Regional Variation in Selected Trace Elements and Heavy Metals in Sheep Wool in Croatia

Regionalne razlike u odabranim elementima u tragovima i teškim metalima u ovčjoj vuni u Hrvatskoj

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REGIONAL VARIATION IN SELECTED TRACE ELEMENTS AND HEAVY METALS IN SHEEP WOOL IN CROATIA

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SUMMARY

The aim of this study was to determine the concentrations of selected trace elements (Cu, Fe, Zn, Mn, Cr) and heavy metals (Cd, Pb, Ni) in sheep wool from three regions of Croatia: Posavina (around Županja), Bilogora (around Grubišno Polje), and the island of Pag. Among the elements investigated, the highest concentrations were observed for iron (Fe 193.09 mg/kg), followed by zinc (Zn 64.03 mg/kg), manganese (Mn 7.06 mg/kg), and copper (Cu 2.59 mg/kg). Very low concentrations (below 1 mg/kg) were observed for nickel (Ni 0.24 mg/kg), chromium (Cr 0.28 mg/kg), lead (Pb 0.02 mg/kg), and cadmium (Cd 0.004 mg/kg). Significant regional differences ($P<0.001$) were observed for almost all elements, except for Cu. Sheep wool from the Posavina region had significantly higher concentrations of Zn and Pb, while wool from Pag had the highest concentrations of Fe, Ni, and Cr. Wool from the Bilogora region had significantly higher concentrations of Mn and Cd compared with the other two regions. Based on the determined concentrations of the selected elements in sheep wool, it can be concluded that all three regions in Croatia are relatively free from significant pollution by the studied elements, as their presence is primarily associated with the underlying bedrock.

Keywords: wool, regions, trace elements, heavy metals, environment

INTRODUCTION

Awareness of the state of the environment has increased substantially in recent decades, prompting researchers to assess pollution levels using various biological and environmental samples, such as soil, animal blood, milk, urine, hair, and wool. In this context, hair and sheep wool have proved to be a good bioindicator of environmental conditions (Martínez-Morcillo et al., 2024). Wool, along with other animal fibers, is easy to collect, as obtaining it is non-invasive, painless, and causes minimal stress to the animal, since it is part of routine zootechnical procedures such as shearing. Furthermore, hair can be easily stored for later analysis, as it does not degrade readily (Janíček et al., 2025). This makes it a stable sample that can be kept at room temperature for long periods without significant changes in its chemical composition. Moreover, it contains high concentrations of trace elements – up to ten times higher – which tend to accumulate in hair, unlike in blood serum or urine (Maugh, 1978). It also enables monitoring of exposure history over time (for example, 2 cm of wool represents approximately 10 weeks of growth; Hawkins and Ragnarsdóttir, 2009), whereas blood reflects only the current status. Therefore, hair is often a better bioindicator than blood, urine, or milk, as it reflects feed quality and environmental conditions (Patkowska-Sokoła et al., 2009).

Although wool and hair offer many advantages for assessing environmental conditions, they often contain external impurities such as soil, feces, and forage particles. Szigeti et al. (2020) note the problem of these impurities, along with uneven mineral intake, when determining the mineral status of sheep. Therefore, washing before analysis is essential, particularly for sheep wool, which is usually dirtier than hair. This is clearly demonstrated by the results of Hawkins and Ragnarsdóttir (2009), who reported a significant difference between the concentrations of trace metals in washed and unwashed sheep wool. For example, the mean Cu concentration decreased from 6.49 μg/g in the unwashed sample to 3.53 μg/g in the washed sample.

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An even greater difference was observed for Zn, with its concentration after washing (128 μg/g) approximately ten times lower than in the unwashed sample (1,858 μg/g). Furthermore, Hawkins and Ragnarsdóttir (2009) demonstrated that washing procedures for wool are element-specific and should not be routinely applied to different elements. They also showed that the order of reagent use can affect the reliability of each washing procedure.

