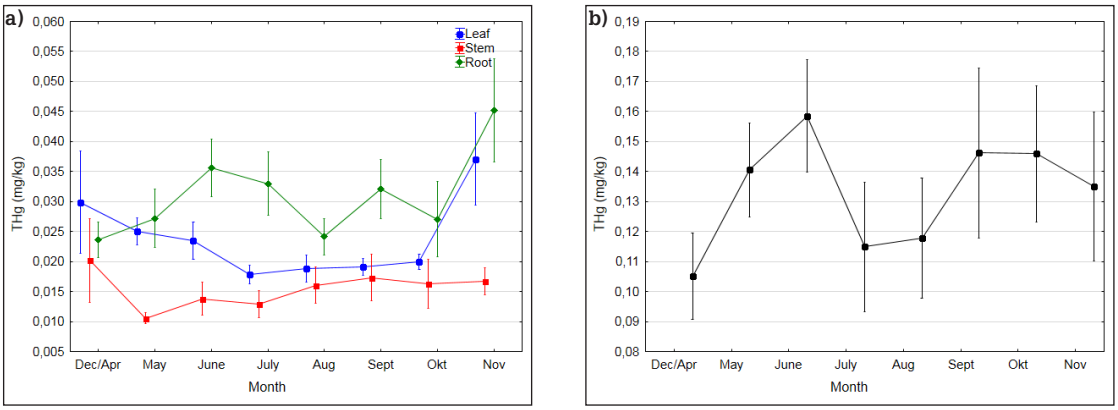

Fig. 13. Mean (± SE) levels of total Hg in a) *S. carpatica* organs and b) soil (K-W H: leaf = 18.5, p = 0.01; stem = 8.25, p = 0.31; root = 9.97, p = 0.2; soil = 5.42, p = 0.61) depending on season.

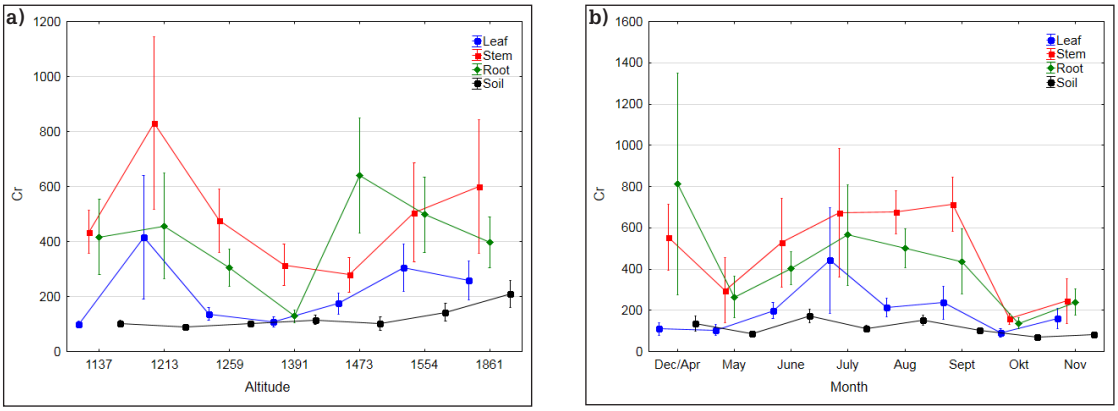

Fig. 14. Mean (± SE) levels of Cr in a) *S. carpatica* organs and soil depending on site indicated by altitude (m a.s.l.) (K-W H: leaf = 16.88, p = 0.01; stem = 2.34, p = 0.88; root = 13.13, p = 0.04; soil = 12.55, p = 0.05) and b) season (K-W H: leaf = 16.9, p = 0.02; stem = 31.24, p = 0.00006; root = 15.13, p = 0.03; soil = 25.97, p = 0.0005).

are recorded in all plant organs and in the soil. It can be observed that Cr increases in the summer and winter months.

Rubidium

Rb concentrations measured in *S. carpatica* organs (Fig. 15a) and in the surrounding soil (Fig. 15b) also varied with position - defined by altitude. The Rb concentration increased and decreased similarly in all organs. The highest amount of Rb was measured in the stem. In contrast, Rb concentrations in the soil were much lower than in the plant. For example, at site 5, the Rb concentration in soil was very low, while it was highest in plant organs. Changes in Rb concentrations were significant in all plant organs and tended to increase with increasing altitude.

Rb concentrations in *S. carpatica* organs (Fig. 16a) and in the surrounding soil (Fig. 16b) also varied seasonally. Rb concentrations in plant organs are significantly lower during the winter months and relatively stable during the rest of the year. Based on the increase in Rb concentration in plant organs in spring, we can speculate that *S. carpatica*

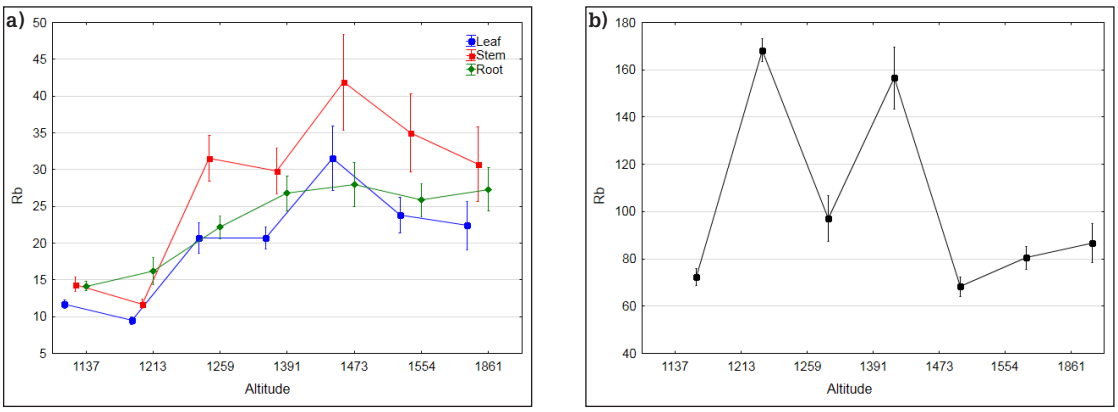

Fig. 15. Mean (± SE) levels of Rb in a) *S. carpatica* organs and b) soil (K-W H: leaf = 55.4, p = 0.00; stem = 52.5, p = 0.00; root = 37.53, p = 0.00; soil = 54.0, p = 0.00) depending on site indicated by altitude (m a.s.l.).

