# Heavy Metal Content in the Soil and Typical Crops of the Pannonian Region of Slovenia

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*Article*

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**Abstract:** Soil contamination and the uptake of contaminants by food crops is a global problem that differs significantly from region to region, with the key factors affecting the contaminants present in local soils being the mineralogical composition of the underlying layers and local human activity. The area of the Pannonian region is known for the fact that agriculture has, historically, played an important role since Roman times, which was particularly influenced by human activity. In this study we performed a preliminary study of the contamination of soil samples across the Pannonian region, to determine the potential presence of harmful contaminants. Both soil and crop samples were analysed for the potential presence of heavy metals, with additional focus placed on the potential presence of microplastics in the region`s soil.

**Keywords:** Soil contamination; Pannonia; soil; food crops; heavy metals; microplastics

## 1. Introduction

Historically, agriculture has been a significant economic activity in the Pannonian region. The fertile plains have supported the cultivation of crops since before Roman times [1,2]. During Roman rule is also when the region, then a province, got its name Pannonia, from the roman word Panis, meaning ''bread'' [3]. Today the region continues to produce several crops, mostly wheat, barley and corn, and represents an important strategic food safety region for Slovenia and neighbouring Austria, Croatia and Hungary [4]. Besides the strong agricultural base, the region also hosts various industrial activities, including manufacturing, processing and energy production. East-Slovenian cities like Maribor, Ptuj and Murska Sobota have industrial zones in sectors such as automotive, machinery, and food processing, that contribute significantly to the regional economy. While limited in scope, the region also saw a short period of oil and coal extraction [5–7].

Due to the strategic importance of the region and the long and diverse history, as well as current industrial activities, it is important to establish a knowledge base on the potential contamination of the soil and its influence on agricultural produce [8–12], as these potential contaminants and pollutants can have adverse effects on the environment, including ecosystem disruption, loss of biodiversity and contamination of water sources. Contaminants in soil can persist for long periods, affecting plants, animals and microorganisms. The uptake of such pollutants into plants, especially those meant for consumption, can pose significant health risks to humans. Soil contaminants, such as heavy metals, pesticides and industrial chemicals, can leach into groundwater or be taken up by plants, eventually entering the food chain [13–15]. Consuming contaminated food can lead to acute or chronic health problems, including poisoning, developmental issues and increased risk of cancer. Understanding, assessing and managing the risks associated with soil and food contamination are

essential for informed decision-making for the development and implementation of key measures. These may include remediation of contaminated sites, implementing agricultural practices to reduce contamination, and monitoring food safety throughout the supply chain [16,17]. Heavy metals are persistent environmental pollutants that can contaminate agricultural soils, impacting crop health and productivity negatively, with elements like Cd, Pb, As, Hg, and Cr being especially toxic at almost any concentration. Some of them are also essential mineral nutrients, like Cu, Zn, and Fe, supporting plant functions at low levels, while their accumulation above optimal concentrations can harm plant growth, and insufficient levels can lead to deficiencies [18].

Monitoring of the content of heavy metals in fertile soils is carried out periodically throughout Slovenia, especially in areas that are particularly exposed due to the potential impact of industrial pollution. Research is carried out by the Agricultural Institute of Slovenia with its subcontractors and project partners. Special attention in research is devoted to water protection areas in Slovenia, as pollution in those areas can be particularly critical for the health of the inhabitants. In research, they focus not only on heavy metals in fertile soils, but also examine the land for other hazardous substances and nitrate nitrogen [21]. In the context of the "Report on soil sampling and measurements of hazardous substances and nitrate nitrogen in the soil within the framework of the official control of the IRSKGLR in 2023" [21] we can read that soil sampling was also carried out in the area of north-eastern Slovenia in the areas that we also covered in our research. In this research by the Agricultural Institute of Slovenia, in the Pomurje area (the Pannonian part of Slovenia), an exceeded copper content value was found in only one area. The content exceeded 148 mg/kg of dry soil, because it represents an already exceeded warning value of excessive pollution, which has a limit of 100 mg/kg of dry soil. No other heavy metal exceedances were detected in this report

Conversely, the monitoring of heavy metals in crops and fruits is not included in the National Monitoring Programme. Instead, most of the available data come from various research studies conducted in specific locations, primarily in areas already known for heavy metal soil contamination, such as gardens near major cities or heavy industrial sites [19–22]. The most concerning pollution affecting human health in Slovenia is linked to the metal production industries. As a result, Zn and Pb are the heavy metals studied most frequently in soils and plants across different regions of Slovenia, including Celje and the Mežiška Valley [23,24]. Additionally, intensive research is being conducted on measures for their decontamination [25,26].

Methods for determining heavy metals in soil include primarily flame atomic absorption spectrometry (FASS), graphite furnace atomic absorption spectrometry (GF-AAS), atomic fluorescence spectrometry (AFS), and inductively coupled plasma-mass spectrometry (ICP-MS). These techniques provide precise detection results and high reproducibility. However, they typically require digestion with strong acids, involve complex and time-consuming pre-treatment steps, and can contribute to environmental pollution [27]. The need for fast and reliable heavy metal detection has led to advancements in XRF and EDX methods, potentially to allow determination of heavy metal content in soil samples without requiring digestion. While those methods offer rapid results, their accuracy is relatively low, making it suitable primarily for early-stage on-site screening of heavy metal pollution. To assess the suitability of SEM and EDS fast determination of C, O, Na, Mg, Al, Si, P, Cl, K, Ca, Ti and Fe in soil, crop and fruit samples, this study was additionally crosschecked with the results of the AAS and spectrophotometric search for P, Mg, K, Na, Fe and Ca.

## 2. Materials and Methods

The soil samples were collected from several locations of the Pannonian region of Slovenia: Gornja Radgona, Zbigovci, Murska Sobota, Stara Cesta, Selo, Mlajtinci and Rakičan. In the survey we included soil for different areas of use. In the case of the confiscation of soil in Mlajtinci, Murska Sobota, Rakičan, it concerns nearby places, where the soil in Mlajtinci was confiscated from a field cultivated by a large agricultural company, while the soil samples from Murska Sobota and Rakičan were confiscated from a field owned by the surrounding individual farmer. The soil in Zbigovci and Stara Cesta were taken from the vineyard area where grapes are grown by a large agricultural company engaged in wine production. The soil from Gornja Radgona was taken from the forest,

which is in the immediate vicinity of the Mura River, which is the largest river in the region. Samples from all sites were collected as composite samples (composed of 10 subsamples) using a 3 cm diameter probe and taking cores for the 0–20 cm depth. The samples, of approx. weight 1 kg, were stored in polyethylene bags and placed in a cooler until transported to the laboratory. Samples of typical crops and fruits from this region were also collected for analysis: apples, pumpkin seeds, barley, corn, potatoes and wheat. The samples were composed of five smaller subsamples, each weighing approx. 1 kg. In the laboratory, the individual samples were mixed thoroughly and then reduced to a final weight of 500 g. This composite sample was then processed further.

