Source-specific risks apportionment and critical sources identification of potentially toxic elements in arable soils combining integrated positive matrix factorization model with multivariate analysis and machine learning classifiers: a case study of the Pannonia Basin

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Abstract

Understanding the source-specific ecological and human health risks and critical sources of arable soils by potential toxic elements (PTEs) is significant for urban contamination control and management. Comprehensive characterization of the arable soils used for organic and conventional agricultural management practice has been done for the first time in the Pannonian Basin, relating the levels of PTEs: As, Cd, Co, Cr, Cu, Ni, Zn, Pb and physicochemical characteristics. Pollution indices such as I_{geo} values for conventional agricultural management practice suggested that the investigated soil samples can be classified as ”unpolluted” or “moderate”, while for organic agricultural management practice samples were classified as “uncontaminated” to “heavy contaminated”. Integrated approaches applying Spearman correlation, positive matrix factorization, and multivariate analysis (PCA) were used to investigate relationships among PTEs and physicochemical properties of soils. PCA revealed that the identified PTEs’ pattern specified their distribution between soil samples intended for organic and conventional agricultural management practice while five different machine learning classifiers: Support Vector Machine, Bayesian Network, Multilayer Perceptron, Random Forest, and J48 which were used to develop test models intended to determine the type of soil agricultural practice have justified their high reliability to distinguish two types of management practice. Three main sources of PTEs were identified: natural, antropogenic, and agricultural sources, which accounted for 63.70%, 19.10%, and 17.20% of the total PTEs content, respectively. According to the occupational health risk assessed for the first time in studied agricultural region no potential non-carcinogenic risk is evidenced, while cancerogenic one was 8.41E-04 indicating potential risk.

1. Introduction

The increasing population and continuing demand for food create a need to make global agriculture production sustainable to supply sufficient amounts of food with more efficient use of resources. Additionally, there is a necessity to change population habits towards more balanced diets to promote better public health mainly through increasing the contribution of fresh fruit and vegetables in the daily diet (Smith et al., 2018). Therefore, it is believed that organic agriculture is a production system that endows the opportunity of the preservation of health of soils, ecosystems, human health and give possible solutions for accumulated problems in conventional agriculture. The purpose of organic agriculture in soil protection and rural development are incorporated in the United Nations following Rio + 20 through the Sustainable Development Goals (SDGs) and EU action plan Biodiversity Strategy (European Commission, 2010). In Serbia, the development of the organic production sector started in 1990 with the aim to promote standards in organic production by following the International Federation of Organic Movement (IFOAM). Serbia adopted EU regulation on organic farming (Council Regulation EC, 2007), made the Law on Organic Production (RS Official Gazette no 30/2010), and established the new Rulebook on controlling and certification in organic production and on organic methods (RS Official Gazette no 95/20). The development of organic agriculture sector in Serbia is very slow, and according to the latest data from 2017, only a small area is used for organic agriculture (Roljević-Nikolić et al., 2017).

All the above-mentioned factors encourage the need to deepen the knowledge on advantages and disadvantages of organic food production over conventional agricultural practice and if possible to distinguish each other based on identified level of PTEs, as the heart of organic agriculture is use of renewable resources, recycling, and reducing use of synthetic pesticides, herbicides, and chemical fertilizers which may have negative effects on the environment and on agricultural products (European Council, 1999). Conventional agricultural practices might be the main source of potential toxic elements (PTEs) pollution which can enter into soils via repeated fertilization and spraying of pesticides up to six or seven times per year, usage of substandard fertilizer and compost, usage of untreated wastewater for irrigation, and industrial activities (Keshavarzi and Kumar, 2019; Kumar et al., 2019). The self-regulating ability of ecosystem is weak, which results in higher concentrations of PTEs than geochemical background values. Moreover, potential heavy elements such as As, Cd, Co, Cr, Cu, Ni, Zn and Pb have a strong tendency to accumulate in soil and weak tendency to degrade, and in accordance can be transferred through food chain (Škrbić et al., 2020). In particular, some potential toxic elements as Cd, As, Ni and Cr, are classified as carcinogenic contaminants-class-I that can cause anemia, neurotoxicity, poisoning, lung cell damage and other breathing problems, while Pb inorganic is classified as carcinogen-class-II, which high levels can affect tissue of the brain and nervous systems (Alves et al., 2017). Thus, agricultural workers working on land can be occupationally expose to potentially toxic elements that can cause non-cancer and cancer risks. Moreover, some authors (Feria et al., 2010) stated that both type of soils can be equally exposed to environmental contaminants, organic soils could even have the same or even higher content of environmental pollutants such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and potential toxic elements. Although, the development of the organic production started at the beginning of the 21st century, to the best of our knowledge, only a few research studies have compared conventional and organic management practices in agricultural soil (Smith et al., 2018) and there is no single study to date that deals with simultaneous determination of PTEs content in soil intended for organic and conventional agricultural management practices (Gasparatos et al., 2011). The comparison of organic and conventional agricultural practices is complicated because there is no regulation dealing with permissible levels of potential toxic elements in soil intended for organic management practices (Gasparatos et al., 2011). Additionally, no detailed information is available on the pollution assessment and possible sources of PTEs in organic and conventional soil in the world.

Based on the above, the aims of the present work were set to a) investigate levels of potential toxic elements and physico-chemical parameters in soils used for both organic and conventional agriculture practice, b) compare obtained: (i) concentrations of PTEs in both soil types between each other's and with the maximum allowed levels set by Serbian national and European countries legislations, and either with the ecotoxicological values set for southern and whole Europe agricultural soils and as well as with the ones obtained for agricultural regions of the Vojvodina Province-Pannonian Basin and (ii) physico-chemical parameters of investigated conventional and organic soil types, c) reveal sources of PTEs in both soil types, d) estimate occupational health risk (non-cancer and cancer risk) and eco-risks for studied soil samples, and e) ultimately for the first time use the machine learning classifiers to develop models for prediction of the type of agricultural management, practice (conventional vs. organic) based on measured physicochemical properties and PTEs content. To the best of our knowledge this is the first comprehensive study dealing with the characterization and application of the integrated statistical approach for identification of the type of arable soil to be used for conventional and organic management practice.

2. Materials And Methods

2.1. Study area

The studied area covers one of the biggest agricultural regions on the Balkans, the Pannonia basin to which also belongs Province of Vojvodina, the northern part of Serbia and south-easter part of Hungary (Mrazovac et al., 2013). The Province of Vojvodina comprising 28% of the total land area of Serbia and 26% of the total population. In the studied area there are fewer villages than in the other regions with relatively low population density (approximately 94 people/km^2) and all villages are connected with roads and communication network. The main factor of economic development in studies region is agriculture. The studied area belongs to steppe-forest zone with a grassland ecosystem, which could be found in North America (Midwestern Plains), Russia (Belyaev, 2007) and China (Peng and Foster, 2007) with highly productive agricultural soil and crop production is dominant because of the fertile soil (Galić et al., 2009). Arable soil has been developed under the forest steppe when the process of technological revolution and need to produce more food caused the conversion of forests which means that the crop yield is cause by soil moisture.

Thus, the climatic conditions are favorable for agriculture production, but insufficient rainfall can be a limitation and it can have influence on yield of agricultural products. Investigated area covers approximately 300000ha of arable soil with the dominant chernozem soil type and the agricultural production is carried out in plain climatic-production zone (Popović and Vasiljević, 2013) with average annual temperature about 10. Detailed sample procedure is given in Text SI-1 Supplementary Material.