Due to these advantages, hair and wool are widely used as bioindicators of environmental conditions and pollution. Owing to its unique structural properties and capacity for long-term accumulation of chemical elements and contaminants, wool can reflect the level of environmental exposure of animals to different pollutants. Consequently, it has been widely employed in environmental monitoring studies, particularly for assessing the presence and distribution of trace elements and other contaminants in terrestrial ecosystems. For example, Patkowska-Sokoła et al. (2009) reported significant differences in the concentrations of biogenic elements in wool samples from Poland, Greece, and Syria. Wool from Syrian Awassi sheep contained up to five times more magnesium (Mg) than that of Polish mountain sheep. Furthermore, wool from Syria had much higher levels of aluminum (Al), iron (Fe), titanium (Ti), and arsenic (As) compared to wool from Europe, indicating the strong influence of environmental and geographical factors on the elemental composition of wool. Similar findings have been reported in Slovakia, where wool analyses have shown clear correlations with local pollution sources. For instance, the Horehronie region exhibits extremely high levels of sodium (Na) due to its proximity to the pharmaceutical industry, while the Šariš region displays elevated levels of iron (Fe) as a result of historical mining activities (Janíček et al., 2025).

However, wool as a bioindicator of environmental pollution has not been used in studies conducted in Croatia, except for the study by Antunović et al. (2010), in which wool was used as an indicator of selenium concentration in sheep. More frequently, particularly in the continental regions of Croatia, tissues of wild animals – primarily roe deer and wild boar – have been used as bioindicators of environmental contamination (Lazarus et al., 2005; Srebočan et al., 2011; Vidosavljević et al., 2025). The lack of studies using sheep wool as a bioindicator may be due to the breed structure of sheep farmed in Croatia, in terms of wool yield and quality. Three main populations can be distinguished according to wool quality: coarse-wool purebred Pramenkas (about 40 μm), crosses of Pramenka and Merino (such as Pag sheep, 28 μm), and purebred Merinos (such as Merinolandschaf, 27 μm; Mioč et al., 2025). In addition, individual breeds are mainly regionally distributed, inhabiting specific geographical areas.

Given the advantages of sheep wool as a bioindicator of environmental pollution, the positive experiences reported by previous studies, and the lack of such research in the Republic of Croatia, this study aimed to determine the concentrations of selected trace elements (Cu, Fe, Zn, Mn, Cr) and selected heavy metals (Cd, Pb, Ni) in sheep wool from three regions of Croatia. Additionally, the study aimed to compare the concentrations of these elements between the investigated regions.

MATERIAL AND METHODS

Sample Collection

Wool samples were collected from three major sheep-breeding regions in Croatia, where sheep are traditionally grazed. In each region, samples were taken from only one dominant breed. The first region was Posavina (around Županja), where Merinolandschaf sheep predominate; the second was the Bilogora region in northern Croatia (around Grubišno Polje), where the Travnik Pramenka breed predominates; and the third was the island of Pag, characterized by the indigenous Pag sheep, located in northern Dalmatia (Figure 1). According to Halamić and Miko (2009), in Posavina (around Županja), Quaternary River and marsh sediments (alluvium) and marsh loess predominate. The soils are mainly hydromorphic, including alluvial soils, eugley, and semigley. This area shows elevated concentrations of arsenic (As) and cadmium (Cd), partly due to anthropogenic input such as industry. Elevated to anomalous concentrations of cobalt (Co) and chromium (Cr) are also present, resulting from material transported by the Bosna River, which drains the central ophiolite zone (ultramafic rocks) in neighboring Bosnia and Herzegovina. Other elements characteristic of the soil in this area are copper (Cu), phosphorus (P), and mercury (Hg). An increase in lead (Pb) is due to the transport of material from the Litija area in Slovenia, a historical mining site. The Bilogora area is largely covered by loess (aeolian sediments), with dominant soil types such as luvisols, which are widespread throughout this hilly region. In this area, high concentrations of sodium (Na) and niobium (Nb) are notable, as direct consequences of the mineral composition of the underlying aeolian sediments. Elevated concentrations of lanthanum (La) are also recorded in soils above the loess in this area. These occurrences are geogenic (natural) in origin. The Island of Pag is part of the Dinaric coastal region, where carbonate bedrock, mainly limestone and dolomite, predominates. Like other Central Dalmatian islands, Pag has elevated copper (Cu) concentrations, regularly exceeding 50 mg/kg. This is often due to long-term intensive agricultural activity, particularly viticulture and the use of copper-based fungicides (Halamić and Miko, 2009).

