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HEAVY METAL CONTENT IN SOILS OF SELECTED HOP PLANTATIONS IN RELATION TO THEIR NATURAL BACKGROUND

VSEBNOST TEŽKIH KOVIN V TLEH IZBRANIH HMELJIŠČ SPODNJE SAVINJSKE DOLINE

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Abstract

Heavy metals (HM) are present in soil naturally *[1]*, due to weathering of the element-rich parent rock and anthropogenic sources (industry, agriculture, traffic, energy production) *[2–4]*. The agricultural source of the increased HM concentrations in soil are HM-containing fertilisers and pesticides. Agricultural soils are often considered polluted, and are, therefore, subject to soil contamination monitoring for food safety reasons. Permanent crops are particularly at risk, due to the intensive and traditional (over)use of pesticides and fertilisers. Hop plantations are a special type of economically important permanent crop in the Lower Savinja region. The product, the dried hop cones, is mainly exported. The cultivation of hops requires intensive soil tillage, fertilisation, and, above all, constant protection of the hop plant by usage of pesticides. According to Slovenian legislation *[5]*, the HM concentration is considered elevated if the HM concentration in the soil is above the limit immission value (LIV), polluted if it is above the warning immission value (WIV), and critically polluted if it is above the critical immission value (CIV). The HM content was analysed in the soils of 10 hop plantations in the Lower Savinja region. The soil samples were

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dried, ground and sieved in the FVO laboratory, and analysed by Bureau Veritas Commodities (Canada) using Aqua Regia extraction to determine the 'pseudo-total content' for 37 elements (Ag, Al, **As**, Au, B, Ba, Bi, Ca, **Cd**, **Co**, **Cr**, **Cu**, Fe, Ga, **Hg**, K, La, Mg, **Mn**, Mo, Na, **Ni**, P, **Pb**, S, Sb, Sc, Se, Sr, Te, Th, Ti, TI, U, V, W, and **Zn**), 10 of which (in the frames) are considered common HM soil contaminants. The HM concentrations in the soils of the hop plantations were within the natural background values *[1]* (below the LIV), with the exception of Cd, Cu and Zn, which were above the LIV in some cases. The Cd concentration was elevated in 90 % (it exceeded the LIV). The hop fields were not contaminated with Cd – as the concentration did not exceed the WIV. The Cu concentration was within the natural background values in 20 % of the hop plantations (well below the LIV), 30 % were elevated (exceeded the LIV), while 50 % were polluted with Cu (the Cu exceeded the WIV). The Zn concentration was below the LIV value in 80 % of the hop plantations, 10 % exceeded the LIV value, while 10 % of the hop plantations were considered to be polluted with Zn (the Zn exceeded the WIV value) *[6]*. As expected, we found that the soils of the hop plantations contained significantly increased, and, in some places, exceeded quantities of Cu and Zn, and in some cases also Cd. Elevated concentrations of HM may also be reflected in other parts of the environment, while the effects on food quality were not detected (i.e., elevated concentrations in beer).

Povzetek

Težke kovine (TK) so naravno prisotne v tleh *[1]* zaradi preperevanja matičnih kamnin, ki so bogate z elementi, ter zaradi antropogenih virov (industrija, kmetijstvo, promet, energijska proizvodnja) *[2-4]*. Kmetijski vir povišanih koncentracij TK v tleh so gnojila in pesticidi, ki vsebujejo TK. Kmetijska tla pogosto veljajo za onesnažena, zato so del monitoringa onesnaženosti tal zaradi zagotavljanja varne hrane. Trajni nasadi so še posebej ogroženi zaradi intenzivne in tradicionalne (prekomerne) uporabe pesticidov in gnojil. Hmeljarski nasadi so posebni ekonomsko pomembni trajni nasadi v Spodnji Savinjski dolini. Pridelek, posušeni hmeljni storžki, se večinoma izvaža. Pridelava hmelja zahteva intenzivno obdelavo tal, gnojenje in predvsem stalno zaščito rastlin. V skladu s slovensko zakonodajo [5] koncentracija TK velja za povišano, kadar koncentracija TK v tleh presega mejno imisijsko vrednost (MIV), za onesnaženo, kadar presega opozorilno imisijsko vrednost (OIV), in za kritično onesnaženo, kadar presega kritično imisijsko vrednost (KIV). Analizirana je bila vsebnost TK v tleh 10 hmeljišč v Spodnji Savinjski dolini. Talni vzorci so bili posušeni, zmleti in presejani v laboratoriju FVO ter analizirani s strani Bureau Veritas Commodities (Kanada) z uporabo ekstrakcijske metode Agua Regia za določanje navidezne skupne vsebnosti za 37 elementov (Ag, Al, **As**, Au, B, Ba, Bi, Ca, **Cd**, **Co**, **Cr**, **Cu**, Fe, Ga, **Hg**, K, La, Mg, **Mn**, Mo, Na, **Ni**, P, **Pb**, S, Sb, Sc, Se, Sr, Te, Th, Ti, TI, U, V, W in **Zn**), od katerih jih 10 (v okvirju) velja za TK, ki onesnažujejo tla. Koncentracije TK v tleh hmeljišč so znotraj vrednosti naravnega ozadnja [1] (pod MIV), z izjemo Cd, Cu in Zn, ki v nekaterih primerih presegajo MIV. Koncentracija Cd je povišana v 90 % (presega MIV). Hmeljišča pa niso onesnažena s Cd – koncentracija ne presega OIV. Koncentracija Cu je znotraj vrednosti naravnega ozadja pri 20 % hmeljišč (močno pod MIV), pri 30 % hmeljišč pa je povišana (presega MIV), medtem ko je 50 % hmeljišč onesnaženih s Cu (koncentracija Cu presega OIV). Koncentracija Zn je pod MIV pri 80 % hmeljišč, pri 10 % presega MIV, medtem ko 10 % hmeljišč velja za onesnažene z Zn (koncentracija Zn presega OIV) *[6]*. Po pričakovanjih smo ugotovili, da tla hmeljišč vsebujejo znatno povišane in v nekaterih primerih celo presežene koncentracije Cu in Zn, ponekod pa tudi Cd. Povišane koncentracije TK se lahko odražajo tudi v drugih komponentah okolja, medtem ko vplivi na kakovost hrane (tj. povišanih koncentracij v pivu) niso zaznani.