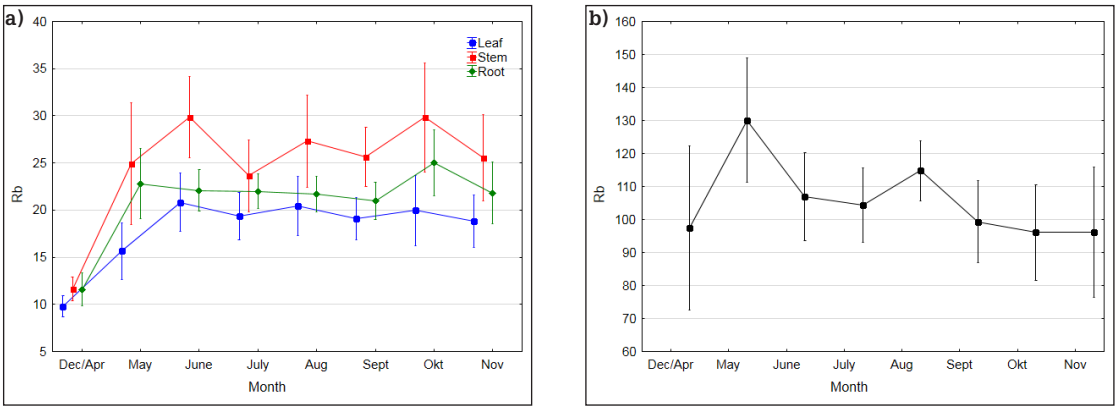

Fig. 16. Mean (± SE) levels of Rb in a) *S. carpatica* organs and b) soil (K-W H: leaf = 9.43, p = 0.22; stem = 9.4, p = 0.22; root = 7.17, p = 0.41; soil = 8.91, p = 0.26) depending on season.

actively utilises Rb during the growth of new shoots and does not retain Rb during the winter months when its metabolic activity is reduced.

Strontium

Changes in Sr concentration measured in *S. carpatica* organs (Fig. 17a) and in the surrounding soil (Fig. 17b) vary between sites with different elevation. Sr concentrations in all plant organs and in the soil changed significantly with altitude. At site 5, Sr concentrations in all plant organs increased significantly, and overall tended to increase in organs with increasing altitude. Soil Sr concentrations show similar changes. We can speculate that the amount of Sr in plant organs depends on the amount of Sr in the soil, and that the predominant mode of Sr uptake by the plant is likely via the root.

Barium

Ba concentrations in *S. carpatica* and its surrounding soil as a function of location - defined by elevation - are shown in Fig. 18a. The lowest Ba con-

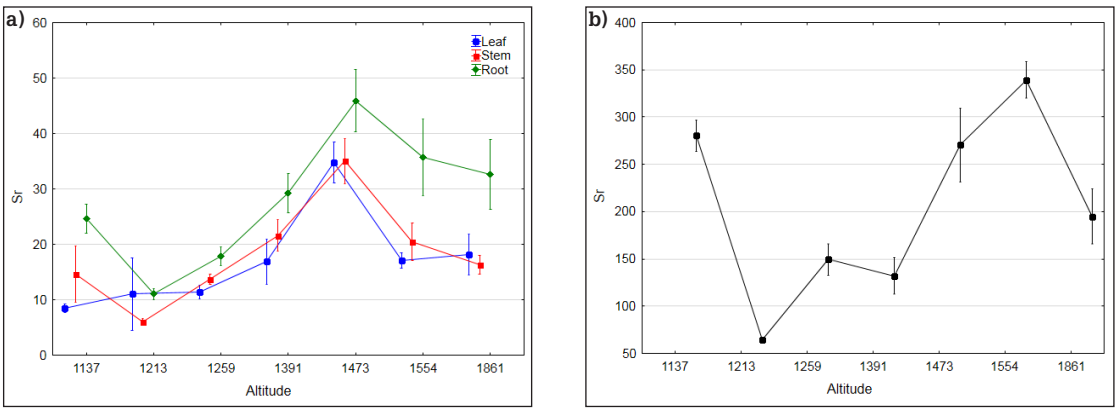

Fig. 17. Mean (± SE) levels of strontium in a) *S. carpatica* organs and b) soil (K-W H: leaf = 51.5, p = 0.00; stem = 56.23, p = 0.00; root = 44.18, p = 0.00; soil = 57.04, p = 0.00) depending on site indicated by altitude (m a.s.l.).

centrations were found in the leaves and the highest in the roots and soil. Near site 5, Ba concentrations increase in the plant and are highest in the root. Significant changes in Ba concentrations dependant on the changing site, were recorded in the leaf, root, and soil. Ba concentrations in *S. carpatica* and its surrounding soil as a function of changing season are shown in Fig. 18b. Ba concentrations are higher in winter and summer months, especially in roots and stems, then decrease in spring and autumn. Significant seasonal changes in Ba concentrations were observed in the leaf and even more so in the stem.