2.2. Laboratory analysis and quality assurance/quality control

Wet digestion method was used to determine the organic matter (OM); method included dichromate with external heat, and titration to assess the content of unreacted dichromate (Mebius, 1960). pH measurements were carried out in ultra-pure water (obtained from a Milli-Q system (Millipore, Molsheim, France)) at a soil/water ratio of 1/2.5 (ISO10390) with potentiometric glass electrode with a pH meter (Hach Instrument, Germany), while soil conductivity was measured in ultra-pure suspension (soil/solution 1/5) (Hach Instrument, Germany). Humus content was determined by the wet oxidation method with $K_2Cr_2O_7$ (Simakov, 1957), while the free calcium carbonate ($CaCO_3$) content was determined by the ISO 10693:1995 volumetric method (Racić et al., 2017).

The previously published method (Škrbić et al. 2018) for analysis of PTEs in soil and dust samples was used in this study. The concentrations of eight potential toxic elements (As, Cd, Co, Cr, Cu, Ni, Pb, and Zn) in the soil samples were determined by graphite furnace atomic absorption spectrometer (Agilent Technologies, Santa Clara, USA) (GFAAS). More about this could be found in Supplementary Material in Section Text SI-2.

Quality assurance/quality control (QA/QC) of the analytical method was conducted in order to provide validation parameters of the applied method for PTEs determination in investigated organic and conventional soil samples. The details about QA/QC can be found in Supplementary Material in Section Text SII-1 and in Table S1.

2.4. Potential ecological risk and pollution levels

To evaluate ecological risk of studied organic and conventional soil samples, geo accumulation index (I_{geo}), contamination factor (CF), integrated pollution load index (PLI), Nemerow integrated pollution index (NIPI) and new modified approach for risk assessment Nemerow integrated risk index (NIRI) that takes into consideration the differences in toxic response factors of PTEs were applied (Škrbić et al., 2022). Therefore, the NIRI revised the undulation of the Er caused by the number of PTEs, and increases flexibility of the NIRI in terms of changes in the number of calculated PTEs, thus, is used for more accurate prediction of pollution level. The equations which were used for calculation of mentioned indices and classifications are given in the Text SIII-1 and in Table S2 (Supplementary Material).

2.5. Health risk assessment

Vulnerability of the farmers to the HEs at studied agricultural region was assessed by methodology recommended by US EPA (US EPA 1989) through the total carcinogenic and non-carcinogenic risks. Exposure of the farmers was calculated for the dermal contact, ingestion and inhalation pathways. Carcinogenic and non-carcinogenic health risks for farmers for harvesting season were assessed using the quantified mean HEs concentrations in samples taken in August in order to get the first insight of the possible health risks as it was already done in study by Škrbić et al., 2021. Equations and the parameters used for calculations of health risks were described in the Text SIV and Table S3 and Table S4 given in the Supplementary Material.

2.6. Statistical treatment of the data

DEL 13.2 Statistica (Tulsa, Oklahoma, USA) and Microsoft Excel 2010 for Windows were used for statistical treatment of the data. For testing variables distribution in a population Shapiro-Wilk test (Sh-W) was used. Spearman correlation analysis was applied to describe the correlation characteristics of PTEs in agricultural soil between organic and conventional agricultural management practice and their correlations with physicochemical properties. Statistical significance difference between means of two types of soil samples was checked by student’s t-test. Multivariate statistical tools such as principal component analysis (PCA) and correlation analysis were used to evaluate the relationship between investigated soil characteristics and levels of PTEs (Škrbić et al., 2010; 2018). PCA was performed with

Varimax rotation, which minimizes the number of variables that are packed with high loads on each component. Additionally, positive matrix factorization (PMF) model was used for confirmation of pollution source apportionment of PTEs (USEPA 2014; Men et al., 2020) as a receptor model that can quantitatively calculate the contribution of possible PTEs sources at each data point and data uncertainty. The detailed explanation and calculations of the model could be found in Text SV-1 (Supplementary Material) and in the US EPA PMF 5.0 User Guide (USEPA, 2014).

2.7. Developing of prediction models based on machine learning classifiers

In order to develop and test the models to be used for prediction of soil agricultural practice (organic or conventional), five different machine learning classifiers were used, i.e. Support Vector Machine (SVM), Bayesian Network (BN), Multilayer Perceptron (MP), Random Forest (RF), and J48. The input data used for development of models are the determined concentrations of PTEs (As, Cd, Co, Cr, Cu, Ni, Zn, and Pb) and the physicochemical properties (pH, conductivity, organic matter content, humus content, and calcium carbonate content) of the studied agricultural soils. These models were developed using Weka 3.8.3 (Waikato Environment for Knowledge Analysis) software (Cohen, 1960). The details of the applied procedure are presented in Supplementary Material in Section Text SVI-1.

3. Results And Discussion

3.1. Physicochemical parameters of organic and conventional soil

The physicochemical properties of investigated organic and conventional soil samples are shown in Table S5 (Supplementary Material). As can be seen from Table S5, the pH values of organic soil samples were in the range of 7.88–9.05, while for conventional soil samples were in the range 7.86–8.97. Most arable soil in Serbia has neutral to alkaline pH (Belić et al., 2014). The presence of base-forming cations associated with carbonates which are found in soils and in water used for irrigation leads to this phenomenon. In general, the determined pH values of the investigated soils for organic and conventional management practice were found to be within the range of acceptable values for cultivation of crops and the availability of nutrients to the plants (Andrades and Martínez, 2014). No statistically significant difference was found between two practices when pH values were compared which was in accordance with the results published by Andrades and Martínez (2014) that also confirmed that the difference is not significant. The electrical conductivity, as the measure of the number of soluble salts in the soil, was found to be from 170 μS/cm to 540 μS/cm in organic soil samples, while for conventional soil EC was in the range from 155 μS/cm to 580 μS/cm. As it could be seen from Table S5, the mean EC value (329 μS/cm) of organic soil samples was higher than for conventional soil samples being 242 μS/cm. To evaluate essential components of agricultural soils necessary for plant cultivation, organic matter content (OM) was examined as the one factor that contributes to biological, chemical and physical properties of the soil. The average organic matter content in the organic soil samples was 8.34%, while for conventional soil samples it was 12.1%. Burning of crop straws and other vegetation (which is more pronounced in conventional agricultural production –demographic habit, although prohibited) has been found to be an important route of increased OM content. Farmers used to apply "burning of crop straw" in order to lower input costs. However, it is important to underline that there was no statistically significant difference in the OM percentage between the organic and conventional soil samples. Additionally, humus content for organic soil samples was from 6.40 to 10.3, while for conventional soil samples was from 6.08 to 10.9. These values indicated that both investigated soil samples are very-humic (Belić et. al., 2014). Although, decrease of humus content, as one of the main characteristics of soil fertility, might be caused by the burning of crop residues in the field, neglect of crop rotation and reduction or long-term omission of the use of organic fertilizers (mainly manure) (Škrbić et al., 2020), the results obtained in this study show rather uniform distribution of humus content in both soil types. Calcium carbonate content for organic soil samples was from 0.41–2.09%, while for conventional it was in range from 0.51–5.46%. Calcium carbonate content in both organic and conventional soil samples indicating that these soils are moderate calcareous in nature and it can have adverse effects on the availability of macronutrients and yield (Belić et. al., 2014).