1 INTRODUCTION

Heavy metals (HM) are present in soils naturally through weathering of the parent rock, but their input can also be anthropogenic through industry, agriculture and transport. Agricultural sources of HM in soil are, among others, pesticides and fertilisers containing HM. HM such as Fe, B, Mn, Zn, Cu, Mo and Ni are important plant and animal micronutrients at low concentrations. However, when the concentrations of these metals increase in the soil they become pollutants, as they can have toxic effects on plants, for example, by inhibiting their growth. Metals that are not macro- or micronutrients are called absolute pollutants *[7]*.

The important Lower Savinja Valley crop is the hop (*Humulus lupulus*, L.), which has been cultivated in the area for a century and a half *[8]* and is used mainly in the brewing industry. Hop production is one of the most intensive forms of agriculture, as intensive plant protection measures are needed to control diseases and pests *[9].*

1.1 Hop growing in Slovenia

In Slovenia, the use of hops for brewing beer was first mentioned around 1160 in the area around Škofja Loka. However, hop production began to develop more intensively in the Savinja valley area after 1870 *[11]*. Hop was cultivated on 1, 625 ha in Slovenia in 2022. Slovenia exports up to 99 % of its hop harvest, which is used mainly for beer production, to foreign markets *[12].* In Slovenia, spraying against pests and diseases is carried out according to the forecast of the requirement for spraying issued by the Institute of Hops and Brewing of Slovenia, based on the tracking of the occurrence of diseases and pests *[10].* In the past, copper preparations were used commonly for the control of fungal diseases in hops, such as hop peronospora (*Pseudoperonospora humuli*), but now only a minimum use of active copper is allowed (3 kg/ha/year). The copper content of hops soils is elevated, due to the longterm use of copper-based fungicides in hops *[9].*

1.2 Basic agricultural soil quality parameters

Soil acidity, expressed as a pH value, influences the solubility of HM in soil more than any other factor, and thus affects their availability to plants *[2]*. The basic cations, especially Mg^{2+} and Ca^{2+}, found in the parent material, have an important influence on acidity of the soil. In the upper soil horizons, acidity is also influenced by the SOM content, which can have a slightly lower pH value. As the soil ages, the upper layers become acidified slowly, due to precipitation that leaches the base cations through the soil profile *[14]*. Other soil properties that depend on soil acidity are buffering capacity, texture, humus content, structure and moisture *[15].*

Soil organic matter (SOM) is made up of organic plant debris such and microbial biomass. In the process of mineralisation, nutrients and energy are released from the SOM, becoming available to plants *[13]*. The SOM content affects various soil properties, such as the water and air properties of the soil, reduction of soil compaction, erosion and soil rooting. It can also improve soil consistency, increase water retention and the absorption rate and drainage capacity of the soil. It affects soil acidity, increasing the soil's ability to bind and exchange nutrients *[13, 14]*.

1.3 Heavy metals in natural and agricultural soils

HM are a group of metals with a high relative density. Pb, Cd, Zn, Cu, Cr, Ni, As, Co and Mo belong to this group of metals and are classified as HMs *[14]*. The metals B, Mn, Zn, Cu, Mo and Ni are micronutrients in small, normal amounts. The concentration range of when a metal is a soil nutrient and when it is a soil contaminant is sometimes very narrow *[16]*.