Preparation for the SEM microscopy was as follows: The apple and potato samples were first cut into slices and freeze-dried before performing the analysis, for preservation of the structures and properties of these samples. The freeze-drying was performed using an FD-200F SERIES lyophiliser (Labfreez Instruments Group Co., Ltd., Beijing, China). The freeze-drying protocol consisted of a freezing period of 8 hours at –40 °C, followed by a drying period of 12 hours, when the pressure was reduced to 1-4 Pa and the temperature was raised to 20 °C. The temperature was then raised to 30 °C and a vacuum was maintained for 30 hours to complete the drying process.

A Scanning Electron Microscope (SEM) equipped with an Energy Dispersive Spectroscope (EDS) was used for the investigations of the soil and crop samples. The used instrument was a Sirion 400 NC (FEI Sirion 400 NC, FEI Technologies Inc., Hillsboro, USA), with an EDS INCA 350 (Oxford Instruments, UK). The soil samples were spread on a graphite tape, adhered to a SEM sample holder and left to dry. The crop samples of pumpkin seeds, barley, corn and wheat were, firstly, milled into smaller particles, before being applied on the SEM holder with graphite tape. Slices of the freeze-dried apple and potato were also applied on matching holders. The samples were coated with Au for 60 seconds before performing the SEM and EDS analysis. 24 EDS spectra were generated from each sample, from which the Mean, Standard Deviation, maximum and minimum values were calculated.

The analysis of P, Mg, K, Na, Fe and Ca in the apple and potato samples was conducted according to ISO 5984:2022 [28] with a spectrometric method and atomic absorption spectrometry. The procedure of sample preparation was as follows: samples were first homogenized - apple and potato were crushed, while wheat, barley, pumpkin seeds and corn were ground in an electric grinder (Gorenje, Velenje, Slovenia). Samples were then dried to constant weight at 105°C in dryer (Memmert, UNB 400, Schwabach, Germany). For futher determination of elements, the samples were ashed in muffle furnace at 530 °C overnight (Nabertherm B150, Lilienthalu, Germany).

The determination of phosphorus content in the apple and potato samples was performed according to ISO 6491:1998 [29] with the spectrometric method. After dissolving the ashed sample in hydrochloric acid (Merck, Germany), and afterwards in nitric acid, a molybdenum vanadate reagent was added to the solution, and the optical density was measured at 430 nm with a spectrophotometer (UV-VIS Agilent 8453, Agilent Technologies, Santa Clara, USA).

Determination of the contents of Mg, K, Na, Fe and Ca was performed according to ISO 6869:2000 [30] after dissolving the ashed sample in HCl (Merck, Germany), using atomic absorption spectrometry (VARIAN Spectra AA-240FS, Agilent Technologies, Santa Clara, USA). The absorptions of the solutions were measured using an air-acetylene oxide flame at the following wavelengths: Mg at 285.2 nm, K at 769.9 nm, Na at 589.6 nm, Fe at 248.3 nm, and Ca 422.7 nm.

The collected soil samples were analysed for the presence and composition of microplastics. Each soil sample was dried in a convection oven at 60 °C for 12 h, the dry soil was sieved up to a 1 mm sieve. 250 g of the sub 1 mm particles were collected and used for the analysis. To separate the microplastic particles from the remaining soil, the sieved powders were dispersed in 0.5 L of a solution of NaCl with a specific density of 1.2 g/mL. The samples were mixed vigorously with a magnetic stir bar for 30 minutes and left to settle for 24 h. The remaining solution was decanted and separated. To increase the yield of microplastic extraction, the process was repeated 3 times, each time adding 0.5 L of a newly prepared NaCl solution. The prepared extracted solutions were additionally digested at 55 °C with the addition of 100 mL of $H_2O_2$, to remove any dissolved or suspended organic components. The suspensions were filtered through Express Plus (PES) 0.45 $\mu$m

pore size filter papers (Merck Millipore, Ireland), using a Sartorius 25 mm glass vacuum filter holder, with a glass frit filter support (Germany). The filter papers were dried overnight in a desiccator.

The dry filter papers were analysed on a PerkinElmer Spotlight 200i FT-IR Micro-scope (PerkinElmer, United Kingdom), connected to a PerkinElmer Spectrum 3 FT-IR/NIR/FIR Spectrometer (PerkinElmer, United Kingdom). 2 image areas with a size of 5000 x 5000 µm were analysed for the potential presence of microplastic particles. The chemical composition of every visible particle was analysed, to determine its material composition.

## 3. Results

The results from the SEM and EDS investigations are shown in Figure 1 for the soil samples and Figure 2 for the crop samples. Tables 1 and 3 show the Mean, Standard Deviation, maximum and minimum values for the obtained 24 EDS spectra from the individual samples. Table 2 shows the overall total average values for all the soil samples combined, while, in Table 4, there are the results of the elemental composition of the crop and fruit samples analysed with the spectrometric and AAS methods.
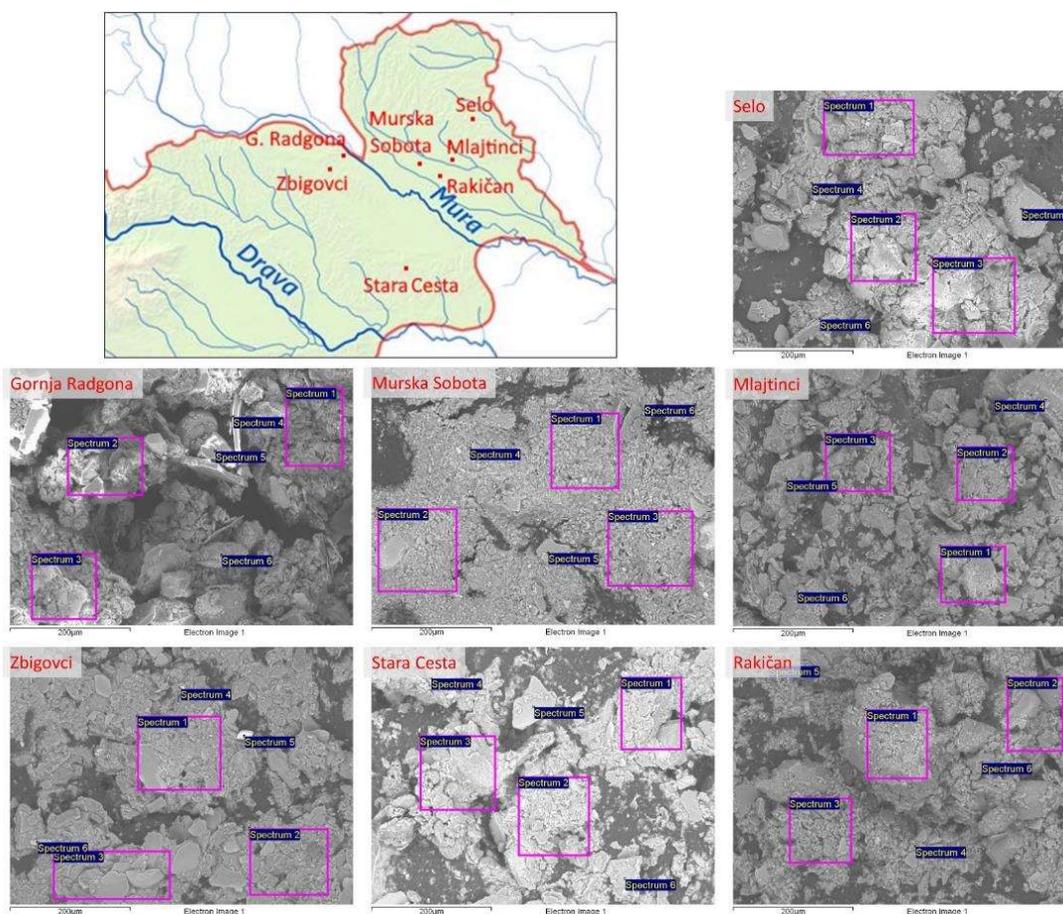