Lead

Pb concentrations in *S. carpatica* and its surrounding soil as a function of site - defined by altitude are shown in Fig. 19a. The detected Pb concentrations were similar in all plant organs and in the soil. Significant changes in Pb concentrations as a function of altitude were recorded in leaf, root, and soil. At the last sampling site, the concentration increased significantly, especially in the soil and in the root. This may indicate that the plant takes up Pb from the soil and accumulates it largely in the root. Fig. 19b shows the Pb concentrations in *S. carpatica* and its surrounding soil as a function of season. The highest concentrations in the plant organs, especially in the root, were observed during the summer months and in early winter. Significant changes in Pb concentrations during the year were only recorded in the leaf.

Titanium and zirconium

The presence of Ti and Zr in organs of *S. carpatica* and soil was not regular. Therefore, only a chi-square test was performed on the observed data in Table 1.

The low p-value < 0.05 indicates a significant association between the organ type or soil and occurrence of detected elements. Thus, we reject the null hypothesis, suggesting that there is a statistically significant relationship between the occurrence of detected elements and the organ type or soil.

Arsenic, selenium, cadmium, tin and antimony

The presence of As, Se, Cd, Sn and Sb in *S. carpatica* organs and soil was not regular. Therefore, only a chi-square test was performed on the observed data in Table 1.

The high p-value > 0.05 indicates a nonsignificant association between the organ type or soil and occurrence of detected elements. Thus, we accept the null hypothesis, suggesting that there is not a statistically significant relationship between the occurrence of detected elements and the organ type nor soil.

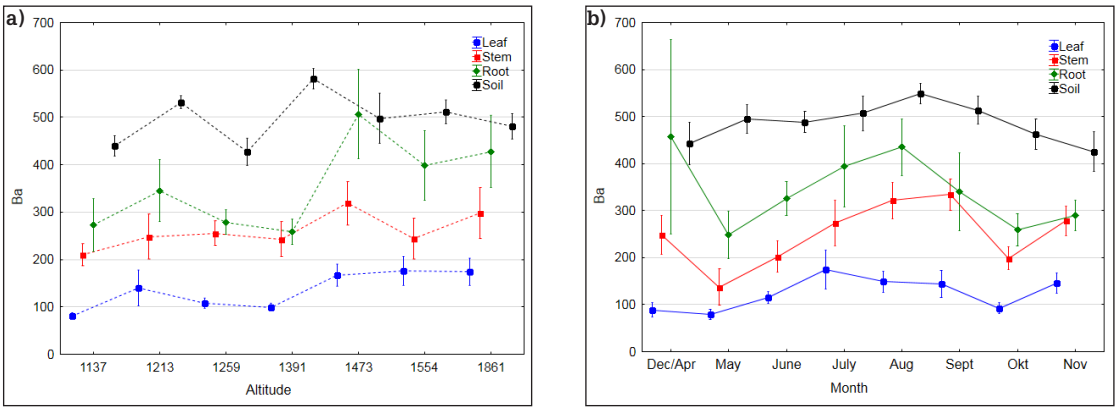

Fig. 18. Mean (± SE) levels of barium in a) *S. carpatica* organs and soil (K-W H: leaf = 24.01, p = 0.0005; stalk = 6.07, p = 0.41; root = 12.63, p = 0.05; soil = 23.9, p = 0.0005) depending on site indicated by altitude (m a.s.l.) and b) season (K-W H: leaf = 14.4, p = 0.04; stem = 25.04, p = 0.0007; root = 7.5, p = 0.37; soil = 10.96, p = 0.14).

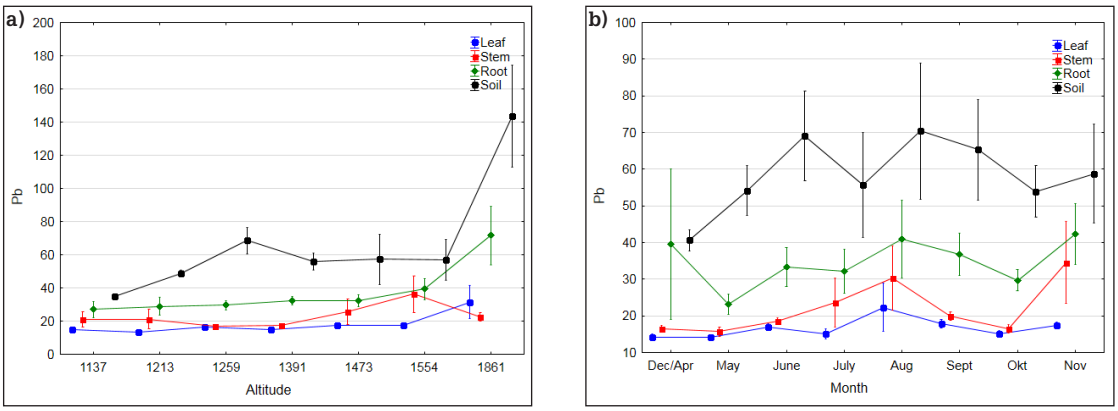

Fig. 19. Mean (± SE) levels of lead in a) *S. carpatica* organs and soil (K-W H: leaf = 30.01, p = 0.00004; stem = 12.05, p = 0.06; root = 25.01, p = 0.0003; soil = 38.28, p = 0.00) depending on site indicated by altitude (m a.s.l.) and b) season (K-W H: leaf = 16.03, p = 0.02; stem = 9.08, p = 0.25; root = 7.82, p = 0.35; soil = 4.31, p = 0.74).

Cobalt, silver

The measured amounts of Co and Ag in *S. carpatica* organs and surrounding soil were in all cases below the detection limit and were therefore insufficient for any analysis.