1.3.1 Influence of anthropogenic factors on soil heavy metal content

Anthropogenic soil contamination is one of the biggest impacts of humans on the environment. The enrichment of soils with chemical elements, especially in industrial areas, is attributed to anthropogenic influences. Other anthropogenic influences on the increase of HM in soils are urban and industrial air emissions, hazardous and special wastes (municipal sludge, industrial effluents, radioactive wastes, etc.), contaminated irrigation or flood waters, mineral and organic fertilisers in agriculture, and FFS and silt from riverbeds and lakes *[1]*. When soils lose their self-cleaning capacity, their physical, chemical and biotic properties deteriorate, and soil fertility is reduced. Such soils are referred to as contaminated soils *[14]*.

1.3.2 Agricultural soil contamination

Agricultural soil contamination is divided into direct and indirect inputs of substances into agricultural soils resulting from agricultural activities. Excessive amounts and bad practice usage of fertilisers and FFS used for prevention and control of hops diseases and pests are the main anthropogenic pollutants on agricultural land *[14]*. The most common metals that pollute soil and, at elevated levels, inhibit plant growth and development, are Cd, Cu, Pb and Hg. Agricultural activity can be a source of pollution, due to the overuse and misapplication of poor-quality fertilisers if they contain HM *[7].* Depending on their composition, fertilisers provide a variety of necessary nutrients that improve plant growth and resistance, as well as increase yields. Organic fertilisers also increase the organic matter content of the soil and improve soil fertility *[16].* The most commonly used fertilisers are based on potassium and phosphorus. In Table 1 below, the classification of the soils is presented, based on soil content of K_2O and P_2O_5.

Table 1*: Soil classification and limit values for phosphorus and potassium according to the AL method*

Nutrient content class	Phosphorous content (P_2O_5) (mg / 100 g)	Potassium content (K_2O) (mg / 100 g)
Class A – Poorly supplied	< 6	< 10
Class B – Medium supplied	6 – 12	10 – 19
Class C – Optimally supplied	13 – 25	20 – 30
Class D – Excessively supplied	26 – 40	31 – 40
Class E – Extremely oversupplied	> 40	> 40

1.4 Soil types in the Lower Savinja Valley

Lower Savinjska is a fertile valley, dominated mainly by young soils that have developed on alluvial deposits, predominantly limestone gravel. Part of the area is still under the influence of the watercourses of the River Savinja, which deposit new sedimentary material, mainly gravels and sands. These sediments have resulted in the development of eutric Cambisols or rendzic Leptosols *[1].* Figure 1 below shows the geological types in the reaserch area graphically.

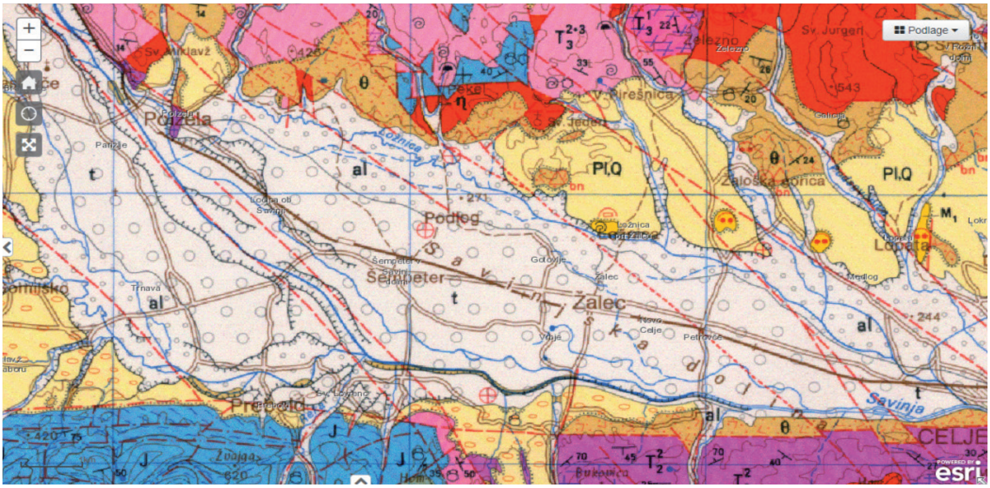

***Figure 1**: Basic geological map of the Lower Savinja Valley*

1.5 Slovenian soil contamination Legislation

Soils in Slovenia are protected by legislation and regulations:

- Regulation on the limit, warning and critical immission levels for dangerous substances in soil (Official Journal RS, nrs. 68/96, 41/04 – ZVO-1 and 44/22 – ZVO-2);
- Regulation on soil quality monitoring (Official Journal RS, nrs. 68/19 and 44/22 – ZVO-2);
- Regulation on operational soil monitoring (Official Journal RS, nrs. 157/22 and 7/23 – correct.);
- Agriculture Act (Official Journal RS, nrs. 45/08, 57/12, 90/12 – ZdZPVHVVR, 26/14, 32/15, 27/17, 22/18, 86/21 – odl. US, 123/21, 44/22, 130/22 – ZPOmK-2, 18/23 and 78/23);
- Environmental Protection Act (Official Journal RS, nrs. 44/22, 18/23 – ZDU-1O and 78/23 – ZUNPEOVE)

Soil contamination is determined according to the Regulation on the limit, alert and critical immission levels of substances in soil *[17]*:

"The limit immission value (LIV) is the level of a particular hazardous substance in soil at which the living conditions for plants and animals are ensured, and the soil fertility and groundwater quality are not impaired."