Figure 1. Locations of collected samples in Croatia.

The sheep in this study were kept in a semi-extensive farming system, grazing freely on natural pastures during the day and in favorable weather conditions. During winter and in unfavorable weather, they were housed in enclosed buildings and fed mainly locally produced hay, with cereals such as maize or barley added as needed. Mineral supplements, in the form of mineral salts, were available ad libitum.

Sampling took place during the regular annual shearing period to avoid unnecessary disturbance to the animals and to ensure the wool represented a full year of growth. The timing of shearing varied by region and was earliest in Posavina for the Merinolandschaf breed, where it took place in March, and slightly later in the other two regions, Bilogora and the island of Pag, for Travnik Pramenka and Pag sheep, in early June. Shearing was carried out with an electric shearing machine by professional shearers. Only female sheep aged 3 ± 0.5 years, with uniform body condition and no visible signs of disease, were included in the study. All animals examined had a uniform coat color (white to slightly yellowish), which reduces the influence of melanin pigment, to which certain metals, such as copper, have a strong affinity (Szpoganicz et al., 2002). A total of 90 fleeces were collected, 30 per breed, and used for the analysis of selected trace elements and heavy metals. After shearing, the fleeces were individually weighed on a digital scale (PCE-HS 50) with a deviation of ±10 grams to determine the annual wool production and the total ash content in the fleece. The entire fleece from each animal, excluding the dirtiest parts from the tail region and lower legs, was then collected and stored in polypropylene bags.

Determination of Ash Content and Mineral Concentration

To remove external surface impurities, all fleeces were first shaken to allow larger impurities to fall away and then washed. The fleeces were washed in warm and cold water to prevent undesirable effects of reagents used during sample preparation on the metal concentration of the wool. Initially, the fleeces were washed in warm water at 30 °C for 30 minutes. The process involved thoroughly soaking the fleeces and occasionally stirring to help dissolve impurities stuck to the wool fibers. After thorough squeezing, the fleeces were washed again in cold water at approximately 15 °C for a further 30 minutes. After washing and squeezing out excess water, the fleeces were dried at room temperature until they reached a constant weight.

To determine the ash content and mineral concentration, a total of 90 fleeces (30 per region) were burned. The washed wool samples were placed in deep porcelain cups and incinerated in an annealing furnace at 550 °C for 8 hours, using a Nabertherm LV 9/11/B510 device (Nabertherm, Germany). After incineration, the proportion of ash obtained relative to the amount of wool burned was calculated for each sample. The concentrations of selected trace elements (copper, Cu; iron, Fe; zinc, Zn; manganese, Mn; and chromium, Cr) and selected heavy metals (cadmium, Cd; lead, Pb; and nickel, Ni) in the wool ash were determined in the laboratory of the University of Zagreb Faculty of Agriculture, Department of Plant Nutrition using an atomic absorption spectrometer (AAS; SOLAAR M5 AAS; Thermo Fisher Scientific, United States) according to the following procedure. A 0.5 g wool ash sample was weighed into the incineration vessel, and 6 mL of HNO_3 and 1 mL of $HClO_4$ were added.

The prepared mixture was incinerated in a microwave oven (CEM Mars 5) and then cooled in a fume hood. After cooling, the sample solution was filtered through filter paper into a 50 mL volumetric flask. The concentration of trace elements and heavy metals in the wool substrate solution was measured directly using an AAS, in accordance with the HRN ISO 11466:2004 standard. The concentrations of Pb, Cd, Ni, and Cr were determined using the GF 95 (Graphite Furnace) method, while the concentrations of Cu, Mn, Fe, and Zn were determined using the FS 95 (Furnace autosampler) method.

Although the concentrations of the solutions for the calibration curve were expressed in μg mL^{-1}, the concentrations of the investigated metals in the wool samples were expressed in mg/kg. The conversion was performed using the following formula:

Conc. element (mg/kg) = (A × Z) / m

Where *A* is the solution concentration read on AAS (μg mL^{-1}); *Z* is the flask volume (50 mL), and *m* is the initial mass of the dry sample (0.5 g).