3.2. Total concentrations of potential toxic elements in organic and conventional soil samples

The basic statistics (mean, median, standard deviation, kurtosis, skewness) of the PTEs concentration are presented in Table 1. The contents of As, Cd, Co, Cr, Cu, Ni, Pb, and Zn ranged from 1.73 to 13.6 mg/kg, from 0.440 to 2.49 mg/kg, from 1.42 to 13.1 mg/kg, from 4.73 to 65.6 mg/kg, from 20.8 to 125 mg/kg, from 6.93 to 31.0 mg/kg, from 3.83 to 67.1 mg/kg, and from 16.1 to 170 mg/kg, with median values of 5.54, 1.47, 7.20, 26.3, 38.7, 25.6, 11.1 and 57.6 mg/kg, respectively. The mean concentrations of PTEs, in decreasing range were Zn (63.7 mg/kg) > Cu (46.1) > Cr (27.5 mg/kg) > Ni (13.2mg/kg) > Pb (13.1 mg/kg) > Co (6.79 mg/kg) > As (6.29 mg/kg) > Cd (1.55 mg/kg). The means of concentrations of investigated PTEs in soil samples were below the maximum allowed concentrations (MACs) set in Dutch standard (Dutch standards, 2000) and the target values established by Republic of Serbia (Official Gazette of the Republic of Serbia, No. 88/2010, 2010) relating the MACs of PTEs in soil, indicating that agricultural soil samples are relatively secure for agricultural production and human health.

Table 1
Descriptive statistics of investigated agricultural soil sample

	As	Cd	Co	Cr	Cu	Ni	Pb	Zn
Mean, mg/kg	6.29	1.55	6.79	27.5	46.1	13.2	13.1	63.7
Median, mg/kg	5.54	1.47	7.20	26.3	38.7	25.6	11.1	57.6
Standard Deviation	3.58	0.339	0.520	12.4	29.5	10.7	1.45	10.4
CV, %	45	29	37	47	53	27	68	89
Kurtosis	-1.27	-1.82	-1.61	4.32	6.94	-2.36	2.16	-0.762
Skewness	0.886	0.481	0.247	1.96	2.54	-0.235	-1.43	0.622
Minimum	1.73	0.440	1.42	4.73	20.8	6.93	3.83	16.1
Maximum	13.6	2.49	13.1	65.6	125	31.0	67.1	170
Background, mg/kg (Ubavić et al., 1993)	2.21	0.51	1.38	2.58	8.93	4.55	14.4	60.3

However, in comparison with the generally accepted background values for agricultural soil of Vojvodina region (Ubavić et., al 1993), the concentration of As, Cd, Co, Cr, Cu, Ni and Zn were 2.84, 3.04, 4.92, 10.7, 5.16, 2.9, and 1.1 times higher, respectively than the background values indicating that these elements could have been enriched in the soil through anthropogenic activities. The soil background values were obtained by analyzing 1600 soil agricultural samples with different physico-chemical properties randomly collected across the agricultural regions of Province of Vojvodina comprising 28% of the total agricultural land area of Serbia. Land was taken at the depth of 0–30 cm (including soil samples in vicinity of Novi Sad) (Ubavić et al., 1993). The same procedure was already applied in the previously published studies regarding the determination of PTEs (Soltani et al., 2015; Tang et al., 2017).

The values of standard deviations of examined PTEs were high as the quantified concentrations showed high heterogeneous distribution in the investigated samples. The highest value of the coefficient of variation (CV) occurred for Zn (89%), indicating a fluctuation which is in relation to the obtained high mean value. The coefficient of variation of Pb and Cu was also high being 68% and 53%, respectively. Chromium, As, and Co with CV values of 47%, 45%, and 37%, respectively, showed moderate variation, while Cd and Ni with CV 29%, and 27% showed low variation.

According to the skewness values, kurtosis values, and Kolmogorov–Smirnov normality test, all studied potential toxic elements were not normally distributed.

Based on published ranges of PTEs for agricultural soils of south Europe (Reimann et al., 2018) and the ones determined for investigated agricultural soils in the Vojvodina province belonging Pannonia Basin, it could be concluded that the upper range of studied soil samples were always several times lower, being approximately 80 (Ni), 50 (As), 20 (Pb), 10 (Co), 10 (Cr), 8 (Zn), 4 (Cd) and 3 (Cu) times lower than the south European upper range, respectively. Moreover, comparing statistically determined median values published by Reimann et al., 2018, with the median values obtained in this study it could be concluded that median values obtained in this study for Cd, Cu, Ni and Zn were 6.68, 2.04, 1.21 and 1.08 times higher, respectively, while for Cr it was almost at the same level. For As, Co and Pb the median values of Serbian agricultural soils attended for both practices were 1.44, 1.40 and 1.89 times lower than statistical median values calculated for south Europe agricultural soils, respectively. Moreover, it is worth mentioning that the mean values for each of the investigated elements for all studied agricultural fields (conventional and organic) were always several times lower than the geochemical (non-toxicological) threshold values determined for southern and whole European agricultural soils (Reimann et al., 2018), being approximately for 7 (Ni), 8 (Pb), 7 (As), 5 (Co and Cr), 3 (Zn), 2 (Cu) times lower, respectively while only the mean value of Cd was in accordance with geochemical trash values for south European agricultural soils. Additionally, considering the determined mean values for studied agricultural soil from Pannonia Basin, and the ranges of defined soil guideline values for PTEs in agricultural soil set in legislations issued by different authorities for European counties, it could be concluded that for the investigated soil samples reported mean values are always several times lower than the upper set range and below the set lower range values with the exception of Cd (taking into consideration only the lowest maximum allowable value set for Hungary and Denmark and (Reimann et al., 2018). All these findings indicated that studied arable soil might be very suitable for agricultural activities as satisfying all requested parameters relating to the presence of regulated potential toxic elements. However, geogenic cooccurrence levels can be highly variable and using geogenic levels from other places or global crustal averages for comparison can be taken with caution. Namely, arable soil physico-chemical parameters are crucial to be set and taken into account in comparison of found concentration level of PTEs, as their mobility and distribution are highly dependent of soil's physico-chemical parameters. Thus, without knowing the pH, conductivity, OM, content of humus and etc., the comparison is only approximative.

3.3. Comparison of the total concentrations of potential toxic elements from two different agricultural management practices

The agricultural soil of Pannonia basin, that belongs to Province of Vojvodina-northern part of Serbia and southern part of Hungary has huge ecological, social and economic potential for agricultural production. The soil texture characteristics, presence of water sources and favorable climate could provide the sustainable agricultural and rural development of the region. Many factors influence the concentration of PTEs in the organic and conventional agriculture soil such as interactive effects of agricultural practices, soil texture, irrigation practice, climatic conditions, time of harvest, as well as the vicinity of the source of contamination of PTEs. Consequently, comparison of PTEs concentrations is very challenging. The main differences between organic and conventional agricultural management practices are use of synthetic chemical fertilizers and pesticides. Namely, conventional agricultural management practice grants the use of synthetic fertilizer, compost, manure, sewage sludge and all available soil additives, while organic agricultural management practice only allows the use of compost and manure. In addition, when the use of pesticides and herbicides is considered, the conventional agricultural management practice allows the use of all approved by the authority's available chemicals, while organic permits only the use of a few pesticides for plant protection mainly chemicals based on copper and sulphur (Borsato et al., 2020). The content of eight potential toxic elements (As, Cd, Co, Cr, Cu, Ni, Pb and Zn) was depicted in Fig. 2. Nevertheless, the soil samples from organic agricultural management practice showed slightly higher mean values of As (7.98 mg/kg), Cd (2.23 mg/kg) Co (8.73 mg/kg), Cr (35.9 mg/kg), Cu (49.7 mg/kg), and Ni (19.7 mg/kg), however, their concentrations are under permissible limits. Moreover, in order to examine statistical differences between management practice Man-Whithey test was applied and it revealed that there are no statistically significant differences between the PTEs determined for conventional and organic practices. Possible source of mentioned PTEs could be found in direct discharge of untreated wastewater (urban and industrial wastewater) into surface water (mainly rivers and irrigation canals, e.g. the Great Bačka canal (Škrbić et al., 2018; Krčmar et al., 2017) and usage of surface water for irrigation (Schröder et al., 2016). Namely, agricultural production in Serbia generally suffers from water shortfall during the growing seasons and it is a common practice in investigated region that the crops are irrigated with surface river and lake waters. The type of water used for irrigation is not well documented, although some villages in Serbia used tap water for irrigation (Antić et al., 2020), while others used low quality surface water (Krčmar et al., 2017; Surdyk et al., 2010). It is known that water used for irrigation of crops for organic agricultural practice can contribute significantly towards the higher concentrations of PTEs such as As, Cd Co, Cr, Cu, and Ni. Moreover, concentrations of Cd vary greatly between investigated sampling locations and the possible sources of Cd could be aerial deposition, phosphate fertilizer and sewage sludge. In Serbia, although it is not recommended, some organic farmers use slowly dissolving phosphate fertilizer which contains Cd. Generally, the mean concentrations of Pb and Zn being 14.3 mg/kg and 63.9 mg/kg, respectively, were higher in conventional soil samples, but always being lower than the ones set by Serbian and by the other European legislations and below geochemical (non-toxicological) background values statistically determined for southern European agricultural soil (Reimann et al., 2018).