"The warning immission value (WIV) is a value at which certain land uses are likely to cause adverse effects or impacts on the environment and human health."

"The critical immission value (CIV) is the level at which contaminated soil is unsuitable for the production of plants for human and animal consumption, and for the retention and filtration of water because of adverse effects and impacts on humans and the environment."

2 MATERIALS AND METHODS

2.1 Description of the research area

The research area extends across the Lower Savinja Valley, from Drešinje village to Poljčane near Braslovče. In this area we selected ten hop plantations, from which soil samples were taken using the "zig-zag" method. The locations of the sampled hop plantations are shown in Figure 2, marked with numbers and circles. The plantations are separated spatially and are located on different soil types, either on brown eutric soils or on brown drift soils.

Figure 2: *Marked locations of the hop plantation [Hmeljišče] soil sample points*

2.2 Sampling, tools and field workflow

Field sampling took place in February and March 2023. The individual soil sample consisted of 20 collected sample units. The sampling locations were distributed evenly across the hopyard in a »zig-zag« pattern, avoiding the extreme edges of the field. A larger shovel was used to excavate a soil profile from 0 to 20 cm deep, and a smaller plastic shovel was used to remove a centimetre-deep strip that could be contaminated with HM from the excavation. The partial samples were pooled into one homogenised representative sample, which was stored in a PVC food bag free of HM.

2.3 Sample preparation for analysis

Sample preparation was carried out in the laboratory of FEP, Velenje. The samples were placed in a glass beaker and shaken carefully to settle, and thus remove any major air spaces. We marked the beakers accordingly with the sample codes. The dryer was set to 105 °C to obtain dry matter of the soil. After drying for 48 hours, the samples were stirred, small pebbles and larger roots were removed, and then sieved. The samples were stored in PVC »zip-lock« bags, labelled with the sample serial numbers. The package also needed a Canadian Import Declaration.

2.4 Laboratory analysis of the samples

The soil samples were analysed by inductively coupled plasma mass spectrometry (ICP-MS) after digestion with a modified *Aqua regia* process (15 g of the sample dissolved in a mixture of acids HCl : HNO3 : H2O = 1 : 1 : 1), resulting in a complete degradation of the soil and the breakdown of even less resistant minerals *[18]*. The laboratory analysis was carried out by a Bureau Veritas accredited laboratory in Vancouver according to ISO 11466:1995 (E) *[18]*. The metals analysed by this method were: Mo, Cu, Pb, Zn, Ag, Ni, Co, Mn, Fe, As, U, Au, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, B, Al, Na, K, W, Sc, Tl, S, Hg, Se, Te and Ga.

Four basic soil parameters were analysed in the Agrochemical Laboratory of the Central Laboratory of the Slovenian Agricultural Institute using accredited methods:

- Soil acidity in $CaCl_2$ (ISO 10390:2021);
- Soil organic carbon content (SIST ISO 14235:1999 MOD);
- Content of plant-available P_2O_5 and K_2O (in-house method of the laboratory) *[20]*

3 RESULTS

3.1 Total HM content in soil samples from 10 hop plantations and comparison with the Limit Immission Values of the Slovenian regulation

For the 10 HM defined by the Regulation on limit, warning and critical immision levels for dangerous substances in soil (hereafter referred as the Regulation) (Cd, Cu, Ni, Pb, Zn, Cr, Hg, Co, Mo and As), we have presented the maximum and minimum levels and their median and mean values

3.1.1 Cadmium (Cd)

The Cd concentration in certain hop plantations exceeded the LIV according to the Regulation. The average Cd concentration in all ten soil samples was 1.2 mg/kg dry soil (in the continuation 'd.s.') and the median of the samples was 1.3 mg/kg d.s.. The lowest content was 0.7 mg/kg soil s.s., and the highest measured content was 1.5 mg/kg soil d.s.. The soils of the hop plantations were not contaminated with Cd, as no plantation exceeded the WIV.