**Figure 1.** SEM and EDS analysis examples of each soil sample, with a map of the marked locations for obtaining the samples (the Pannonian region of Slovenia).
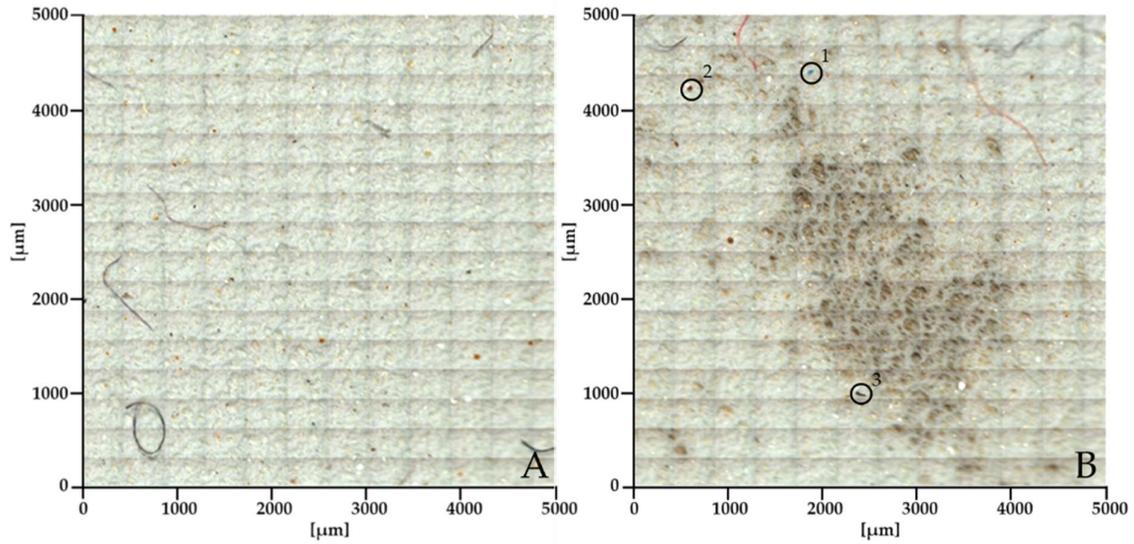
**Figure 2.** Stitched FTIR microscopy images of residues taken from the **G. Radgona** soil sample.
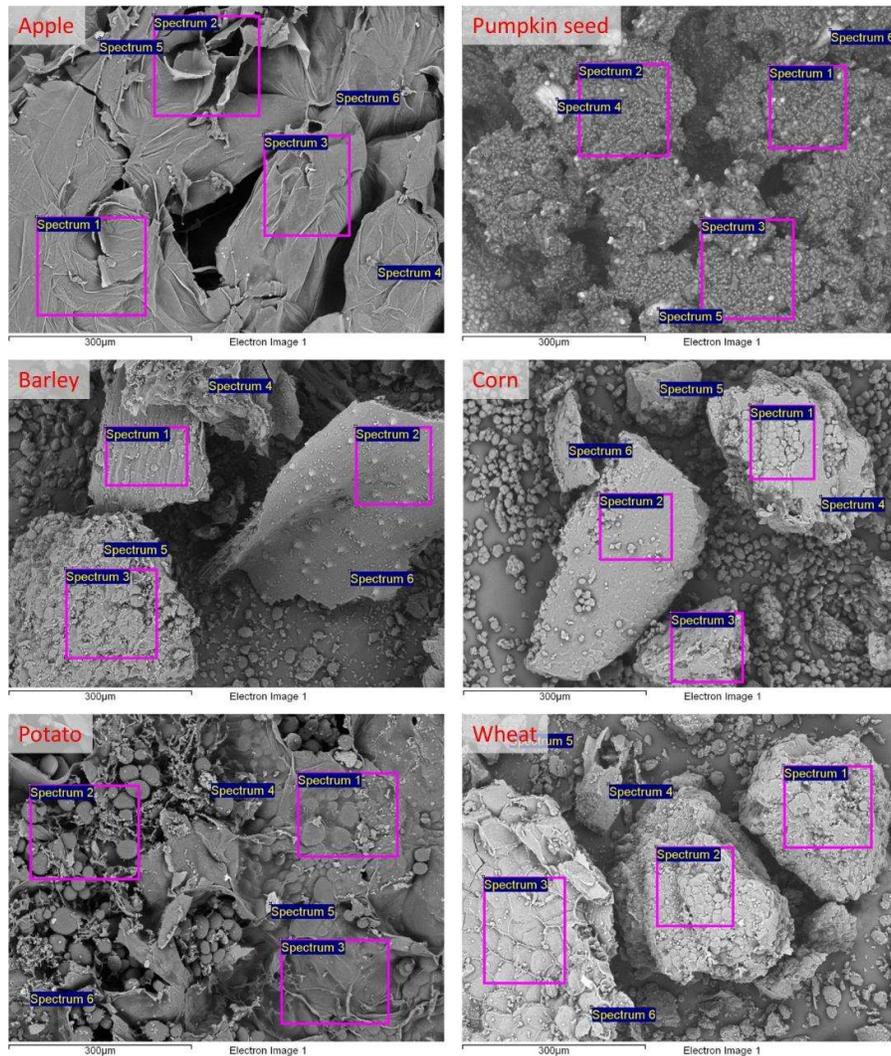