Higher concentrations of Pb and Zn in conventional soil samples could be associated with usage of fertilizers (mainly phosphate fertilizers), pesticides which are frequently used in the Province of Vojvodina and vehicle emissions (Surdyk et al., 2010). Phosphate fertilizers are used for tomatoes and pepper crops. Moreover, it is common practice in Serbia that vegetables are treated with insecticide against fungal disease and weeds. Also complex fertilizers such as N:P:K-10:5:40, N:P:K-24:12:12, $MgSO_4$ can contain Pb and Zn in trace amounts (Simić, 2017). Student's t-test was applied to examine statistically significant differences between the PTEs concentrations in organic and conventional soil. The results of t-test indicated that there was no significant difference in the concentrations of PTEs between organic and conventional agricultural practice. Additionally, the use of different agricultural fertilizers does not significantly increase total PTEs content in the soil above background levels (Rutkowska et al., 2009).

3.4. Correlation between physicochemical properties and total concentrations of PTEs

Investigation of the correlations among soil properties and PTEs content is helpful tool for analyses of the impact of various human activities which could be associated with increase of PTEs in agricultural soil. Hence, Spearman correlation was applied in order to recognize if the relationship between soil pH, OM, EC, humus content, $CaCO_3$, and PTEs in investigated soils samples existed. The results of correlation analysis are presented in Table S6, Supplementary Material. Generally, soil pH showed a positive correlation with As, Cd, Co, and Cr. Slightly significant positive correlations between pH and As, Cd, Co and Cr could be attributed to the same source or the associated form of the mentioned elements in which they are slightly mobile. The level of Cu, Pb and Zn are negatively correlated with pH (although not significantly) indicating that these elements are present in chemical form(s) that are more mobile in investigated agricultural soils. Moreover, the obtained results demonstrated that there is no correlation ($p < 0.05$) between most of investigated PTEs and very important soil physicochemical properties OM, conductivity, and humus content. Organic matter showed a strong positive correlation only with humus content and $CaCO_3$. The results of this study showed that there are very few correlations between examined soil characteristics. Higher concentration levels of Cu and Zn are correlated with lower levels of Pb. Zinc was found to have the highest level in investigated soils and the high correlated with EC indicating the that the chemical form of Zn is present in parent material.

Additionally, significant strong positive correlations were observed between particular groups of PTEs in investigated agricultural soils. Strong positive correlations (0.86–0.71) were observed for Cd with Co, Co with Cr, As with Cd, and moderate positive correlation (0.44–0.56) between Co with As and Cd. Strong positive correlations between particular PTEs may indicate their similar source (Reimann et al., 2018).

3.5. Source identification of PTEs

A combination of multivariate statistics using PCA and positive matrix correlation (PMF) was applied to explore possible sources which contribute to increasing of PTEs quantity in investigated agricultural soils. It is important to mention that no statistically significant difference between two agricultural practices was found. Therefore, PMF was carried out on the whole dataset (without any separation of input data) obtained for both agricultural management practices. Additionally, biplot was used to reveal the relationship between sampling locations, potential toxic elements content and physicochemical properties.

3.5.1. Positive matrix correlation analysis (PMF)

For identification and quantification of pollution sources of PTEs PMF was applied. The results obtained from the PMF model are shown in Fig. 3. Factor 1 contributed to 63.7% of the PTEs in the investigated soil samples and contained loadings for Cu (99.2%) and Zn (58.2%). The obtained mean concentrations of Cu and Zn slightly exceeded background concentrations (Ubavić et al., 1993). Moreover, Cu and Zn showed lower CV values, Table 1, in comparison with the CV of other PTEs. Based on statistics (Table 1) it could be concluded that Cu and Zn probably have the same origin (natural sources). Hence, F1 may represent natural sources, such as pedogenic processes and soil parent materials.

Factor 2 accounting for 19.1% of the total contribution, and it was weighted only on Pb (46.3%). Lead had a high CV value, indicating anthropogenic sources. In Serbia, emissions from motor vehicles have been regarded as the main source of Pb in urban and agricultural soil over the years (Guo et al. 2014). All sampled locations were in vicinity of the roads, so F2 could be associated with vehicle emission. Studies of Guo et al. (2018) and Cui et al. (2018) confirmed that vehicle exhaust emission accounts for almost two third of total Pb global emissions.

Factor 3 accounting for 17.2% of the total contribution and was dominated by Ni (77.7%), Cr (72.3%), Co (68.8%), Cd (59.4%), and As (56.6%). The use of pesticides, organic manures, and usage of surface water (in which untreated wastewater is directly discharged (Pedrazzani et al., 2019) for irrigation, generally provide considerable amounts of these elements (Zhang et al., 2014, Salem, 2021). Moreover, as it was mentioned earlier, it is a common practice in Serbian agricultural production of vegetables and fruits to apply large-scale fertilizers and pesticides, which results in PTEs accumulation in soils. Fertilizers based on NPK, as well as phosphate fertilizers, copper sulphate, iron sulphate, and manure from animals that contains Cd, Co, Cu, As, and Zn as impurities are the usual culprits for the enrichment of soil with PTEs (Alloway, 2013). Therefore, F3 is associated with agricultural activities and applied practices (Fei et al., 2020). Thus, critical source identification achieved by performing source-specific analysis should be considered when managing pollutant sources to decrease the perniciousness of contaminants.

3.5.2. PCA analysis

PCA analysis clearly showed separation of two principal components, the first principal component represented the 42% of the total variance. The biplot was used to illustrate and to reveal hidden similarities between locations from which organic and conventional agricultural management practice were conducted i.e., to investigate PTEs and soil physicochemical properties, Fig. 4. PCA analysis revealed that As, Cd, Co, Cr, and Ni were quantified in higher concentrations in soil samples from organic agricultural management practice, while higher concentrations of Pb and Zn were observed in soil samples from conventional agricultural management practice. Pb and Zn differentiate the samples on the second principal component (17% of total variance). Thus, the identified PTEs' pattern specified their distribution between soil samples intended to be used for conventional and organic soil practice.

Green points represent samples from organic agricultural management practice, while blue points represent samples from conventional agricultural management practice. The biplot even shows distribution between investigated sampling locations and PTEs which point out some difference in their composition. Hence, from Fig. 4, it can be seen that two groups were extracted. The first group represents strong correlation mostly among samples from organic agricultural management practice with EC, and As, Cd, Co, Cr, Cu, and Ni concentrations, while the second group is highly correlated with samples from conventional agricultural management practice and pH and $CaCO_3$. This was mainly due to slightly higher concentrations of As, Cd, Co, Cr, Cu, and Ni in organic soil.