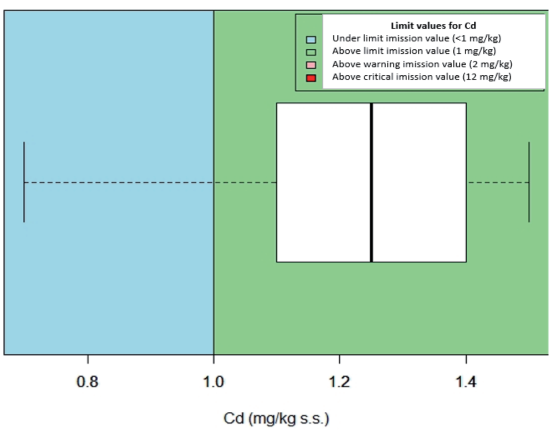

Figure 3: *Cd concentration in the selected hop plantations and immission values*

3.1.2 Copper (Cu)

The mean Cu value was 94.90 mg/kg soil d.s. and the median value was 102.70 mg/kg soil d.s. The highest measured Cu content was 131.5 mg/kg d.s., while the lowest Cu content was 52.9 mg/kg d.s.. In 3 out of the 10 hops, the LIV was exceeded, while, in the remaining 5 out of the 10 hops, the Cu content was above WIV, and, therefore, were contaminated.

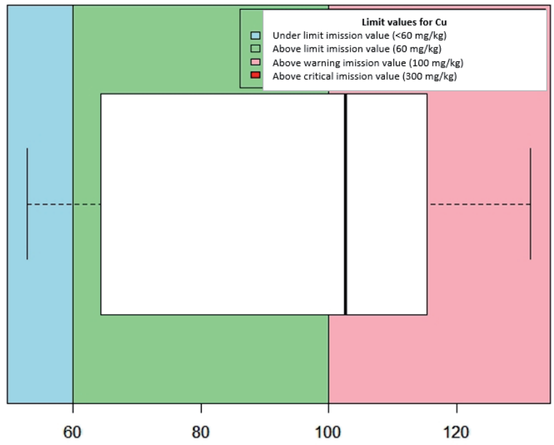

Figure 4*: Cu concentration in the selected hop plantations and immission values*

3.1.3 Zinc (Zn)

The median Zn content of the samples was 167.5 mg/kg d.s. and 147 mg/kg d.s.. The highest measured content was 303 mg/kg d.s. soil, while the lowest level was 94 mg/kg d.s.. The Zn concentration in 8 out of the 20 hops was under the LIV and were free from Zn contamination. In the one remaining hop sample, the Zn content was above LIV, meanwhile, in one hop sample the Zn content was above the WIV, resulting in Zn contamination.

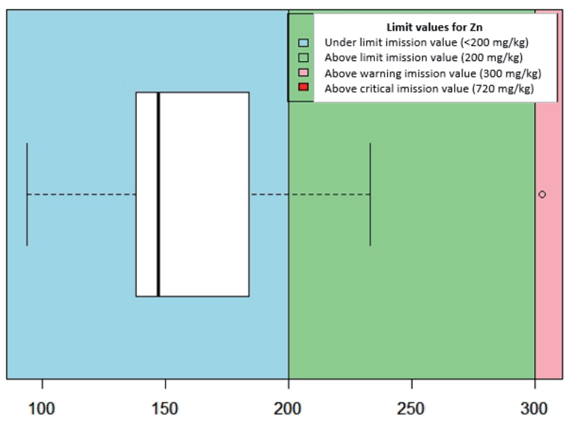

Figure 5: *Zn concentration in the selected hop plantations and immission values*

3.1.4 Other heavy metals included in the AQ251 analysis

The mean Nickel (Ni) value in the hops was 25.7 mg/kg d.s.. The lowest concentration was 15.7 mg/kg d.s. and the highest value was detected at 37 mg/kg d.s.. The LIV for Ni was not exceeded, thus confirming that the hop plantation soils were not contaminated with Ni.

The average Lead (Pb) content in the samples was 45.7 mg/kg d.s.. The highest level of lead was 82.6 mg/kg d.s. and the lowest level was 32.1 mg/kg d.s.. The Pb concentration in the samples did not exceed the LIV, therefore, the soils of the hop fields were not contaminated with Pb.

The mean value of Chromium (Cr) was 24.8 mg/kg d.s.. The highest level of Cr was 37 mg/kg d.s. and the lowest detected value was 16.0 mg/kg d.s.. The soils in the hop plantations analysed were uncontaminated with Cr, because the values did not exceed the LIV.

The mean Mercury (Hg) value in all 10 soil samples was 0.1 mg/kg d.s.. The Hg content in the samples was extremely low, and did not exceed the level of 0.2 mg/kg d.s.. The lowest measured level was 0.07 mg/kg d.s.. The Hg content did not exceed the LIV in the hop samples and therefore the soil was not Hg uncontaminated.

The mean Cobalt (Co) concentration in the samples was 11.60 mg/kg d.s.. The Co content ranged from 8.60 mg/kg d.s. to 14.70 mg/kg d.s.. The Co levels in the soil of all the sampled hop plantation areas were below the LIV, therefore, the soil of the hops was not contaminated with Co.