Discussion

The chemical composition of plants, in particular the uptake and accumulation of various elements, plays a crucial role in their growth, development, and interaction within ecosystems. In this study we aim to summarise the results of our research on the chemical composition of the Carpathian snowbell (*Soldanella carpatica*), focusing on the uptake and accumulation of chemical elements in its organs, and to understand the mechanisms governing the uptake, translocation, and sequestration of the biogenic elements P, S, Cl, Ca, K, Ni, Mn, Fe, Cu, Zn, and Mo, and potential pollutants Hg, Cr, Ti, Rb, As, Se, Sr, Zr, Ag, Cd, Sn, Sb, Ba, and Pb in *S. carpatica*.

As winter and spring samples are collected either as autumn samples preserved under snow or in conjunction with new spring samples may play a role in the increased concentration of certain elements (biogenic or contaminants) in plant organs during the winter and spring months. In such samples, the concentrations of each element may be higher because they have already gone through a whole growing season during which they have accumulated and gradually deposited the element. In addition, these samples have remained under snow cover, which may have increased the amount of the element in question on the surface of the plant organs. Therefore, if such samples are mixed with new shoots, misleading results may be obtained from this period.

In this work, the effect of soil pH on the uptake of chemical elements by the plant was not analysed, but pH was determined on randomly selected samples from each sampling site. This pH is only mentioned in the discussion part of the work because, after evaluating the results of the analysis and comparing them with the work of other authors, we found that soil pH might be an important factor in the mobility of the different elements in the soil. The test was carried out using the following procedure: 2 g of dried and grounded soil was shaken for one minute in a test tube containing 5 ml of distilled water, and the solution was then filtered using filter paper. An indicator paper (Ref: 1010F00021) was dipped into the resulting leachate and its colour compared with the sample scale. The resulting pH values of the seven Javorová Valley sampling sites ranged from 5 to 7 (i.e., the soils were observed to range from acidic to neutral).

Essential nutrients

Sulfur

The high concentrations of sulphur in the soil (Fig. 1b) suggest that the main source of S is the soil, as is also confirmed by Barker and Pilbeam (2015). However, the movement of concentrations in soils does not directly correspond to the movement of concentrations in plant organs, so we can assume that atmospheric deposition of S also plays a role in plant uptake (De Kok 1990). At site 4 (Fig. 1a) we observe reduced S concentration in the root, so we can assume a reduced S accumulation in this organ. De Kok (1990) reported in his work that a similar phenomenon was observed with high atmospheric concentrations of H_2S and SO_2, suggesting that in some situations S is accumulated more from the atmosphere by leaves and stems than from the soil. We can support this statement with the results from the second site, where S accumulation is increased in the leaf and stem (Fig. 1a), whereas it is lower in the root (Fig. 1a) and lowest in the soil (Fig. 1b) among all sites. Similar results are shown in the winter months (Fig. 2a), where S accumulation is high in all organs but low in the soil. Anlauf *et al.* (1987) carried out a study showing that SO_2 concentrations in the atmosphere are higher in winter than in summer.

Chlorine

The highest Cl concentrations were measured in the stem (Fig. 3b), so we can assume that Cl accumulation is mainly in the stem. In general, plants accumulate Cl mainly in leaves and stems (Barker and Pilbeam 2015). Although some sources claim that plants take up Cl mainly from the soil (Barker and Pilbeam 2015; Taiz and Zeiger, 2015), the results of this research show that Cl concentrations in the soil (Fig. 3a) were lower than in plant organs. White and Broadley (2001) argue that the natural supply of Cl to the soil is rainwater, and that the movement of Cl in the soil is largely determined by water flow. Based on our results, we see that soil Cl concentrations (Fig. 3a) remain constant; however, stem and leaf concentrations are significantly elevated at the second site. It is therefore possible that this is due to natural water flow, as site 2 is in a place where increased natural water flow is possible. At the same time, we can assume that *S. carpatica* can also take up Cl directly from precipitation. The possible dependence of the amount of Cl in the plant on rainwater is also shown by the results of increased Cl concentrations in stem and leaf during the summer months (Fig. 4a, b), when rainfall is more frequent. It can therefore be concluded that the supply of Cl to the plant is likely rainwater and may be taken up by the roots from the soil (White and Broadley 2001), but is mobile within the plant and, in *S. carpatica*, accumulates mainly in the stem.

Calcium

Calcium concentrations in all plant organs and in the soil do not differ significantly. White and Broadley (2003) and Yang and Jie (2005) argue that Ca generally enters the plant from the soil solution via the roots. Kirkby and Pilbeam (1984) argue in their research that the known physiological disorders resulting from localised Ca deficiency in the plant are due to inadequate Ca distribution in the plant rather than limited uptake. Therefore, it can be assumed that the distribution of Ca throughout the plant is similar in all organs without any disturbance in the uptake of this element. At site 4 (Fig. 5a), the Ca concentration decreases both in the soil and in all

plant organs, suggesting a relationship with a factor manifested at this site. This may be due to the specific geological subsoil. Several studies have reported that the elemental composition of the soil is determined by the parent rock (He *et al.* 2005; Alloway 2012; Yadav *et al.* 2023). At the same time, Sapek (2014) reported that the Ca concentration in the soil solution is significantly higher in acidic soils. Thus, the dependence of soil Ca concentration on soil pH can also be assumed. On the other hand, Bowen and Dymond (1955) found that sandy, acid soils contain relatively low amounts of Ca. In the geological map of Javorová Valley we observed that Site 4 has a sandy subsoil geologically. The elevated Ca concentration in *S. carpatica* and the surrounding soil is mainly observed in the summer months, which may confirm that Ca is mainly supplied to the soil and the plant by precipitation (Sapek 2014), which is frequent during this period.