**Figure 2.** SEM and EDS analysis examples of each crop sample.

**Table 1.** Elemental composition of the soil samples, obtained from the EDS analysis.

| | | C | O | Na | Mg | Al | Si | P | K | Ca | Ti | Mn | Fe | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Selo** | **Mean** | 4.57 | 56.16 | 0.56 | 0.73 | 8.91 | 23.30 | 0.00 | 2.39 | 0.29 | 0.16 | 0.00 | 2.95 | 0.00 |
| | **SD** | 3.69 | 4.36 | 1.07 | 0.65 | 4.57 | 6.09 | 0.00 | 2.01 | 0.37 | 0.23 | 0.00 | 2.13 | 0.00 |
| | **Max** | 11.79 | 68.21 | 5.14 | 2.50 | 17.41 | 42.04 | 0.00 | 9.13 | 1.34 | 0.67 | 0.00 | 8.20 | 0.00 |
| | **Min** | 0.00 | 50.17 | 0.00 | 0.00 | 0.00 | 16.37 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **Gornja** | **Mean** | 11.28 | 49.02 | 0.75 | 1.96 | 6.50 | 16.78 | 0.04 | 1.49 | 2.46 | 0.37 | 0.02 | 9.33 | 0.00 |
| **Radgona** | **SD** | 6.42 | 13.55 | 1.05 | 2.41 | 2.83 | 5.84 | 0.13 | 1.40 | 2.98 | 1.58 | 0.11 | 17.36 | 0.00 |
| | **Max** | 21.58 | 61.41 | 3.70 | 9.69 | 11.16 | 32.79 | 0.56 | 6.50 | 11.14 | 7.91 | 0.55 | 83.41 | 0.00 |
| | **Min** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.27 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **Murska** | **Mean** | 5.01 | 52.11 | 0.62 | 1.18 | 9.74 | 18.23 | 0.13 | 2.32 | 0.57 | 2.99 | 0.02 | 7.10 | 0.00 |
| **Sobota** | **SD** | 4.06 | 6.59 | 0.96 | 0.74 | 3.55 | 5.52 | 0.19 | 1.98 | 1.09 | 9.18 | 0.09 | 7.75 | 0.00 |
| | **Max** | 12.27 | 61.60 | 3.92 | 4.11 | 15.34 | 27.61 | 0.59 | 7.12 | 5.53 | 42.43 | 0.47 | 35.58 | 0.00 |
| | **Min** | 0.00 | 29.36 | 0.00 | 0.00 | 0.36 | 0.65 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.58 | 0.00 |
| **Mlajtinci** | **Mean** | 4.78 | 50.81 | 0.36 | 0.83 | 7.93 | 16.95 | 0.07 | 2.01 | 0.20 | 5.83 | 0.61 | 9.63 | 0.00 |
| | **SD** | 4.95 | 8.81 | 0.76 | 0.47 | 4.02 | 9.74 | 0.19 | 1.83 | 0.30 | 11.31 | 1.74 | 10.31 | 0.00 |
| | **Max** | 21.18 | 61.06 | 3.14 | 1.77 | 14.67 | 49.23 | 0.73 | 6.66 | 1.13 | 35.25 | 8.05 | 42.00 | 0.00 |
| | **Min** | 0.00 | 21.72 | 0.00 | 0.00 | 0.42 | 0.91 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **Zbigovci** | **Mean** | 9.99 | 49.97 | 0.16 | 0.94 | 7.30 | 14.73 | 0.10 | 1.86 | 0.35 | 2.32 | 0.00 | 8.92 | 3.36 |
| | **SD** | 16.34 | 8.06 | 0.42 | 0.63 | 4.28 | 7.12 | 0.24 | 1.59 | 0.60 | 7.31 | 0.00 | 9.83 | 11.23 |
| | **Max** | 66.89 | 60.11 | 1.92 | 2.11 | 16.27 | 25.98 | 0.78 | 7.03 | 2.58 | 30.31 | 0.00 | 32.73 | 45.12 |
| | **Min** | 0.00 | 21.90 | 0.00 | 0.00 | 0.00 | 2.16 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| **Stara** | **Mean** | 4.40 | 53.57 | 0.30 | 0.95 | 10.26 | 22.01 | 0.02 | 2.25 | 0.16 | 0.31 | 0.00 | 5.75 | 0.00 |
| **Cesta** | **SD** | 4.22 | 3.52 | 0.53 | 1.17 | 3.81 | 5.61 | 0.10 | 2.22 | 0.28 | 0.47 | 0.00 | 4.00 | 0.00 |
| | **Max** | 13.60 | 57.68 | 1.72 | 4.66 | 17.92 | 41.80 | 0.50 | 8.08 | 1.03 | 1.92 | 0.00 | 18.53 | 0.00 |
| | **Min** | 0.00 | 42.51 | 0.00 | 0.00 | 1.55 | 13.49 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.73 | 0.00 |
| **Rakičan** | **Mean** | 7.60 | 53.19 | 0.60 | 0.88 | 7.02 | 16.21 | 0.07 | 1.09 | 0.49 | 2.47 | 0.12 | 10.28 | 0.00 |
| | **SD** | 4.53 | 4.79 | 1.31 | 0.63 | 3.12 | 8.54 | 0.18 | 0.82 | 0.63 | 5.87 | 0.49 | 12.78 | 0.00 |
| | **Max** | 13.71 | 63.94 | 6.30 | 2.39 | 11.45 | 32.59 | 0.70 | 2.96 | 2.86 | 20.92 | 2.45 | 46.37 | 0.00 |
| | **Min** | 0.00 | 43.24 | 0.00 | 0.00 | 0.84 | 1.10 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.62 | 0.00 |

All values are in weight%.

**Table 2.** Elemental composition of the soil, for all the soil samples combined (the Pannonian region of Slovenia).

| | | C | O | Na | Mg | Al | Si | P | K | Ca | Ti | Mn | Fe | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Total** | **Mean** | 6.80 | 52.12 | 0.48 | 1.07 | 8.24 | 18.31 | 0.06 | 1.91 | 0.65 | 2.06 | 0.11 | 7.71 | 0.48 |
| | **SD** | 8.02 | 8.10 | 0.94 | 1.21 | 4.01 | 7.67 | 0.17 | 1.80 | 1.47 | 6.84 | 0.72 | 10.62 | 4.40 |
| | **Max** | 66.89 | 68.21 | 6.30 | 9.69 | 17.92 | 49.23 | 0.78 | 9.13 | 11.14 | 42.43 | 8.05 | 83.41 | 45.12 |
| | **Min** | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.27 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

All values are in weight%.