The mean concentration of Molybdenum (Mo) was 0.7 mg/kg d.s.. The Mo content of all the hop samples was extremely low and did not exceed 0.8 mg/kg d.s., while the lowest Mo content was 0.5 mg/kg d.s.. The Mo levels did not exceed the LIV, and the soils of the hops were free from Mo contamination.

The Arsenic (As) concentrations in all 10 samples did not exceed the LIV. The mean level in the samples was 9.4 mg/kg d.s. The highest measured As content was 12.30 mg/kg d.s., while the lowest As content was 7.5 mg/kg d.s.. The soil of the hops was not contaminated with As.

3.2 Standard soil analysis

Soil acidity is defined as the pH value, and it is measured in a $CaCl_2$ solution. The pH value varied depending on the hop plantations. The average pH value in the hop fields was pH 5.9. Hop 1 (pH 5.5), Hop 7 (pH 4.8) and Hop 8 (pH 4.5) had the lowest pH value among the 10 hop plantations. The highest pH value was pH 7.3.

The available phosphorus content varied between the hop plantations, with large differences between the lowest and highest levels. The average plant-available phosphorus (P_2O_5) content was 67.7 mg/100 g d.s.. The highest phosphorus content was 115 mg/100 g d.s., while the lowest content was 27 mg/100 g d.s.. The results revealed that 90% of the hop plantations fell into Class E (extreme phosphorus content), and none of the samples was in Class A (poor content) or Class B (medium content).

The average plant-available potassium (K_2O) content of hop-growing soils was 35.3 mg/100 g d.s.. The highest content was 59 mg/100 g d.s. and the lowest potassium content was 14 mg/100 g d.s.. In this case, 40% of the hops fell into Class E (extreme potassium content), and two out of the 10 hops sampled fell into Class B (medium content).

The median soil organic matter (SOM) content in the hops soil was 2%. The highest content was 3.6%, while the lowest content was 1.9%, which was detected in two out of the 10 sampled hops.

4 DISCUSSION

4.1 Comparison of the results of HM in the soils of the hop plantations with the study of the Geochemical background and upper limit of natural variability of 47 chemical elements in the topsoil of Slovenia

In the study of the Geochemical Background and threshold of 47 Chemical Elements in Slovenian topsoil *[1]* (hereafter referred to as the 'GB study'), systematic sampling was carried out in a 5 x 5 km mesh over the whole territory of Slovenia. A total of 817 samples were collected at depths ranging from 0 to 10 cm, for which the median and upper limits of natural variability were calculated. The results of our study were compared with the results for Slovenia as a total and for the spatial unit of the Interior Basins.

The comparison revealed that the metal contents of Hg, Tl, Bi, Mo, Th, Sc, Ga, Ag, Cr, K, Ti, Na, Al, Fe did not exceed the median values obtained in the GB study. The levels for the metals Cd, Au, Ba, Mn, Cu, Zn in the hops exceeded the values obtained in the GB study. The content values in hop plantation soils for the metals Co, Sr, La, Ni, Pb, Ca exceeded the values of the GB study for Slovenia as a whole, but not the values for the Interior Basins, while the values for the metals U and Mg exceeded the results of the GB study for the Interior Basins, but were lower compared to Slovenia as a whole. The causes of elevated concentrations of these metals vary. In the case of Cd, we assume that the cause was the fertilisation with low quality mineral fertilisers enriched with Cd. Ca and Fe are also added by the application of some fertilisers, but they are also present in the soil naturally, being important micro- and macro-nutrients necessary for optimal plant growth and development. The metals Th, Sc and Ga are also present naturally. As the eutric cambisols in the Lower Savinja Valley are formed on calcareous limestone gravel and sand, the agricultural soils may also have higher Mn, Cu and Zn contents. Soils on carbonate parent material also tend to have higher levels of the metal U *[1].* One of the reasons for the elevated levels is the use of Pb and Cu-based plant protection products in the past. In addition to all these possible agricultural soil pollutants, anthropogenic pollution from various industries, combustion and local pollution should not be neglected *[14].* It should also be considered that the proximity of Celje and the smelting industry, which is a well-known source of atmospheric Cd and Zn deposition in the area, also contributes to the higher HM content in the hops. Despite the higher Cu content in the hop plantation soils, according to a study *[23],* the Cu content of the spring hop crop is low, at only 2.3 mg/kg fresh weight. It can be concluded that hops do not absorb excessive amounts of either Cu or Zn *[23].* Research in Italy has shown that HM such as As, Cd and Pb may be present in beer, but do not pose a threat to consumers' health as the levels are so low *[19].*