Statistical Analyses

Data preparation, preliminary analyses, and statistical data analyses were performed using the R software environment (version 4.3.1; R Core Team, 2023). Data preparation prior to the analysis was performed using the tidyverse package (Wickham et al., 2019), while a descriptive and inferential statistical analysis was performed using the rstatix package (Kassambara, 2023a). Prior to the analysis, the model assumptions were checked, such as the following: no significant outliers (rstatix package), normality with QQ plot (ggpubr package (Kassambara, 2023b) and sphericity with Mauchly's test (rstatix package). When all assumptions were met, an ANOVA was performed with the rstatix package, while post hoc tests were performed with the emmeans package (Lenth, 2024). To reduce the type I error, the Bonferroni test was performed to correct the p-value.

RESULTS AND DISCUSSION

Diet quality and environmental pollution are key factors affecting the productivity and health of breeding animals, as reflected in the concentrations of macro- and microelements in animal tissues, organs, and hair or wool (Dove, 2010; Stapay et al., 2023; Janíček et al., 2025). Total ash content (%) and concentrations (mg/kg) of selected essential microelements and heavy metals determined in the wool of sheep raised in three different regions of Croatia are presented in Table 1.

Table 1. Descriptive statistics of ash content (%) and concentrations (mg/kg) of selected essential trace elements and toxic heavy metals in sheep wool

Tablica 1. Opisna statistika udjela pepela (%) i koncentracije (mg/kg) odabranih esencijalnih mikroelemenata i teških metala u ovčjoj vuni

Parameter / *Pokazatelj*	n	x̄	SD	Min.	Max.	Med.	CV, %
Ash / Pepeo	90	3.514	1.209	0.194	6.928	3.344	34.40
Fe	90	193.092	28.502	135.457	239.272	199.490	14.76
Zn	90	64.032	17.895	13.340	108.800	63.860	27.95
Mn	90	7.062	1.920	3.553	12.214	6.658	27.19
Cu	90	2.592	0.458	1.525	3.928	2.544	18.70
Ni	90	0.236	0.091	0.101	0.456	0.230	38.77
Cr	90	0.278	0.111	0.095	0.507	0.302	39.89
Pb	90	0.023	0.013	0.009	0.065	0.017	58.37
Cd	90	0.004	0.002	0.001	0.008	0.004	36.96

n – number of observations; x̄ – mean value; SD – standard deviation; Min. – minimum value; Max. – maximum value; CV – coefficient of variation

Table 1 shows that the average ash content in the washed fleece was 3.514%, which is significantly higher than the values reported by Patkowska-Sokoła et al. (2009) for sheep wool from Greece (2.736 %), Poland (2.649 %), and Syria (2.522 %). The noticeably higher ash content in the wool may result from the different breeds of sheep, as well as from using the entire fleece to calculate ash content in this research, rather than only a few gram samples. Among the elements investigated, the highest concentrations were found for iron (Fe 193,092 mg/kg), followed by zinc (Zn 64.032 mg/kg), manganese (Mn 7.062 mg/kg), and copper (Cu 2.592 mg/kg). Very low concentrations (below 1 mg/kg) were observed for nickel (Ni 0.236 mg/kg), chromium (Cr 0.278 mg/kg), lead (Pb 0.023 mg/kg), and cadmium (Cd 0.004 mg/kg). The Fe values determined in this study are relatively high compared to those reported by Patkowska-Sokoła et al. (2009) for Poland (approximately 22.03 mg/kg) and Greece (approximately 76.70 mg/kg), Behrem et al. (2022) for Turky (29.34 mg/kg), Janíček et al. (2025) for Slovakia (ranging from 17.61 to 71.83 ppm depending on the region), and Aydin (2008) for Turkey (117.42–120.52 μg/g). In contrast, Ramírez-Pérez et al. (2000) reported mean Fe levels in sheep wool in Mexico of around 291.22