**Table 3.** Elemental composition of the crop samples, obtained from EDS analysis.

| | | C | O | Na | Mg | Al | Si | P | Cl | K | Ca | Ti | Fe | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Apple** | **Mean** | 489.32 | 461.86 | 4.10 | 1.48 | 8.41 | 19.54 | 0.00 | | 9.31 | 1.99 | | 3.98 | 1000 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | SD | 134.52 | 100.35 | 12.45 | 1.62 | 21.38 | 56.06 | 0.00 | | 5.96 | 2.34 | | 4.90 | |
| | Max | 763.60 | 697.40 | 57.70 | 7.00 | 77.00 | 252.30 | 0.00 | | 32.50 | 8.60 | | 15.80 | |
| | Min | 150.80 | 230.30 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | | 0.00 | 0.00 | | 0.00 | |
| Barley | Mean | 521.76 | 396.94 | 1.11 | 1.19 | | 40.77 | 0.01 | 5.95 | 27.96 | 1.87 | | 2.42 | 1000 |
| | SD | 109.92 | 74.58 | 1.73 | 1.36 | | 93.74 | 0.07 | 7.59 | 22.83 | 2.46 | | 3.21 | |
| | Max | 653.60 | 513.00 | 7.80 | 5.30 | | 391.00 | 0.40 | 29.60 | 101.30 | 11.70 | | 13.10 | |
| | Min | 162.90 | 188.30 | 0.00 | 0.00 | | 0.00 | 0.00 | 0.00 | 3.30 | 0.00 | | 0.00 | |
| Corn | Mean | 566.45 | 422.61 | 0.80 | 1.80 | | | 0.00 | | 3.40 | 0.65 | | 4.31 | 1000 |
| | SD | 65.68 | 65.32 | 0.96 | 3.93 | | | 0.00 | | 3.68 | 0.86 | | 12.45 | |
| | Max | 709.90 | 511.20 | 3.60 | 20.90 | | | 0.00 | | 14.30 | 3.00 | | 67.00 | |
| | Min | 483.20 | 283.20 | 0.00 | 0.00 | | | 0.00 | | 0.00 | 0.00 | | 0.00 | |
| Potato | Mean | 351.71 | 434.26 | 1.74 | 10.17 | 30.87 | 83.69 | 0.03 | 2.89 | 37.23 | 10.89 | 8.67 | 27.85 | 1000 |
| | SD | 134.26 | 82.33 | 4.26 | 11.22 | 36.28 | 107.84 | 0.15 | 6.23 | 30.35 | 37.84 | 34.81 | 36.82 | |
| | Max | 538.90 | 563.70 | 25.80 | 50.80 | 113.60 | 419.50 | 0.90 | 27.90 | 138.40 | 230.50 | 167.00 | 118.30 | |
| | Min | 67.40 | 167.30 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 3.90 | 0.00 | 0.00 | 0.00 | |
| Pumpkin seed | Mean | 746.98 | 226.05 | 0.40 | 4.90 | | | | 6.16 | 11.65 | 2.39 | | 1.45 | 1000 |
| | SD | 77.78 | 71.11 | 0.66 | 6.55 | | | | 11.43 | 17.79 | 4.98 | | 3.02 | |
| | Max | 890.70 | 392.50 | 2.50 | 26.00 | | | | 47.80 | 93.20 | 18.60 | | 14.30 | |
| | Min | 559.80 | 87.90 | 0.00 | 0.00 | | | | 0.00 | 0.00 | 0.00 | | 0.00 | |
| Wheat | Mean | 577.83 | 413.33 | 0.80 | 0.90 | | | | 0.13 | 4.56 | 0.78 | | 1.70 | 1000 |
| | SD | 62.15 | 58.80 | 1.23 | 1.23 | | | | 0.67 | 5.60 | 1.60 | | 3.09 | |
| | Max | 677.50 | 507.40 | 4.60 | 4.80 | | | | 3.60 | 22.00 | 7.60 | | 15.90 | |
| | Min | 490.20 | 320.10 | 0.00 | 0.00 | | | | 0.00 | 0.00 | 0.00 | | 0.00 | |

All values are in g/kg, calculated from the weight% obtained from the EDS analysis.

**Table 4.** Elemental composition of the crop and fruit samples, obtained from spectrometric and AAS analyses. The analyses were performed in the dried and ashed samples (dm – dry matter).

| | Ash [g/kg dm] | P [g/kg dm] | Mg [g/kg dm] | K [g/kg dm] | Na [g/kg dm] | Fe [mg/kg dm] | Ca [g/kg dm] |
|---|---|---|---|---|---|---|---|
| **Apple** | 19.77 | 0.87 | 0.34 | 8.01 | 0.43 | 67.8 | 0.29 |
| **Barley** | 29.26 | 3.26 | 1.18 | 4.90 | 0.05 | 301.3 | 0.24 |
| **Corn** | 12.42 | 2.32 | 0.71 | 3.51 | 0.02 | 24.5 | 0.03 |
| **Potato** | 54.56 | 2.64 | 1.14 | 24.10 | 0.30 | 146.9 | 0.42 |
| **Pumpkin seed** | 45.15 | 9.97 | 4.30 | 8.34 | 0.06 | 285.0 | 0.21 |
| **Wheat** | 16.91 | 3.44 | 1.09 | 4.20 | 0.02 | 24.5 | 0.03 |

The main constituent elements in the soil were C, O, Al and Si, with Fe and Ti metals. Lower values of K, Mg, Na, Ca, Mn and P were detected in the samples as trace elements. In the soil sample at the location of Zbigovci, Zr was detected additionally, which was not found in the other samples.