Additionally, data mining was applied to develop and test the models intended to determine the type of agricultural production (for conventional or organic) based on determined PTEs concentrations and physicochemical properties of the soil.

3.5.3. Machine learning classification models

Table 2 presents the results of the models developed for prediction of soil agricultural practice (organic or conventional). As can be seen from Table 2, generally, better accuracy was obtained when all measured data were included (pH, conductivity, organic matter, humus content, $CaCO_3$ content and PTEs concentrations) for almost all tested clarification models. The accuracy of the RF classification model for both data sets (with and without physicochemical properties) was 100%. Like the RF, the J48 classification algorithm showed equal accuracy of the model (93.75) for both data sets. Opposite to the previously discussed models (RF and J48), classification model NB displayed the lowest accuracy for both data sets (87.5%). SVM and MLP classification algorithms showed equal accuracy (93.7%) for data set with included physicochemical properties and PTEs concentrations while the accuracy of the MLP classification model with only included concentrations of investigated elements was the lowest being 81.2%. As can be seen from Table 2, the values for Kappa coefficient as a measure of the agreement between the predicted and observed categorizations of the dataset with physicochemical properties included were equal for models SVM, MLP, J48 or higher for RF model.

Table 2
Classification performances of the dataset for the evaluated classification models

Performance measure	**SVM[b]**	**NB[c]**	**MLP[d]**	**RF[e]**	**J48**
Organic vs. conventional without physicochemical properties					
Accuracy (%)	87.5	87.5	81.2	100	93.7
Kappa coefficient	0.75	0.75	0.62	1	0.87
MAE[a]	0.12	0.13	0.19	0.15	0.062
Organic vs. conventional with physicochemical properties					
Accuracy (%)	93.75	87.5	93.7	100	93.7
Kappa coefficient	0.87	0.75	0.875	1	0.875
MAE[a]	0.062	0.12	0.11	0.195	0.062

As the Weka software can perform model comparison in the light of statistical evaluation, the five developed models based on the data set consisting of physicochemical properties and concentrations of PTEs were statistically compared. The statistical evaluation was performed at a 0.05 confidence interval. The obtained results for F-values were 0.97, 0.97, 0.94, 0.97 and 1 for MLP, SVM, NB, J48, and RT models, respectively. Thus, based on the results revealed by F-values there were no statistically significant difference among the evaluated models at the 0.05 level. Therefore, all five developed models could be successfully used for separation of lands for conventional and organic management practice based on the concentration levels of eight investigated PTEs and five physicochemical parameters of studied soil samples.

4. Risk Assessment

4.1. Limitations and implications

The mean values of single-element indices for conventional and organic agricultural management practice I_{geo} and CF were presented in Fig. 5, Fig. 6 and Table S7 (Supplementary Material). The I_{geo} values for conventional agricultural practice were in following descending order: Cr > Cu > Co > Cd > As > Zn > Ni > Pb. Chromium and Cu had higher I_{geo} values indicating that soils were moderately contaminated ($1 < I_{geo} \leq 2$, degree 2). Moreover, for other PTEs soil samples were recorded as uncontaminated ($0 < I_{geo} \leq 1$, degree 1). Descending order of I_{geo} values for organic agricultural management practice were Cr > Co > Cu > Ni > As > Cd > Zn > Pb. I_{geo} indices for organic agricultural management practice were classified as degree 1 (Zn, Ni, Cd, As and Pb), degree 2 (Co and Cu), and degree 3 (Cr) which indicated heavy contamination for Cr according to the I_{geo} value. Based on CF values contamination by human activities (CF > 1) for major of investigated PTEs was found with exception of Pb in both agricultural practice. On the other hand, in conventional agricultural management practice As, Cd, Cu and Ni were classified as moderate contamination (CF of 3–6), whereas Cr showed very high contamination (CF > 6). For organic agricultural management practice, only values of CF obtained for Pb indicated low contamination, while CF for Co and Cr showed considerable contamination.

The individual I_{geo} values for Cr in all analyzed samples were ranged from 0.368 (sample no. 11) to 5.10 (sample no. 20), and 12.5%, 37.5%, 33.33%, 12.5% and 4.17% of all investigated samples were classified as uncontaminated to moderately, moderately, moderately to heavily, heavily and extremely polluted, respectively. When I_{geo} values of Cd were taken into consideration obtained range was from 0.175 (sample no. 10) to 2.34 (sample no.5) and 83.34%, 8.33% and 8.33% of sampling location were classified as uncontaminated to moderately, moderately and moderately to heavily polluted. According to the I_{geo} values for other investigated PTEs all studied location were classified as unpolluted to moderately polluted, Fig. 5. The individual values of CF for conventional and organic agricultural management practice ranged from 0.142 (Pb-sample no.10) to 11.41 (Cr-sample no.1) and from 0.282 (Pb-sample no.17) to 25.43 (Cr-sample no.20), respectively (Fig. 6).

According to the CF values for Pb, only location no.12 (2.84) was moderately polluted while all other locations were classified as low contaminated with CF values being lower than 0.463. Based on the CF values, Cr could cause very high contamination for organic agricultural practice, while 30.77% and 69.23% of convention soil locations were considerable and very high contaminated, respectively. On the other hand, calculated CF values of As, for conventional management practice indicated that 7.70%, 76.92% and 15.38% were low, moderate and considerable polluted, while 18.18%, 72.72% and 9.10% of studied fields for organic agricultural practice were moderate, considerable and very high polluted, respectively. Furthermore, CF values of Cu were ranged between 2.34 (sample no. 2) to 14.02 (sample no.14), and 15.38%, 61.54% and 23.08% of locations for conventional production, and 9.10%, 72.72% and 18.18% of organic locations were moderately, considerable and very high contaminated, respectively.

Relating calculated CF values for Cd and Ni, it was indicated that 30.78% of locations for conventional agricultural practice and no one for organic management practice were low polluted. Additionally, only one of the all studied locations based on CF values for Cd was very high contaminated (sample no. 4), while majority of the studied locations were moderately contaminated. However, 36.36% locations for organic production based on CF values for Ni was very high polluted with no one intended for conventional production. Moreover, CF values of Co, ranged between 1.03–6.82, indicated that only 15.38% of locations for conventional production were moderately while the rest were considerable contaminated. In the case of organic locations, the CFs were between 5.33–6.87, with 45.45% and 54.55% of studied fields being considerable and very high polluted, respectively. The average PLI value for organic agricultural management practice was found to be 3.12, while for conventional agricultural management practice was 3.05. Since the average PLI was above unity for all studied samples, deterioration of site quality for investigated region is noticed based on applied background values of the studied PTEs in Serbian arable soils (Ubavić et al., 1993) used in the risk estimation. Moreover, if the integrated risk that takes into account the influence of the number of studied PTEs has calculated, the mean value of the NIPI was 8.14 indicating that the majority of the sites are strongly polluted. Furthermore, the mean value for NIRI in the studied area was 91.2 indicating considerable risk. However, based on the calculated NIPI and NIRI values only conventional location no.10 with NIRI of 20.68 and NIPI of 2.44, indicated low risk, while the other conventional locations were under considerable (61.54%) and high (30.77%) risk, respectively. Moreover, taking into consideration, locations used for organic agricultural practice, based on NIRI values 45.45%, 45.45% and 9.10% were under considerable, high and extreme risk, respectively, while based on calculated values of NIPI all locations were strongly polluted. Namely, as it is mentioned earlier integrated risk is significantly influenced by the number of calculated potential toxic elements and toxic response factors being the highest for As and Cd. Thus, the values of the NIRI in this study were largely influenced by concentrations of As and Cd.