Potassium

The potassium content of *S. carpatica* and surrounding soils differs. Plants take up K mainly from the soil (Barker and Pilbeam 2015; White *et al.* 2021). Our results show that soil K concentrations (Fig. 6a) are variable, but K concentrations in plant organs (Fig. 6a, b) are not always fully proportional. An important factor influencing soil K availability is the parent rock (He *et al.* 2005; Alloway 2012; Yadav *et al.* 2023), its weathering, and the associated soil composition. Pal *et al.* (2002) and Manning (2010) report that one of the ways K enters the soil is through weathering or dissolution of feldspars in rocks and soils. These are found, for example, in granitic rocks or as particles in sands. Pal *et al.* (2002) also report that K concentrations in sands are relatively high, while Manning (2010) mentions a slower and less efficient release of K from granitic rocks than directly from feldspar particles that may be part of sands. For example, in Fig. 6a we see that soil K concentrations were elevated at the second and fourth sites. At these sampling sites the soil had a sandy character. At the same time, in our results we observe a significant increase in K concentrations in plant organs during the summer months, when precipitation is usually more intense. Mackay and Barber (1985) found that as soil moisture increased within the optimum, diffusion increased and thus K^+ uptake by the rhizosphere was higher, but when soil moisture exceeded the optimum, the amount of oxygen in the soil decreased and thus root growth was slowed, resulting in lower K^+ uptake by the plant. This is a potential explanation for increased K levels in the organs of *S. carpatica*, but not in the surrounding soil. The highest K concentrations were found in the stem and similar results were also reported by Xu *et al.* (2018) when testing K accumulation in agricultural crops.

Manganese

Manganese concentrations in *S. carpatica* organs varied similarly, with the highest values measured at site 4 (Fig. 8a). Here, Mn concentrations were almost four times higher than at site 1 and site 5. According to Barker and Pilbeam (2015), plants take up Mn exclusively from the soil, specifically from the soil solution, in the form of Mn^{2+}. At this site (site 4), soil Mn concentrations were elevated, but were higher at site 2, where, in contrast, plant Mn concentrations were significantly lower. The most likely reason for these variations in soil Mn concentrations is soil type - specifically the proportion of soil organic matter and soil pH (Sims 1986; Obrador *et al.* 2007). In most acidic soils with a pH below 5.5, there is an increased concentration of soluble Mn^{2+}, the form of Mn that can be absorbed by plants (Kogelmann and Sharpe 2006; Millaleo *et al.* 2010). The results of the soil pH test showed a pH of 6–7 at site 2 and a pH of around 6 at site 4, so this claim is not confirmed. Page and Feller (2005), based on an experiment on *Lupinus albus*, found that Mn tends to accumulate mainly in roots and stems, from where it is transferred to photosynthetically active leaves. Thus, based on all the findings, we may conclude that the distribution of Mn in the plant is uniform, as confirmed by similar concentrations and their movement in the different organs of *S. carpatica* (Fig. 8a, b). In the graph showing the effect of seasonality (Fig. 8b) on Mn concentrations in *S. carpatica*, the changes were not as pronounced as in the graph showing the effect of sampling sites (Fig. 8a). Mn concentrations in plant organs increased during spring and summer. In their work, Wildová *et al.* (2021) reported that increased Mn concentrations in leaves of three different trees occurred during the growing season and with increased precipitation. Page and Feller (2005), in an experiment with wheat, reported that Mn from the roots was mainly distributed to the shoots. This could be the reason for the increased Mn concentrations in the root during the growing season (Fig. 8b), as *S. carpatica* is a hemicryptophyte (Kochjarová *et al.* 2016) and thus grows new shoots from the root (Raunkiaer 1934).

Iron

The highest Fe concentrations in *S. carpatica* were measured in the root and its surrounding soil. Fe concentrations in both soil and all plant organs increased significantly around site 2 (Fig. 9a, b). According to Schmidt (1999) and Barker and Pilbeam (2015), soil is the main source of Fe for plants, which is taken up by the roots. Dicotyledonous plants, which include the family Primulaceae (Xu *et al.* 2017), take up Fe in its ferrous form Fe^{2+} (Lindsay and Schwab 1982). It is likely that the increase in soil Fe concentrations, (e.g., at site 2; Fig. 9b), is due to reduced soil pH. McCauley *et al.* (2009) report that micronutrients such as Fe are more available in soils with a pH in the range of 5–7. As mentioned above, the results of the soil pH test showed a pH of 6–7 at site 2. It can therefore be concluded that the conditions for the presence of Fe in the soil were optimal. Due to seasonality, Fe concentrations in *S. carpatica* were highest in the root, especially in summer. Conversely, soil Fe concentrations decreased during the summer months. However, the relationship between seasonality and Fe accumulation in the plant has not been clearly demonstrated (Barker and Pilbeam 2015).

Zinc

Zinc concentrations were significantly higher in the root and surrounding soil of *S. carpatica* than in the remaining plant organs. Dinh *et al.* (2015) observed similar results in an experiment on *Thlaspi arvense*. The arbuscular mycorrhizal fungi (AMF) could be an explanation for this increased concentration of Zn in the root of *S. carpatica* (Zubek *et al.* 2018). Christie *et al.* (2004), Hildebrandt *et al.* (2007) and Zhu *et al.* (2001) state in their research that under high soil Zn concentrations, colonisation of roots by AMF can lead to reduced accumulation of Zn (and other metals) in plant tissues. At the same time, we observe an increase in Zn concentrations in all plant organs around site 4 (Fig. 11a, b). At this site there are also significant changes in the concentrations of other elements, especially Mn and Ca. In an experiment with *Noccaea caerulescens*, Dinh *et al.* (2015) observed a reduction of P and Ca concentrations in shoots by up to 50% at elevated Zn concentrations. As mentioned above, Ca concentrations were significantly reduced at site 4 (Fig. 11a), which could be one of the factors influencing the elevated Zn concentrations at this site. Another factor could be soil pH. According to Sims (1986) the distribution of Mn and Zn is strongly influenced by soil pH, where at a pH below 5.2 these two elements were dominant. As mentioned above, the soil pH was 6–7 at site 2 and around 5 at site 7. We could therefore conclude that the concentrations of Zn in the soil may be related to the soil pH, as the concentrations were highest at site 2 and 7.