The results from the microplastic analysis of the soil samples are shown in Figures 2–8, with detailed images and the FTIR spectra of the various particles detailed in the Supplementary Material S1.
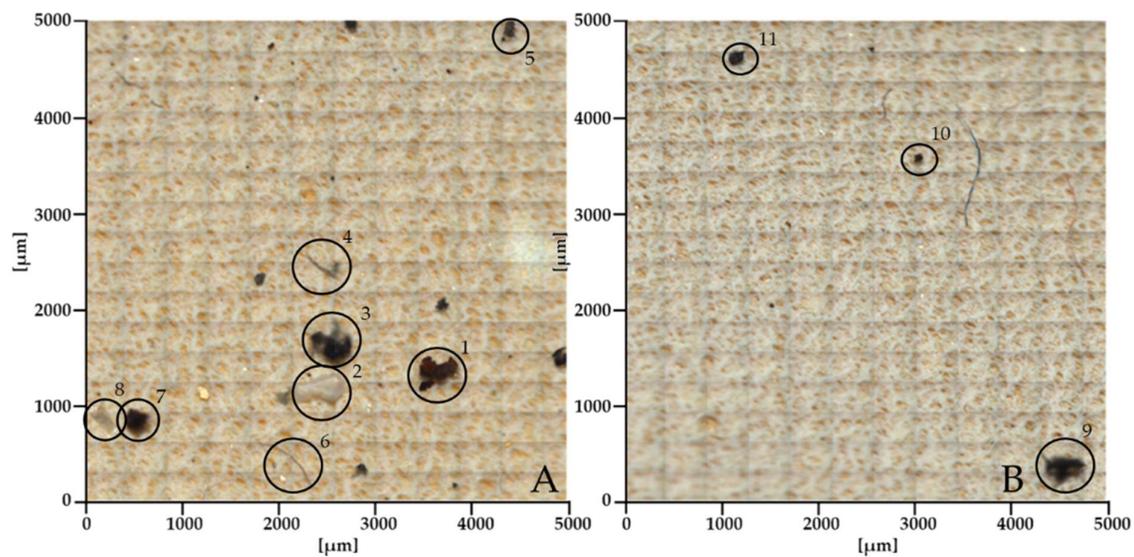
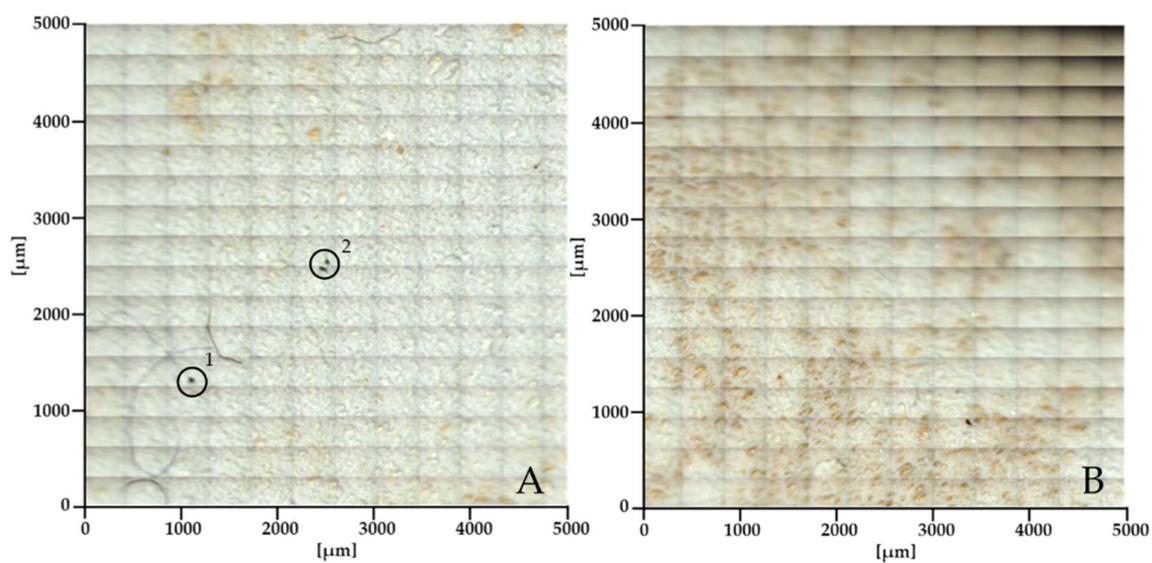**Figure 3.** Stitched FTIR microscopy images of the residues taken from the **Murska Sobota** soil sample.



**Figure 4.** Stitched FTIR microscopy images of residues taken from the **Mljatinci** soil sample.
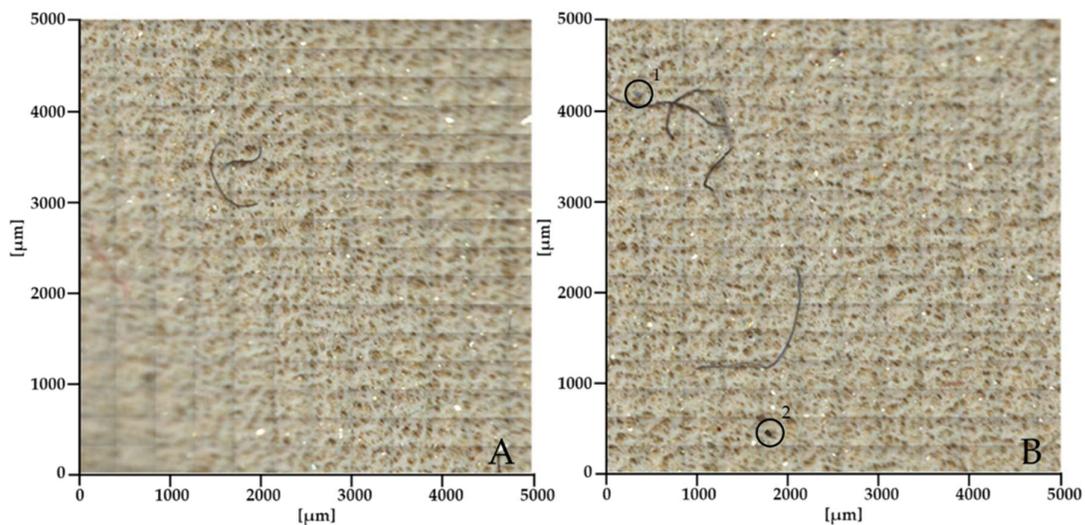
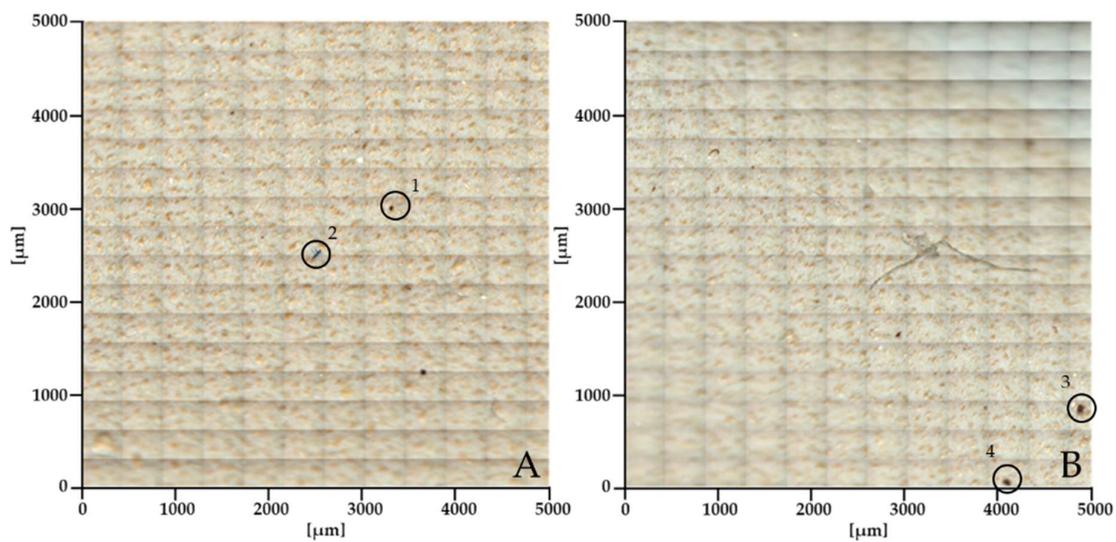**Figure 5.** Stitched FTIR microscopy images of residues taken from the **Rakičan** soil sample.