On the other hand, based on the comprehensive survey of PTEs concentration ranges, mean, median, geochemical values, maximums allowed concentrations of PTEs set by European regulatory bodies for European agricultural soils (Reimann et al., 2018) and the determined levels of PTEs in agricultural soils from the northern part of Serbia and southern part of Hungary belonging to the Pannonian Basin (Table 1) it might be concluded that evaluation of risk by using the indices such as I_{geo}, CF, PLI, NIPI and NIRI with the accepted background values from Ubavić et al. (1993) might not give the real picture of the state of the agricultural soils. Namely, application of the estimated indices may overestimate the risk what is confirmed by the finding in this study, particularly considering that mean values determined for investigated soil samples in this study were several times lower for the most of PTEs than the geochemical (non-toxicological) threshold values determined for southern and whole European agricultural soils (Reimann et al., 2018).

Additionally, the geochemical threshold values published for European agricultural soils are several times higher (being approximately for (Cr) 111, (Cu) 40, (Co) 27, (Ni) 25, (Pb) 22, (As) 20, and (Cd and Zn) 3 times higher) than the background values determined for Serbian agricultural soils (Ubavić et al., 1993). However, in European scale, the variation in the natural background concentrations of all investigated elements in agricultural soil samples is much larger than any anthropogenic impact (Reimann et al. 2018). Thus, it can explain the fact that direct comparisons of PTEs concentrations with accepted background values provides one side view relating elements levels control, and might fails to adequately interpret the level of risk of those PTEs can pose (Fei et al. 2022). Anyhow, the indices also should be taken with precaution in the case of agricultural soil PTEs risk estimation. Namely, the proper choice of PTEs background concentrations is crucial, particularly taking into consideration the definition of "ambient background" given in ECHA, 2008 (Reimann et al., 2018) as "the sum of the natural background of an element and diffuse anthropogenic input in the past or present, without the massive influence of point sources" which indicates that the chosen background values depend also of time the soil samples were taken. Moreover, if taken into account, the proposed indication limits of food chain contamination for standard texture soils for selected elements (Cd, Ni and Pb) at pH higher than 6.5 (Vacha et al., 2014), as was the case for the investigated arable soils, it could be concluded that in this study the determined levels of Cd, Ni, and Pb, were 1.29 times for Cd, 15.2 times for Ni and 22.90 times for Pb lower than the proposed indication limits of the ones. Moreover, if the limit values of phytotoxic risk elements (Ni, Cu and Zn) (Vacha et al., 2014), which indicate the plant growth inhibition that results in significant yield reduction, are taken, it was revealed that the mean concentration levels determined in this study were lower 15.2 times for Ni, 6.51 times for Cu and 6.28 times for Zn than the set phytotoxic risk limits. Thus, generally, considering the proposed data for indication limits of food chain contamination and phytotoxic risk it could be concluded that there are no any risk relating food chain contamination and plant growth inhibition with studied elements. These, additionally, support the fact that the application of indices might not give the real picture of the state of the agricultural soils and can overestimate potential risks (Reimann et al., 2018; Škrbić et., 2010; Sakan et al., 2015). Therefore, the use of proper geochemical trash hold values is crucial and should be set by regulatory bodies of each region based on definition given in (Reimann et al., 2005.) to adequately manage the ecological and health risks for sustainable production (Fei et al. 2022).

4.2. Occupational health risk assessment

Potential toxic elements accumulated in agricultural soil may cause negative effects on farmer's health because farmers are exposure to PTEs during harvesting and land cultivation. Researchers around the world have reported that pollution by PTEs in the soil can contribute the etiology of oral cancer and cause neurological, cardiovascular and autoimmune diseases (Wang et al., 2020). To assess the exposure of the farmers in studied agricultural region to non-carcinogenic and carcinogenic risks were calculated by using the USEPA health risk recommended method (US EPA 1989). The health risk assessment was based on three exposure pathways: agricultural soil to farmers via inhalation, ingestion and dermal contact. The total HI expressed as a sum of different exposure routes of the farmers to heavy elements was 4.46E-01, which indicates no adverse non-carcinogenic human health effects on farmers health (HI < 1) in entire studied area. Hazard quotients calculated for individual potential toxic elements were the following decreasing order Cr > Cu > As > Co > Pb > Ni > Cd. The order of hazard quotients routes of exposure was as follows ingestion > dermal > inhalation. Accidentally ingestion of agricultural soil seems to be the dominant exposure route for the farmers in investigated agricultural region so it is suggested that during stay in field farmers wear protective masks. Moreover, potential total carcinogenic risk (TCR) estimated via ingestion, inhalation, and dermal exposure for farmers was 8.41E-04 indicating potential risk because 1 in 10,000 people may develop cancer from lifetime exposure to carcinogenic hazards.

Findings obtained in this study are in accordance with study by Wang et al. (2020). In order to keep on with the protection of farmer's health risks, fertilizers and traffic emissions as a source of the PTEs must be subjected as priority management in agricultural activities and agricultural activities must be designated as a priority pollution source.
/p>

Conclusion

The sector of organic agriculture is constantly growing, but still represents a small part in the global agriculture (in Europe 22%). In Serbia and Hungary, the percentage of agricultural areas under organic production is increasing day by day and this is the first study comparing the concentrations of PTEs in soils intended for organic and conventional agricultural management practices. Agriculture could be the key for sustainable development due to multiple effect on economic (in order to provide fibred, foodstuffs, bio-fuels, source of incomes), social (impact on quality of life and health) and on environment (in order to protect water, soil, climate and biodiversity) but sustainable management is required. Based on obtained results in this study it could be concluded that arable soil used for conventional agricultural management practice could be also used for organic agricultural production due to low concentrations of PTEs and as there is no statistical significance between the level of PTEs and physicochemical parameters in two types of arable soil. Besides, applied statistical approaches: PCA and models developed for prediction of soil types based on data manning classifiers confirmed clear distinguish between soil types based on PTEs patterns and physico-chemical parameters of. It could be concluded that there are not any risks relating to food chain contamination and plant growth inhibition by the studied PTEs. However, potential total carcinogenic risk (TCR) estimated via ingestion, inhalation, and dermal exposure for farmers was 8.41E-04 indicating potential risk because 1 in 10,000 people may develop cancer from lifetime exposure to carcinogenic hazards. Thus, health risk assessment based on PTEs concentration indicated that farmer's health during stay in agricultural field might be endangered. The obtained results demonstrate that in perspective of food safety, the usage of surface water for irrigation should be under control as the surface water quality directly influence on enrichment of some PTEs even in organic agriculture. In future perspective the improvement of water management should be taken as a major goal and to raise land area dedicated to organic agriculture because still large percentage of arable land is under conventional use. Additionally, present manuscript can be used to encourage farmers and researchers to inform public about pollution status in agricultural sector. Moreover, critical source identification achieved by performing source-specific analysis should be considered when managing pollutant sources to decrease the perniciousness of contaminants.