mg/kg, while Patkowska-Sokoła et al. (2009) reported 513.17 mg/kg in the wool of sheep from Syria. These iron values in sheep wool indicate the varying availability of this element in different parts of the world, which primarily depends on its presence in the soil as well as in the feed that sheep intake while grazing (Patkowska-Sokoła et al., 2009). The observed average Zn concentrations were slightly lower than those reported in Poland, Greece, and Syria (Patkowska-Sokoła et al., 2009), and in Turkey (Aydin, 2008; Behrem et al., 2022). The average Mn concentration (7.06 mg/kg) was higher than the values found in Turkey (Aydin, 2008), Poland, and Greece (Patkowska-Sokoła et al., 2009), but significantly lower than those determined in sheep wool in Syria (22.93 mg/kg; Patkowska-Sokoła et al., 2009) and Turkey (27.61 mg/kg; Behrem et al., 2022). The copper values determined were similar to those in Turkey (Aydin, 2008; Behrem et al., 2022) but significantly lower than those reported in other European countries (Patkowska-Sokoła et al., 2009; Janíček, 2025). The average Pb and Cd values were significantly lower than those reported by Patkowska-Sokoła et al. (2009) and Aydin (2008). The Cr values in this study were also lower than those reported by Aydin (2008) for Turkey. Comparison of Ni with other studies was not possible as values for this element were not reported.

Table 2 shows the influence of the region on the ash content and the concentration of the investigated elements in the sheep wool. Wool ash content was lowest in the Bilogora region (2.533 %) compared to Posavina and the island of Pag (3.916 % and 3.824 %, respectively). Statistically significant differences in wool ash content are probably influenced by breed, as each region is associated with a different sheep breed. Patkowska-Sokoła et al. (2009) reported varying ash contents in sheep wool depending on region and breed: Karagounico (Greece) at 2.736 %, Polish Mountain Sheep (Poland) at 2.649 %, and Awassi (Syria) at 2.522 %, but differences between regions were not as pronounced as in our study.

Table 2. The effect of the breeding area on the ash content (%) and the concentration of the heavy metals (mg/kg) in sheep wool

Tablica 2. Utjecaj uzgojnoga područja na udio pepela (%) i koncentracije teških metala (mg/kg) u ovčjoj vuni

Indicator / *Pokazatelj*	Posavina	Island of Pag	Bilogora	**Level of significance** / *Razina značajnosti*
	LSM ± SE	LSM ± SE	LSM ± SE	
Ash / *Pepeo*	3.916 ± 0.192[a]	3.824 ± 1.999[a]	2.533 ±1.999[b]	P<0.001
Fe	200.34 ± 2.55[b]	219.69 ± 2.55[a]	159.78 ± 2.55[c]	P<0.001
Zn	74.466 ± 2.83[a]	67.872 ± 2.83[a]	52.014 ± 2.83[b]	P<0.001
Mn	7.514 ± 0.298[a]	5.379 ± 0.298[b]	7.713 ± 0.298[a]	P<0.001
Cu	2.595 ± 0.089	2.541 ± 0.089	2.603 ± 0.089	n.s.
Ni	0.236 ± 0.010[b]	0.332 ± 0.010[a]	0.155 ± 0.010[c]	P<0.001
Cr	0.333± 0.008[b]	0.370 ± 0.008[a]	0.138 ± 0.008[c]	P<0.001
Pb	0.040 ± 0.001[a]	0.015 ± 0.001[b]	0.016 ± 0.001[b]	P<0.001
Cd	0.004 ± 0.0002[a]	0.003 ± 0.0002[b]	0.006 ± 0.0002[c]	P<0.001

LSM ± SE: least squares mean ± standard error; Labels [a, b, c] within a row indicate statistically significant differences between regions; n. s. – no significant difference / *LSM ± SE: sredina najmanjih kvadrata ± standardna pogreška; oznake [a, b, c] unutar retka označavaju statistički značajne razlike između regija; n. s. – nema značajne razlike.*

The results presented in Table 2 indicate significant regional differences in the investigated elements, due to biogeochemical origin and differences in the vegetation of the specific regions where the sheep graze. This is consistent with observations from Slovakia (Janíček et al., 2025) and Turkey (Aydin, 2008). Almost all investigated elements showed statistically significant differences between regions, except for Cu, whose values were not statistically different.