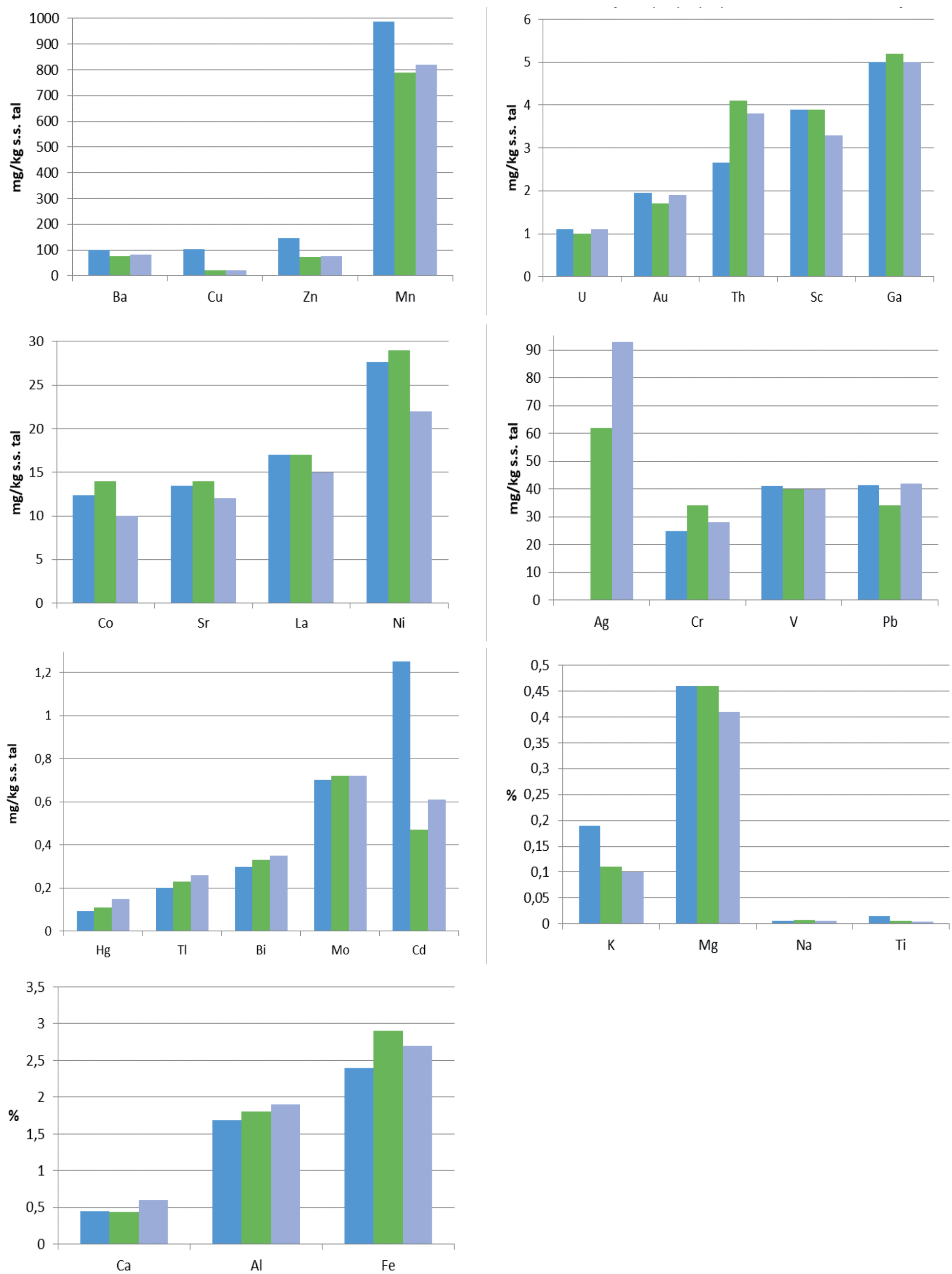

***Figure 6:** Combined results of the hop plantation soil HM content (blue column) compared to the study of the Geochemical Background for Slovenia as a total (grey column) and for the spatial unit of the Interior Basins (green column).*

5 CONCLUSIONS

Ten hop plantations were sampled for their agricultural soils. A sample from one hop plantation consists of 20 subsamples taken along the hop plantation at a depth of 0-20 cm. 37 metals (Mo, Cu, Pb, Zn, Ag, Ni, Co, Mn, Fe, As, U, Au, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, B, Al, Na, K, W, Sc, TI, S, Hg, Se, Te, and Ga) were analysed at the Bureau Veritas accredited laboratory in Vancouver. Ten metals (Cd, Cu, Ni, Pb, Zn, Cr, Hg, Co, Mo and As) were compared with the Slovenian legislation on limit values . The results of the metal contents were also compared with the Geochemical background and upper limit of the nature of variability of 47 chemical elements in the topsoil of Slovenia in the Interior basins and Slovenia as a whole.