Declarations

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Figures

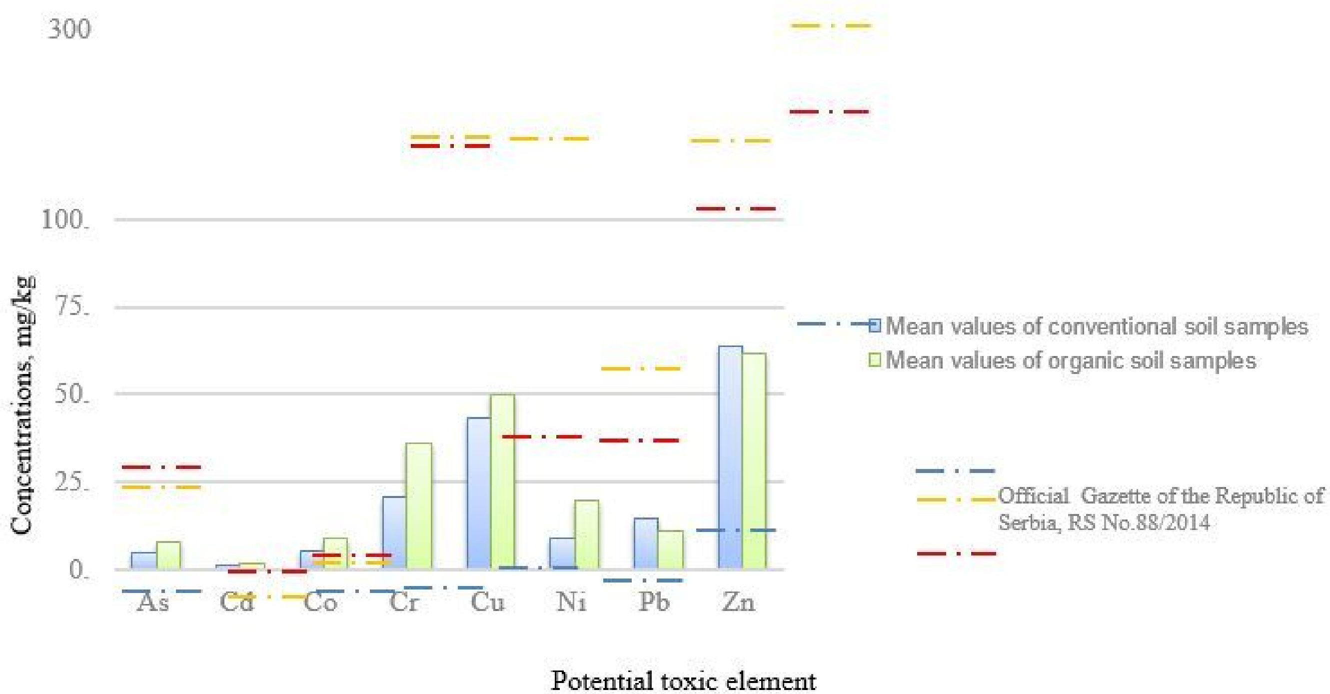

Figure 1

Fig 2. Comparison of PTEs concentrations in the soil samples used in organic and conventional practice

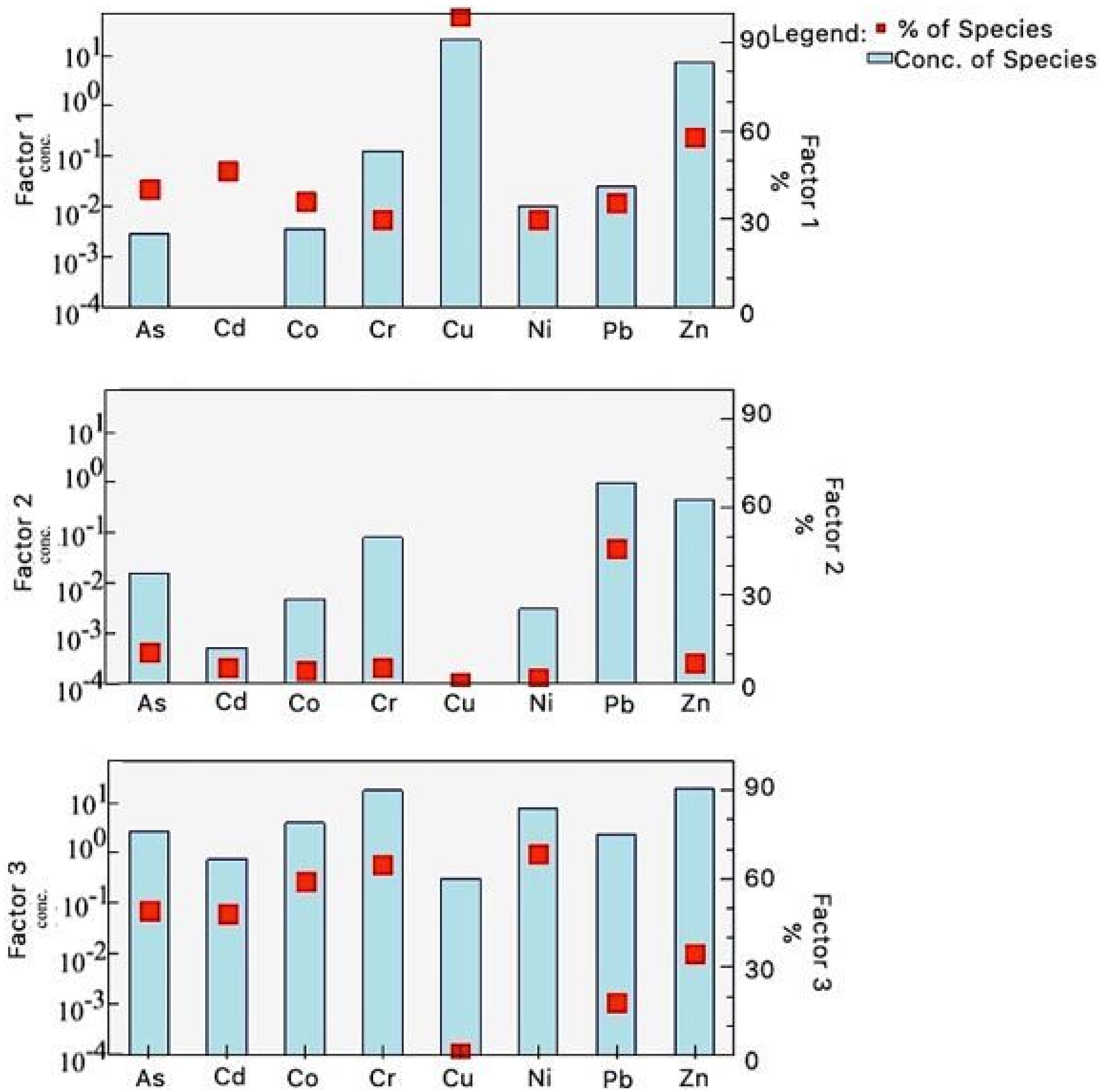

Figure 2

Fig 3. Source contributions of investigated potential toxic elements obtained from PMF model