Phosphorus, nickel, copper, and molybdenum

The elements P, Ni, Cu and Mo were rarely detected by the XRF spectrometer in *S. carpatica* and its surrounding soil, and therefore it was not possible to perform a visual statistical analysis of these elements. Contingency tables of these elements were constructed, and chi-square tests were performed to determine whether the presence of a given element depended on the type of plant organ or the soil in which it was detected. This may indicate that these elements are present in low concentrations in the plant and its surrounding soil. However, it is possible that this irregularity was due to insufficient plant or soil sample material, and the XRF spectral analysis method did not capture enough backscattered radiation of the element in question for the instrument to unambiguously assess its presence (Potts 1987). However, it must be remembered that each chemical element has a certain minimum level of identification when using the ED-XRF spectrometer. In particular, P has a high minimum level of identification. The complexity of the chemical composition of plant tissues treated as analytical matrices is considered to be the main reason why there is no single answer to the question of how to qualitatively and quantitatively determine relevant phosphorus compounds, despite the use of a relatively high-quality ED-XRF spectrometer (Wieczorek *et al.* 2022).

After nitrogen, the second most common limiting macronutrient affecting plant growth is phosphorus, which is mainly taken up by the plant from the soil (Schachtman *et al.* 1998), but this element has only rarely been identified in *S. carpatica* (Table 1). However, as mentioned above, these results are not reliable due to the high minimum level of phosphorus identification by the ED-XRF spectrometer. We can speculate that the cause of this irregularity may also be due to the frequent presence of P in the soil in forms that are not cumulative for plants (Schachtman *et al.* 1998; Holford 1997). It can therefore be concluded that the availability of P to the plant may depend on its availability in the soil (Xiao *et al.* 2009). Unfortunately, in this study we do not have sufficient and credible data to assess the presence and accumulation of this element.

Since nickel is considered a trace element (Yusuf 2011), its presence was detected only a few times in the organs of *S. carpatica* and in the surrounding soil. It was most frequently detected in the soil (6 times out of a total of 90 samples) and in the root (5 times out of a total of 88 samples) (Table 1). Based on these results, we assume that the source of Ni uptake by the plant is the soil, especially the soil solution (Yusuf 2011). Temp (1991) states in his work that Ni uptake decreases at higher pH values of the soil solution. Experimental soil pH values from our sampling sites were in the range of 5.0–7.0. Panda *et al.* (2007) reported that Ni^{2+} uptake by *Lathyrus sativus* species increased up to pH 5.0 and further decreased with increasing pH up to 8.0, which may also be the reason for the low Ni uptake. Another reason for reduced Ni uptake may be the competition of Ni^{2+} ions with other essential metal ions when taken up by the roots (Yusuf 2011). In general, the uptake of heavy metals by plants is influenced by the calcium ion Ca^{2+}. For example, Ca^{2+} decreased Ni^{2+} uptake in *Arabidopsis bertolonii*, whereas it increased Ni^{2+} uptake in *Berkheya coddii* (Gabbrielli and Pandolfini 1984; Boyd and Martens 1998).

The presence of copper was slightly more frequent than other elements analysed by the chi-square test. The detected presence had a success rate of almost 50% in all plant organs (Table 1). According to Barker and Pilbeam (2015), plants mainly take up Cu from the soil, and its availability in the soil is strongly influenced by the pH of the soil (Yruela 2009; Barker and Pilbeam 2015). Cu is more available in acidic soils, (i.e., soils with low pH), because the soil solution of such soils contains more Cu ions that are acceptable to plants. The availability of Cu in soils starts to decrease above pH 7.0 (Barker and Pilbeam 2015). As mentioned above, the experimentally determined soil pH at our sampling sites was in the range of 5.0–7.0, so we can assume that this factor may influence the presence of Cu in *S. carpatica* and its surrounding soil, as the presence in both plant and soil was close to 50% (Table 1). According to Yruela (2009) and Jarvis and Whitehead (1981), the availability of Cu in the soil is also influenced by the nitrogen supply. Plants growing in high N soils also require a greater supply of Cu (Yruela 2009). However, in this work, the presence and amount of N is not analysed, so we cannot apply this theory.

The detected presence of molybdenum (Table 1) was also frequent, in all plant organs Mo was present in more than 50% of the cases. Heuwinkel *et al.* (1992) carried out an experiment on tomato plants which showed a significantly increased uptake of

Mo in the absence of P. However, we cannot evaluate this fact in this study due to the insufficient data on P identification mentioned above. According to Reddy *et al.* (1997) the availability of soil Mo to plants is strongly influenced by soil pH. They claim that in neutral or slightly alkaline soils, Mo is highly soluble, and thus available to plants as MoO_4^{2-}. However, once the pH starts to decrease (values of around 5.0– 5.5), the availability of Mo also starts to decrease sharply (Reddy et al. 1997). This is more or less true for our soil pH values which, as mentioned above, were in the range of 5.0–7.0. We can therefore assume that the availability of Mo in the soil is probably sufficient for *S. carpatica*, even if its presence was not always detected.