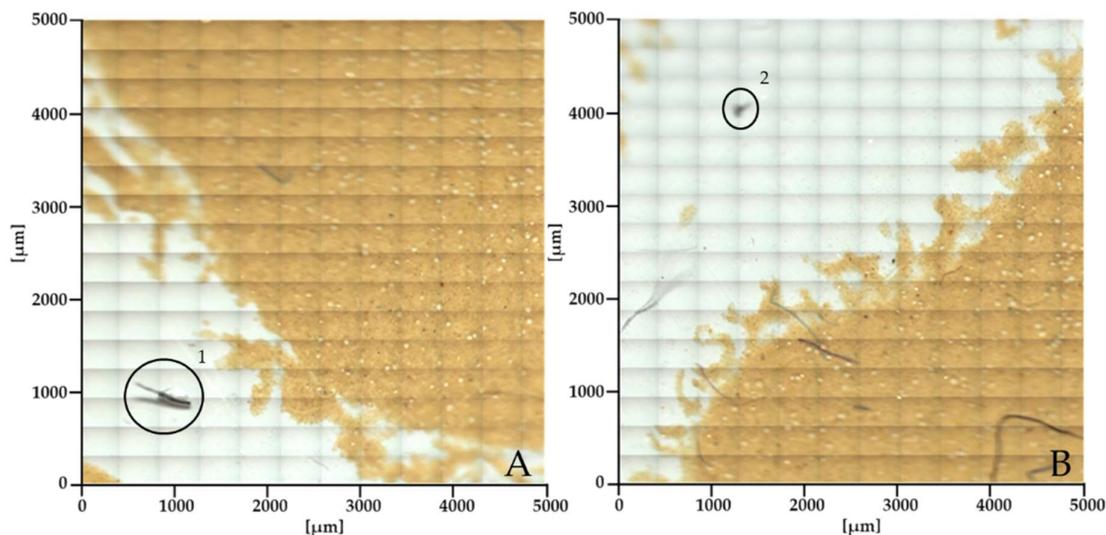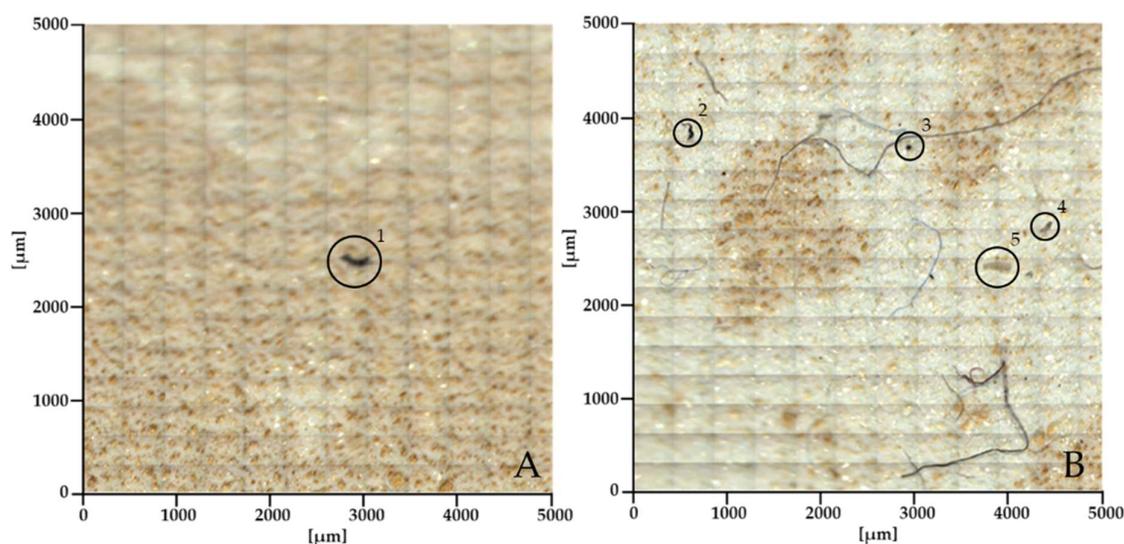**Figure 6.** Stitched FTIR microscopy images of residues taken from the **S. Cesta** soil sample.

**Figure 7.** Stitched FTIR microscopy images of residues taken from the **Selo** soil sample.



**Figure 8.** Stitched FTIR microscopy images of residues taken from the **Zbigovci** soil sample.

The crop samples contained mainly C and O from organic matter, along with varying smaller amounts of Na, Mg, Al, Si, P, Cl, K, Ca, Ti and Fe. Al and Si were present in the apple, barley and potato samples, along with Ti and Fe also being present in the potato sample. The other elements of Na, Mg, P, Cl, K and Ca had lower values in the samples, below or around 1 wt.%.