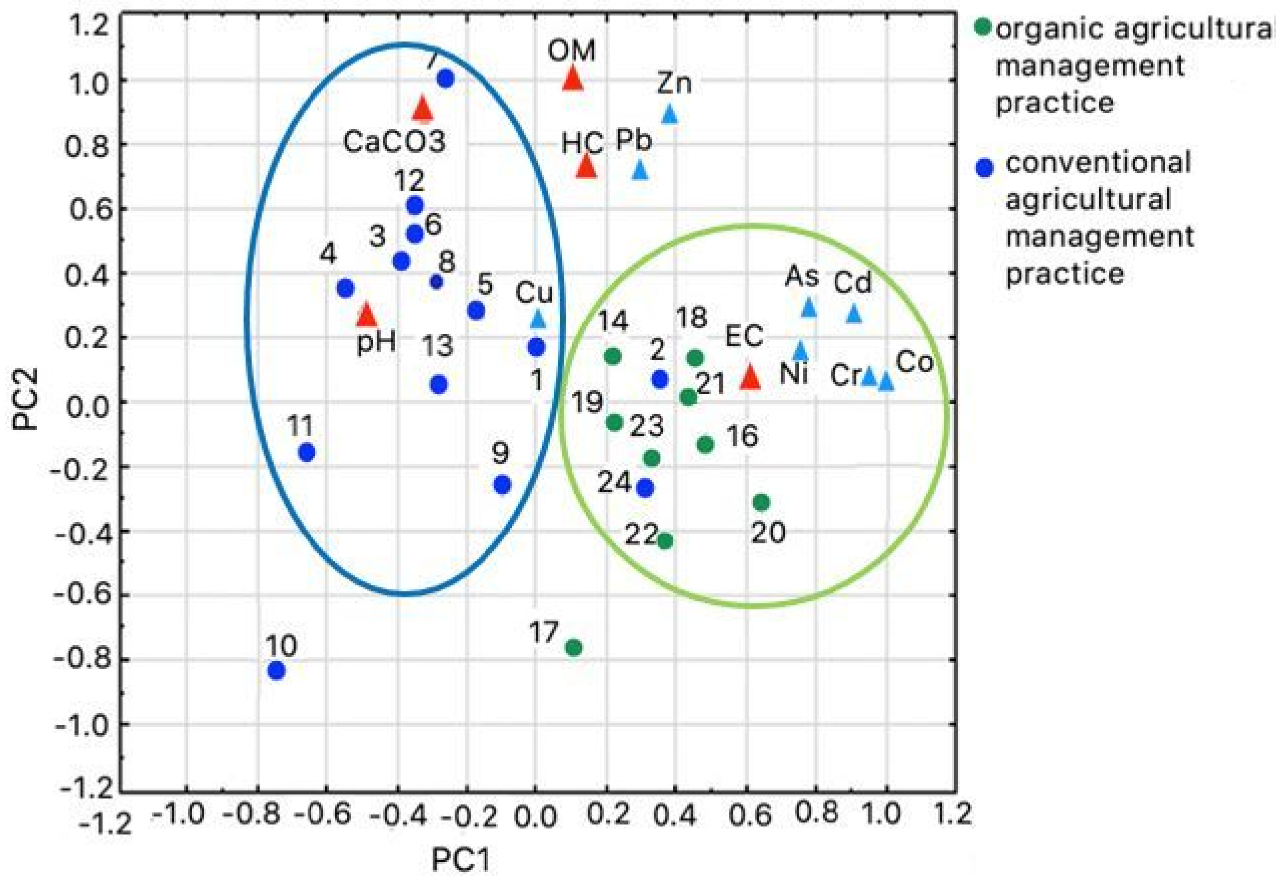

Figure 3

Fig 4. PCA biplot obtained for soil physicochemical properties, PTEs content and samples from organic and conventional agricultural management practice

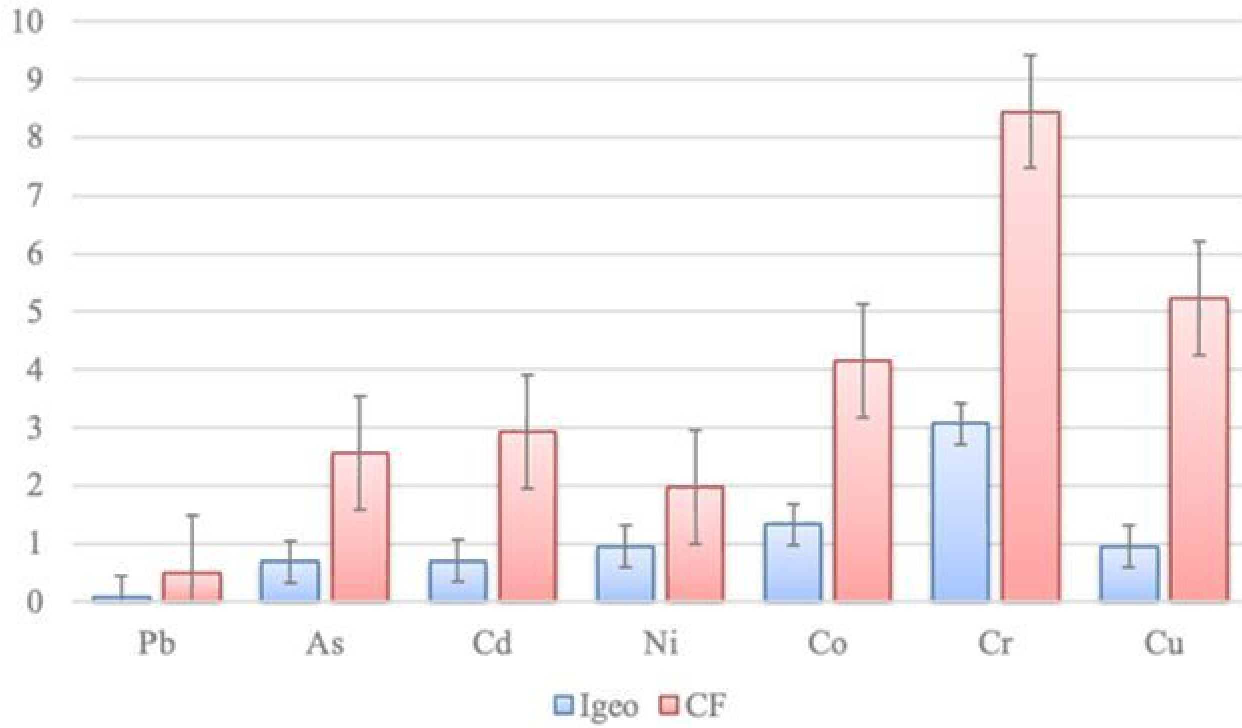

Figure 4

Fig 5. Geoaccumulation indices and contamination factor class distribution of studied PTEs for mean concentrations in agricultural soil

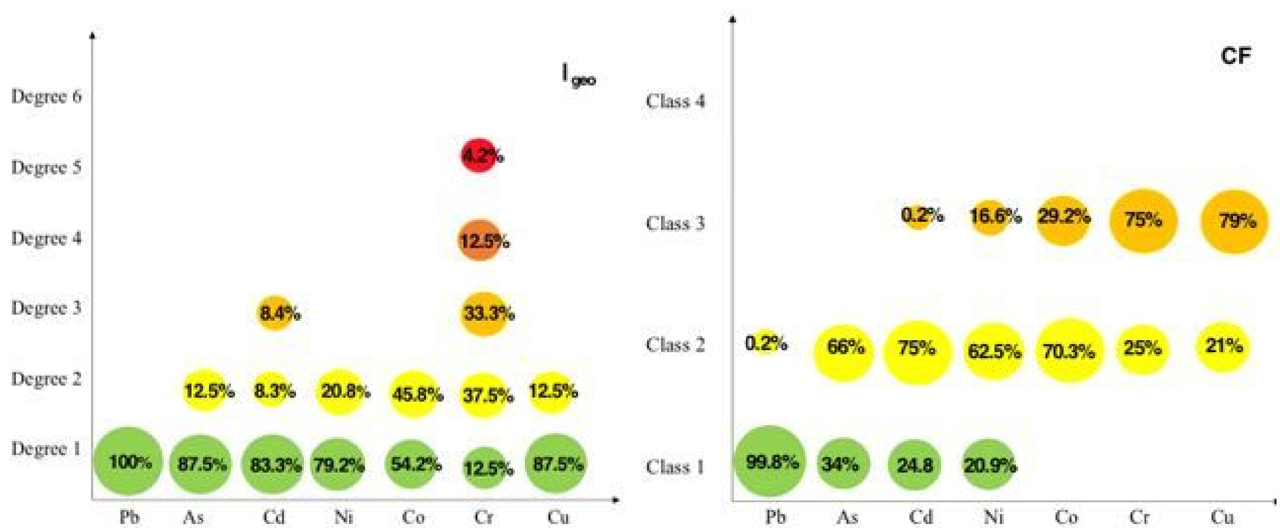

Figure 5

Fig 6. Geoaccumulation indices and contamination factor class distribution of studied PTEs for mean concentrations in agricultural soil

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