Potential pollutants/harmful elements

Mercury

Hg accumulation was highest in soil (Fig. 12b) at 0.08 mg/kg and was also highest at site 7, the sampling site at the highest elevation. Hg levels detected in roots followed a similar trend. Kimáková *et al.* (2020) reported that industry in Slovakia also contaminates high mountain ranges, such as the High Tatras, through north-westerly air currents. In all plant organs, Hg concentrations remained at approximately the same level despite the change in location and increasing altitude. However, a slight increase in Hg levels was also observed in stems and leaves at site 7. The highest values were measured in the root, followed by the leaf, and finally in the stem. Hronec (1996) reported that Hg concentrations decrease in the following order: leaf, stem, grain, tuber, and fruit. He goes on to say that the availability of plant-available Hg in the soil is generally low and tends to accumulate in the roots, creating a 'barrier' to further Hg progression and accumulation in other plant organs. He also argues that Hg accumulated by above-ground plant organs is mostly of atmospheric origin. The results of the experiment by Kimáková *et al.* (2020), on the other hand, showed that plants take up Hg mainly from the soil, emphasising that the plant-soil system is influenced by the amount of soil organic matter, soil reactions, and the genotype of the plant under study. AMF could be another explanation for the slightly higher accumulation of Hg in the root. According to Miransari (2011), AMF can phytostabilise heavy metals in the soil and absorb and detoxify heavy metals themselves. In this way, AMF can help the host plant to survive heavy metal stress. The results of Hg concentrations in different plant organs of the same family show a similar trend (Kimáková *et al.* 2020), so we can assume that other species of the Primulaceae family may also take up and accumulate Hg similarly to *S. carpatica*. Yin *et al.* (1996) and Kimáková *et al.* (2020) also report that soil pH is an important factor influencing Hg adsorption to soil. Maximum Hg adsorption occurred in acid soils with a pH between 3.0 and 5.0 (Yin *et al.* 1996). Experimentally determined soil pHs from *S. carpatica* sampling sites ranged from 5.0 to 7.0, with the lowest pH of 5.0 found at site 7, the site where Hg concentrations were elevated in plant organs, particularly roots and soil.

Due to seasonal changes, Hg concentrations in roots and leaves increased mainly during the winter months and increased slightly in late spring and early summer - with the retreating snow and its gradual melting. Kimáková *et al.* (2020) write that during the spring months the proportion of mobile Hg compounds increases with low temperatures and increased humidity. However, the collection of spring samples mixed with autumn samples (or those that survived the winter under snow) may again play a role in these results.

Chromium

Differences between chromium concentrations in *S. carpatica* and the surrounding soil were not pronounced. They remained at almost the same level at all sampling sites in the soil (Fig. 14a), except at site 7 where the concentration increased slightly. Soil Cr concentrations followed a similar trend with changing seasons. Shahid *et al.* (2017) and Sharma *et al.* (2020) reported that Cr accumulates most in plants in the roots due to its low mobility in roots compared to other heavy metals. Barančíková (1998), in her partitioning of heavy metals, states that Cr has maximum mobility in soil at a pH of less than 5.5. Our results show the highest concentration in the stem and leaf at site 2, where the pH is around 6.5, but the increase in soil concentration occurs at site 7, where the pH is around 5.0. Shahid *et al.* (2017) report that translocation to aerial shoots is very limited and depends on the chemical form of Cr in the tissue. He goes on to say that translocation and distribution of Cr in the plant depends on the oxidation state of Cr ions in the plant species and on its concentration in the growth medium. In *S. carpatica*, however, Cr concentrations were higher in the stem than in the root, especially at site 2, where elevated Cr concentrations were also measured in the leaf but were found to be slightly elevated in the root (Fig. 14a). This suggests a possible atmospheric deposition of Cr in this area.

Rubidium

Rubidium showed an increasing trend in all plant organs of *S. carpatica* (Fig. 15a) depending on the sampling site, (i.e., Rb increased with increasing altitude). The highest values were measured in the soil (Fig. 15b), but the concentrations in the plant followed the opposite trend. For example, at sites 2 and 4, Rb concentrations were highest in the soil, but in all plant organs at these sampling sites, the concentrations were either the same as at the previous sampling site or the concentrations showed a slightly decreasing trend. Conversely, when Rb concentrations decreased in the soil (sites 3 and 5), they increased in the plant. Helmke and Sparks (1996) state in their paper that Rb is usually not found as a pure mineral in soil unless it comes from the parent rock. They argue that Rb is mainly found in soil as trace amounts of other compounds, particularly in feldspars and micas, or adsorbed to the soil solid phase, particularly by illite. From the geological map of the Javorová Valley we observed that the parent rock of Site 2 and 4 consists of deluvial-proluvial clay sediments, interspersed locally

with gravels and sands, which supports the thesis of elevated Rb concentration at this sampling site. Läuchli and Epstein (1970) suggest that the uptake and transport of Rb by plants is very similar to the mechanism of potassium transport. Helmke and Sparks (1996) state that the availability of K in the soil is also dependent on the parent rock and that Rb may be partially replaced by K in plants as their properties are similar. In addition, figure 7a shows that soil K concentrations were also elevated at sites 2 and 4. Aschmann and Zasoski (1987), in their experiment on the uptake of Ni^{2+} and Rb^{+} by oat plants (*Avena sativa*), found that the uptake of both elements is strongly influenced by temperature, (i.e., the uptake of these elements decreases with decreasing temperature). In Fig. 16a we can see that the concentration of Rb in all plant organs of *S. carpatica* was lowest during the winter and spring months, (i.e., the coldest months). This may be related to another factor observed by Tanada (1962). He found that bean roots grown under soil Ca deficiency absorbed more Rb at a faster rate than those grown under higher soil Ca levels. In the presence of Ca, the uptake decreased significantly. Figure 6b shows that Ca concentrations in *S. carpatica* are relatively high in the winter months, while Rb concentrations are lowest in the winter months (Fig. 16a). For the rest of the year, Rb concentrations in plant organs and soil were at nearly the same level.