In the present study, relatively high concentrations of Fe were observed, with statistically significant differences among all three regions (Table 2). These values are significantly higher than those recorded in sheep wool from other European countries, such as Poland (22.03 mg/kg), Greece (76.70 mg/kg; Patkowska-Sokoła et al., 2009), and Slovakia (17.61–71.83 ppm; Janíček et al., 2025). However, they are very similar to the Fe values found in sheep wool in Turkey (119.04–182.52 μg/g; Aydin, 2008), but still significantly lower than the extreme values reported in sheep wool in Syria (513.17 mg/kg; Patkowska-Sokoła et al., 2009).

The determined concentrations of Zn in sheep wool show regional differences, with the highest values in Posavina (74.466 mg/kg) and Pag (67.872 mg/kg), and a statistically significantly lower concentration in Bilogora (52.014 mg/kg). The Zn concentrations found in all three regions in this study were consistent with reported values for Turkey (73.94–87.08 μg/g; Aydin, 2008) and for Syria, Greece, and Poland (73.62 mg/kg, 75.02 mg/kg, and 88.80 mg/kg; Patkowska-Sokoła et al., 2009), or were slightly lower, as on the island of Pag (67.872 mg/kg) and especially in the Bilogora region (52.014 mg/kg).

Although Behrem et al. (2022) reported a similar average Zn concentration (82.90 mg/kg) in the wool of Central Anatolian Merino sheep, the range of values was very wide (9.80–383.60 mg/kg), which may be attributed to the large age differences among the animals studied (less than 6 to over 42 months).

The Mn concentrations were highest in Bilogora (7.713 mg/kg), followed by Posavina (7.514 mg/kg), and were statistically significantly higher than those observed on the island of Pag (5.379 mg/kg). The determined concentrations of Mn in all regions in Croatia were significantly higher than those in Turkey (0.44–0.95 μg/g; Aydin, 2008) and Poland (3.37 mg/kg; Patkowska-Sokoła et al., 2009). They are most similar to those from Greece (4.43 mg/kg) but remain well below the Syrian and Turkish extremes of 22.93 mg/kg and 27.61 mg/kg, respectively (Patkowska-Sokoła et al., 2009; Behrem et al., 2022).

Copper is the only element with uniform values across the studied regions, ranging from 2.541 to 2.603 mg/kg. These values fully agree with results from Turkey (Aydin, 2008; 2.45–3.64 μg/g; Behrem et al., 2022; 3.79 mg/kg), but are about half those found in Poland (5.30 mg/kg), Greece (6.79 mg/kg; Patkowska-Sokoła et al., 2009), and Slovakia (up to 7.54 ppm; Janíček et al., 2025).

The concentrations of trace elements (Ni and Cr), although very low, were statistically significantly different between the studied regions (Table 2). The lowest concentrations were found in the Bilogora region (Ni: 0.155 mg/kg; Cr: 0.138 mg/kg), while the highest were recorded on the island of Pag (Ni: 0.333 mg/kg; Cr: 0.370 mg/kg). The relatively high concentrations of Ni and Cr in sheep wool from the island of Pag are attributed to elevated levels of these elements in the soil, as the coastal region is characterized by a carbonate geological substratum (limestones and dolomites) and high average values of these elements in the soil (median values: Ni: 74.6 mg/kg; Cr: 121 mg/kg; Halamić and Miko, 2009). In a Turkish study, Ni was below the detection limit regardless of the method used, while Cr ranged from 0.23 to 1.20 μg/g (Aydin, 2008).