*3.1. Soil Sample Results*

Significant residues of manmade textile fibres are visible in both images. While points 1 and 2 on image B seem visually to be polymer based, the small size prevented the acquisition of a clear spectrum. The spectral analysis of point 3 corresponded to natural cotton. *Detailed images and FTIR spectra in the Supplementary Material under: 1. G. Radgona.*

On both images a there is a minimal residue of manmade textile fibres with the exception of point 4, that has the characteristic spectrum of spandex. Both images show a significant residue of microplastics, based mostly on PE (points 3, 5, 8 and 11) and degraded PVC (points 1 and 7). With minor residues of polyester detected at point 8 and PTFE detected at point 2 (most likely residue from

the magnetic stir bar). *Detailed images and FTIR spectra in the Supplementary Material under: 2. Murska Sobota.*

The soil sample taken from Mljatinci had almost no microplastic contamination, although the few visible residues were too small to extract a decent FTIR signal. *Detailed images and FTIR spectra in the Supplementary Material under: 3. Mljatinci.*

The soil sample taken from Rakičan had almost no microplastic contamination and some contamination of synthetic fibres. *Detailed images and FTIR spectra in the Supplementary Material under: 4. Rakičan.*

The soil sample taken from S. Cesta had almost no microplastic or synthetic fibre contamination. *Detailed images and FTIR spectra in the Supplementary Material under: 5. S. Cesta.*

The soil sample taken from Selo had moderate fibre residue and some larger microplastic residues identified via FTIR spectrum as polyester urethane (points 1 and 2). *Detailed images and FTIR spectra in the Supplementary Material under: 6. Selo.*

The soil sample taken from Zbigovci had moderate fibre residue (points 1-3) and some smaller microplastic residues identified via the FTIR spectrum as PE (point 4). *Detailed images and FTIR spectra in the Supplementary Material under: 6. Zbigovci.*

*3.1. Crop Sample Results*

## 4. Discussion

*4.1. Soil Sample Results*

Oxygen is the most abundant element in soil, while Si and Al are the second and third most abundant [31]. These are followed by the fourth most abundant element, Fe, which is important for plants and animals, for the biogenesis and functioning of chlorophyll, energy transmission, metabolism of cells, fixation of nitrogen and respiration of plants [32]. The element constituent values for the analysed soil in Tables 1 and 2 correspond with these characteristics. Ti is favourable for plant growth, with available commercial fertilisers containing Ti, used for improving crop production [33].

Parent material/mineralogy are key soil-forming factors, along with climate, biota, relief, and time, as mineral soils—typically composed of more than 95% mineral particles—influence many soil properties significantly [34]. Agricultural practices disrupt the natural nutrient cycling in soil, with intensive cultivation and crop harvesting depleting plant nutrients and organic matter, leading farmers to apply soil amendments (like fertilisers, lime) to maintain fertility [35]. This effect can be also observed in the elemental composition of soil samples from our study, since the soils from forest (Gornja Radgona) and vineyard (perennial) production (Zbigovci) had higher contents of organic matter than samples from intensive crop production (Mlajtinci, Rakičan). Additionally, in the forest, higher concentrations of Ca and Mg were observed, presumably because these elements are not harvested regularly as in intensive agricultural production in other areas. Contrarily, higher concentrations of P and K were determined in the samples from intensive agricultural production (Mlajtinci, Stara Cesta), as these soils are also fertilised intensively. The Fe concentration was highest in forest soils, but also some agricultural soil had high concentrations of this element. The total iron concentration in soil is usually around 2.5% [36], while the average content of this element in the Pomurje soil in our study was higher, 7.71%, and the average in Slovenian soil is 3.80 [37]. On the composition of elements like O, Na, Al, Si and Ti, soil use seems to not have great influence, but are mostly dependent on the parent material. Zr was found only in the sample from a vineyard (Zbigovci), in extremely high concentrations (average 3.36 wt.%) that exceeds the average content in soils, which is 90-850 mg/kg Zirconium content of soil, and is inherited mainly from the parent rocks [38]. Although there are many anthropogenic sources of zirconium possible for soil contamination (nuclear fallout, ceramic dusts and heavy metal mining, improper waste dumping, abandoned industrial activity sites, incidental release) [39], the source of this element in our case is not known and requires further research, but is most probably derived from phosphate fertilisers that are also well known sources of Zr [40].

The analysis of potential microplastic contamination showed relatively low microplastic contamination from non-textile sources in the region, with the exception of the sample area of Murska Sobota. The town of Murska Sobota is, on average, more industrialised, with a significant polymer processing industry that has potentially contributed to the localised higher microplastic contamination. The relatively high degree of textile fibre contamination may be due to the local human activities. A main source may be the water runoff from washing machines. While all possible steps were taken to minimise the potential contamination with fibres from the researchers' clothes, this possible source of contamination cannot be disregarded.

*4.2. Crop Sample Results*

Elements of interest in the crop samples were also Al, Si, Ti and Fe, excluding the other elements with trace values. The potato sample had comparable values of Al, Si, Ti and Fe, as the overall values of these elements in the soil (Table 3, potato sample and Table 2). This suggests an uptake of these elements from the soil inside the potato. Al and Si were also found in the apple sample, with similar ratios between these elements, as they are found in the soil. Only Si was found in the barley sample. The results of elemental analysis with atomic spectroscopy (Table 4), in comparison with the EDS analysis (Table 3) revealed that the latter was not able to detect all the important elements present in crops and fruits fully, among them P, K, Fe, Mg and Na; only K was the element detected in all plant tissues. Those elements are otherwise widely present in crops and fruit, with the concentration varying regarding the plant species and variety, growth conditions and soil properties, and plant tissue analysed [41–43]. The lack of determination might be related to the very low concentration of those elements in the freeze-dried tissue (EMS analysis), while the elements analysed in ash were highly concentrated in the procedure of the sample preparation and quantified successfully with ASS and spectrophotometrically (Table 4). The SEM analysis was more reliable for detection of the elements in the soil samples.

**5. Conclusions**

The results of the elemental composition of soils from the Pomurje region can generally be classified in to two different categories, those being mainly soils from forests that are richer in Mg and Ca, and soils where intense agricultural production occurs, where higher concentrations of P and K are typical for artificially fertilised soils.

One key outlier was a region rich in Zr, the source of which requires a more detailed study of the area's mineral composition and localised human activity.

In general, the region sems to be slightly richer in Fe, with an average content of 7.71% than the Slovenian average of 3.80 %.

Despite intense agricultural use, the region sems to be relatively free from microplastic contaminations, as only a minimal quantity was extracted from the soil samples. A key outlier was the sample taken in Murska Sobota, a larger town that has a pronounced plastic processing industry, dealing in the rotational moulding of large products.

The potato and apple crops showed a distinct similarity of element composition as the soil they were planted in.

While the EDX analysis was sufficiently accurate when analysing the soil samples, the same was not observed in the organic crop samples where the EDX analysis failed completely to detect the relevant elements in the crop samples.

The low detection rate of EDX was most likely a compounding effect of low concentration, sample porosity, low sample conductivity, which necessitates the use of a conductive Au coating to improve imaging.

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