Strontium

Strontium concentrations in plant organs of *S. carpatica* (Fig. 17a) increased with increasing altitude and varied almost equally. The highest concentration measured was at site 5. Isermann (1981) reported in his book that Sr uptake decreases in the presence of Ca^{2+} and that the whole uptake mechanism depends more on the total Ca^{2+} and Sr^{2+} concentration together in the soil than on the Sr^{2+} concentration alone. In the case of *S. carpatica*, this is likely not the case, as the Ca (Fig. 5a) and Sr (Fig. 17a, b) concentrations are rather similar. Günther and Schroeder (1968) suggest that Sr^{2+} uptake is lower in soils with high clay content than in soils with higher organic matter content. Figure 17b shows that Sr concentrations decrease at sites 2 and 4. According to the geological map of Javorová Valley we observed that these two sites have deluvial-proluvial clay sediments, locally interspersed with gravels and sands.

Barium

The highest concentrations of barium were found in the substrate, followed by concentrations in the root (Fig. 18a). With increasing altitude, Ba concentrations in all plant organs of *S. carpatica* tended to increase slightly (Fig. 18a). In their study, Abreu *et al.* (2012) reported that Ba mobility was higher in acidic soils. The results of our analysis of Ba concentrations (Fig. 18a) as a function of site (altitude) show the lowest Ba concentration in the soil at site 3, where the highest pH was found among all sites. The highest Ba concentration was found at site 4 with a soil pH of 5. Nogueria *et al.* (2010) observed Ba accumulation in maize plants in soils with much lower Ba concentration and low pH (5.1–5.7). Ba concentrations in *S. carpatica* at site 4 are much lower in roots and other plant organs (Fig. 18a), while soil Ba concentrations are highest (Fig. 18a). In addition, soil Ba concentrations behaved in exactly the opposite way to soil Ca concentrations. Menzie *et al.* (2008) and Abreau *et al.* (2012) suggest that the two elements may interact, with the presence of Ca reducing Ba concentrations. Ba concentrations as a function of seasonality (Fig. 18b) were highest in the soil but did not show significant changes in concentrations throughout the year. They increased slightly in summer, particularly in August and decreased between autumn and spring. In plant organs (Fig. 18b) these elements increased in winter and summer and decreased in spring and autumn. Böhmová and Šoltés (2017) found an increase in Ba concentrations in *Fallopia japonica* during flower formation. S. carpatica has a spring blooming season (Kochjarová *et al.* 2016) and, in contrast, Ba concentrations in the plant were reduced during this period.

Lead

Pb concentrations were similar in plant organs, but the highest Pb concentrations were found in the root (Fig. 19a). In the soil, Pb concentrations were higher than in the plant (Fig. 19a). In agreement with Asati *et al.* (2016), this suggests that terrestrial plants tend to take up Pb from the soil and subsequently retain it in the roots. Another explanation could be AMF, which can accumulate Pb, and since they are part of the plant roots, it may appear that Pb accumulates more in the root. A similar phenomenon was also observed by Adeyemi *et al.* (2021) in soybean plants, where AMF helped to retain Pb in the roots without significant Pb translocation to the rest of the plant. Concentrations in *S. carpatica* organs and in the substrate continued to increase slightly with increasing altitude, with the highest concentrations (except in the stem) occurring at site 7, the highest altitude sampling site. Concentrations in the stem decreased at this site. According to Dauer *et al.* (2007) and Richardson and Friedland (2016), metals are more mobile in soils with lower pH. Site 7, where Pb concentrations are elevated, has a soil pH of 5. However, site 4 also has a pH of 5 and Pb concentrations are not elevated there. Zhou *et al.* (2019) found that pH values were significantly negatively correlated with Pb concentrations in soil organic horizons. Therefore, it is possible that this is the reason for the elevated concentrations at site 7. They further stated that the results showed an increasing trend in topsoil Pb concentrations with increasing elevation. Stankwitz *et al.* (2012) and Zechmeister (1995) noted that forests at higher elevations may receive higher annual precipitation and cloud cover, and that deposition of contaminants also increases at higher elevations. Based on our results, we see increasing Pb concentrations in leaves at site 7 (Fig. 19a), which may also indicate increased atmospheric deposition of Pb. Pb concentrations were also highest in soil and roots in response to the change in season (Fig. 19b). Soil Pb concentrations were highest in

August and lowest in winter and spring. In roots, Pb concentrations were also elevated in August, but higher concentrations were found in the winter months and in November. Prodaj and Kompišová Ballová (2021) conducted a similar study on blueberry in the Low Tatras at two different sites and found that at the first site (Chochula), the highest Pb levels were recorded in October and the lowest in June. On the other hand, at the second site (Prašivá), they observed lower Pb concentrations in October and higher Pb concentrations in June. They suggested that this may be due to differences in weather conditions, or differences in growth and development of individual blueberry plants. Shparyk and Parpan (2004) suggest that element accumulation may also be highly influenced by slope position and snow cover.

Conclusion

This study focused on obtaining data on the concentrations of biogenic and potentially toxic chemical elements in the Western Carpathian, alpine endemic species - Carpathian snowbell (*Soldanella carpatica*), which was collected for two years in the Javorová Valley in the High Tatras. We found that biogenic elements in *S. carpatica* were distributed and accumulated fairly evenly in all plant organs, with a few exceptions where elements accumulated significantly more in the stem. In particular, chlorine and potassium accumulated in this way. Zinc behaved differently from the other biogenic elements, accumulating most in the root. All potential pollutants accumulated primarily in the root (or were potentially impacted by AMF), and somewhat less in the stem, or nearly equally in both. The concentration of all potentially toxic elements was significantly higher in the soil than in the plant itself, with exception of chromium, where the concentration was higher in the plant than in the soil.

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