Based on a comparison of the median levels for ten metals (Cd, Cu, Ni, Pb, Zn, Cr, Hg, Co, Mo and As) with the limit values in the Regulation, we found that two metals, Cu and Zn, exceeded the WIV in several samples. Cu contaminated 50% of the tested hops, while only one hop plantation was contaminated with Zn. Only Cd exceeded the LIV according to the Regulation in 90% of the sampled hops. The other metals which are covered by the Regulation, did not exceed the LIV in any of the samples taken. The soil of the hop plantations is in agricultural use, which means that the elevated metal levels may also be due to the long-term use of mineral or organic fertilisers and FFS containing Cu, Cd and Zn. Metals used in the past still accumulate in the soil, reflecting the history of farming and the use of different chemical inputs in the hop fields, as they are not leached out, but accumulate in the soil over the years. However, elevated HM levels in soils can also be attributed to anthropogenic sources of pollution, as the soils of the hops in the Lower Savinja Valley have been exposed to various levels of HM pollution in the past. Among other sources, contamination of the soil by HM from various industries in the area of Žalec and Celje cannot be excluded. The possibility of soil contamination in the past, especially with Cd, can also be attributed to the burning of lignite and the proximity of the Zinc smelting industry in the nearby city of Celje. The urbanisation of the Lower Savinja Valley is also estimated to have contributed to the higher HM content in soil, while the possibility of soil contamination by traffic must also be considered in the soils of traffic corridors. In conclusion, higher HM levels in the soils of the hop plantations in the Lower Savinja Valley are estimated to be the result of a combination of industrial, agricultural, urban and other anthropogenic activities in the past and present.

The metals Cu and Zn, which were found at elevated levels in the hops soils, do not pose a risk to the consumer. From the study on the final products - beer, the contents of HM were extremely low and did not threaten the consumer. There were also no significant levels of these HM in the hop plant itself, through which they could pass from the soil to the hop cones and to the final product. The metals in question are bound to soil particles (clay minerals and soil organic matter) in the soil, and are therefore difficult to leach out of the soil. However, when soil properties change (reduced SOM content or increased soil acidity), the HM become mobile again and available to the plants.

The most ideal and optimal soils for growing hops are moderately acid soils in the pH range from 6 to 6.7 *[21]*. The conducted study showed that 60% of the hopgrowing areas are in the suitable class for growing hops in terms of soil acidity. The remaining 30% of hop soil sampled had pH values from 4.5 to 5.5, and 10% of the hop soil samples had a pH value above 7.2. There are several reasons for lower acidity in soils. These include leaching of cations out of the soil, acid precipitation and neutralisation during the growing season. Soil acidity is also influenced by cropping, which removes the base cations from the soil, especially Ca^{+} and Mg^{+}. In addition, the use of acid-acting mineral fertilisers can also contribute to soil acidification *[15]*.

The analysed hop plantations are generally well supplied with plant-available K_2O and P_2O_5. According to the soil supply classification, the soil samples fell into the classes of medium to extreme soil content. In the case of phosphorus, out of the 10 hops analysed, 10% belonged to class D, with excessive content, and as much as 90% to class E, meaning extreme soil content. In the case of potassium, of the total of 10 hops analysed, 20% were in class B, medium soil content, 20% in class C, optimal content, 20% in class D, excessive soil content, and 40% in class E, meaning extreme content. The elevated levels are most likely due to the overuse of potassium- and phosphorus-based fertilisers. In agricultural lands where increased levels are measured, limited fertiliser application is recommended, and where values are extreme, complete restriction of fertiliser application is advised for the next 5 to 10 years *[22].*

For further research, it would be beneficial to identify additional hop plantations that contained higher levels of metals in the soil. At the same time, for food safety reasons, it would be recommended to check the mobility of HM in soil and their uptake by agricultural plants (hops), as well as the HM content in the produce (hop cones) and food (beer).

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Nomenclature

(Symbols)	(Symbol meaning)
HM	Heavy metals
FEP	Faculty of Environmental Protection
SOM	Soil organic matter
RS	Rebublic of Slovenia
ZVO	Environmental Protection Act
LIV	Limit immission value
WIV	Warning immission value
CIV	Critical immission value
d s.	Dry soil
Ag	Silver
Al	Aluminium
As	Arsenic
Au	Gold
B	Boron
Ba	Barium
Bi	Bismuth
Ca	Calcium
Cd	Cadmium
Co	Cobalt
Cr	Chromium
Cu	Copper
Fe	Iron
Ga	Gallium
Hg	Mercury
K	Potassium
La	Lanthanum
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
Na	Sodium
Ni	Nickel
P	Phosphorus
Pb	Lead
S	Sulphur
Sb	Antimony
Sc	Scandium
Se	Selenium
Sr	Strontium
Te	Tellurium
Th	Thorium
Ti	Titanium
Tl	Thallium
U	Uranium
V	Vanadium
Zn	Zinc