The concentrations of the heavy metals lead and cadmium also differed statistically significantly between the studied regions in Croatia. Cadmium concentrations in soil are relatively similar across all three investigated regions, ranging from 0.003 to 0.006 mg/kg. In central Croatia, which includes the Bilogora region, elevated and anomalous cadmium concentrations have been recorded in the hilly areas of Žumberak Mountain and Samoborsko Gorje (near Rude), as well as in the western part of Ivanščica Mountain. These concentrations are of geogenic origin. Increased concentrations have also been observed in a narrow belt on floodplain sediments of the Sava River (Posavina region), both upstream and downstream from Županja, probably due to anthropogenic cadmium input into the soil from industry (Halamić and Miko, 2009). This is reflected to some extent in the concentrations of cadmium in sheep's wool, which were statistically significantly higher in sheep from the Bilogora area and from the area along the Sava River. The determined concentrations of lead in wool are also influenced by the concentration of lead in the soil. In the Posavina region, the median soil lead concentration is 145 mg/kg, significantly higher than in the other two regions (Central Croatia: median 27 mg/kg; Coastal Croatia: median 48.7 mg/kg). Elevated concentrations have been observed on the banks of the Sava River downstream of Županja (Halamić and Miko, 2009), which coincides with the breeding area of the sheep from which the wool samples were collected. However, the values determined for Pb (0.015–0.040 mg/kg) and Cd (0.003–0.006 mg/kg) are extremely low compared to other studies. For example, research conducted by Patkowska-Sokoła et al. (2009) found concentrations of Pb and Cd in Poland, Greece, and Syria (2.25 and 0.134 mg/kg; 2.32 and 0.342 mg/kg; 2.46 and 0.294 mg/kg, respectively) to be higher. In Turkey (Aydin, 2008), detected levels of Pb were 0.42–1.52 μg/g, and Cd 0.06–0.17 μg/g, which are also higher than the values determined in the present research in the three different regions of Croatia.

Although comparing the results of this study with those of others is somewhat ungrateful due to differences in sheep breeds and methods of determining individual elements in wool, the concentrations of selected elements found in sheep wool suggest that the studied areas in Croatia are ecologically exceptionally well preserved from pollution, especially from contamination by heavy metals such as Pb and Cd.

CONCLUSION

The results of this study confirmed that sheep wool is a reliable bioindicator of environmental exposure to trace elements and heavy metals. Statistically significant regional differences were found, primarily reflecting the geochemical background rather than anthropogenic pollution. If pollution is defined as anthropogenic influence, Posavina shows the highest exposure indicators. In contrast, Bilogora is the cleanest region, with the lowest total mineral load and the least exogenous contamination. The island of Pag is a unique example of a region strongly influenced by natural factors, mostly geological substrate, rather than pollution. In general, low concentrations of toxic elements such as lead and cadmium indicate that the studied regions in Croatia are ecologically well preserved. The results contribute to the limited knowledge on the application of sheep wool as a bioindicator in Croatia and provide a basis for future research and systematic monitoring of the state of the environment.

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REGIONALNE RAZLIKE U ODABRANIM ELEMENTIMA U TRAGOVIMA I TEŠKIM METALIMA U OVČJOJ VUNI U HRVATSKOJ

SAŽETAK

Cilj ovoga istraživanja bio je utvrditi koncentracije odabranih elemenata u tragovima (Cu, Fe, Zn, Mn, Cr) i teških metala (Cd, Pb, Ni) u vuni ovaca uzgajanih u tri hrvatske regije: Posavini (oko Županje), Bilogori (oko Grubišnoga Polja) i na otoku Pagu. Među istraživanim elementima utvrđena je najveća koncentracija željeza (Fe 193,09 mg/kg), zatim cinka (Zn 64,03 mg/kg), mangana (Mn 7,06 mg/kg) i bakra (Cu 2,59 mg/kg). Utvrđene su vrlo male koncentracije (ispod 1 mg/kg) nikla (Ni 0,24 mg/kg), kroma (Cr 0,28 mg/kg), olova (Pb 0,02 mg/kg) i kadmija (Cd 0,004 mg/kg). Značajne regionalne razlike ($P < 0,001$) utvrđene su za gotovo sve elemente, osim za Cu. U ovčjoj vuni s područja Posavine utvrđena je značajno veća koncentracija Zn i Pb, dok je u vuni s otoka Paga utvrđena najveća koncentracija Fe, Ni i Cr. U vuni iz Bilogore utvrđena je značajno veća koncentracija Mn i Cd u usporedbi s ostalim regijama. Budući da je njihova prisutnost prvenstveno povezana s temeljnom stijenom, na temelju utvrđenih koncentracija odabranih elemenata u ovčjoj vuni može se zaključiti da su sve tri istraživane regije u Hrvatskoj relativno slobodne od značajnoga onečišćenja proučavanim elementima.

Ključne riječi: vuna, regije, elementi u tragovima, teški metali, okoliš

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