Scientific Papers. Series A. Agronomy, Vol. LXVII, No. 1, 2024
ISSN 2285-5785; ISSN CD-ROM 2285-5793; ISSN Online 2285-5807; ISSN-L 2285-5785

LAND USE IMPACT ON SELECTED CHEMICAL PROPERTIES OF HUMOFLUVISOLS IN PERI-URBAN AREA IN ZAGREB (CROATIA)

Aleksandra BENSA[1], Ivan MAGDIĆ[1], Jana KRKALO[2], Nikolina JURKOVIĆ BALOG[1], Aleksandra PERČIN[1]

[1]University of Zagreb, Faculty of Agriculture, Svetošimunska cesta 25, 10 000, Zagreb, Croatia
[2]University of Zagreb, Faculty of Agriculture, MS student of Agroecology, Svetošimunska cesta 25, 10 000, Zagreb, Croatia

Corresponding author email: imagdic@agr.hr

Abstract

The objective of the study was to assess the effects of different long-term land uses on the basic chemical properties and contamination of Humofluvisols by potentially toxic elements (PTE). A total of 20 top soil samples (0-30 cm) were collected in the peri-urban area of Zagreb within cropland (CROP), orchard (ORCH), vegetable garden (VEGA), and urban park (UP). A significantly lower pH value was determined in ORCH compared to the other land use types. The UP had a significantly higher soil organic carbon (SOC) content than agricultural soils. The P_2O_5 and K_2O concentrations were significantly lower in UP compared to agricultural soils. The As, Cu, Pb, and Zn concentrations were the lowest in UP. Significantly higher Cu concentrations were determined in ORCH compared to other agricultural soils. The soils of UP, CROP, and VEGA had PTE concentrations below the maximum permissible concentrations. Only three soil samples from ORCH were contaminated by As and Zn. Tillage, fertilization, and the application of pesticides were presumably the reasons for altered soil chemical properties and reduced soil quality of agricultural soils.

***Key words**: agriculture, available nutrients, pH, potentially toxic elements, soil organic carbon.*

INTRODUCTION

Land management practices modify the environment, including soil quality and productivity (Jiang et al., 2006; Grieve, 2011; Bogunović et al., 2020; Assefa et al., 2020). Agriculture production implies tillage, fertilization, and the application of pesticides that can significantly alter particular soil properties. It affects soil organic carbon (SOC) content (Lehtinen et al., 2014; Barančikova et al., 2016), pH (Ge et al., 2018), and the status of physiologically active nutrients (Bogunović et al., 2017; Margenot et al., 2018; Kumar et al., 2024).
Apart from the change in basic chemical soil properties, an additional problem in agricultural soils is contamination with potentially toxic elements (PTE) (Huang et al., 2008; Toth et al., 2016; Rashid et al., 2023). Their origin in soils is both natural (geogenic and pedogenic) and anthropogenic. Fertilizers and pesticides applied to agricultural soils are significant sources of PTEs (Kabata Pendias and Mukherjee, 2007). The elevated level of Cu concentrations in soils under permanent crops, due to long-term application of Cu–based fungicides, is the most commonly observed and widely documented problem in the literature (Li et al., 2005; Brunetto et al., 2017; Ballabio et al., 2018; Fu et al., 2020). Furthermore, enrichment of agricultural soils with other heavy metals such as As (Alexakis et al., 2021; Kobza, 2021) and Zn (Park et al., 2011) was also documented.
Humofluvisols are widespread in alluvial deposits and are characterized by fluvic material within the soil profile. The heterogeneity of parent material results in variable soil properties and fertility (Husnjak, 2014). In general, these soils are characterized by deep ecological depth, loamy texture, favourable water-air relations, neutral to weakly alkaline reactions, and medium SOC content. Grundwater level varies below a depth of 1 m without causing problems with water-air relations in the rhizosphere zone. Furthermore, the capillary rise of groundwater prevents the lack of physiologically active water in drier months (Vukadinović and Vukadinović, 2011).

Therefore, these are fertile soils that are intensively used in agriculture. In Croatia, Humofluvisols occupy 86670.9 ha, out of which 83.4% are used in agricultural production (Husnjak, 2014).
Agriculture near urban areas is an important source of food for local markets in several cities around the world (Zasada, 2011; Opitz et al., 2015; Dieleman, 2017). There are few socioeconomic and environmental benefits of peri-urban agriculture (Brinkley, 2012; Fereira et al., 2018). However, there are some concerns as well regarding food safety (Boente et al., 2017; Kesharvazi et al., 2018) and the degradation of biodiverse ecosystems and the services these systems provide (Wilhelm and Smith, 2017).
The general aim of the study was to assess the effects of different long-term land uses on the properties of Humofluvisols in the peri-urban area of Zagreb. The specific goals were to: (i) determine selected chemical properties in top-soil samples under different land use types; (ii) compare analysed soil properties among land use types; and (iii) evaluate soil contamination by selected PTEs.

MATERIALS AND METHODS

Study area

The study was conducted in the northeastern part of the city of Zagreb in central Croatia (Figure 1). Four study sites were selected in the surroundings of the University of Zagreb, Faculty of Agriculture: cropland (CROP), orchard (ORCH), vegetable garden (VEGA), and urban park (UP), as shown in Figure 1.

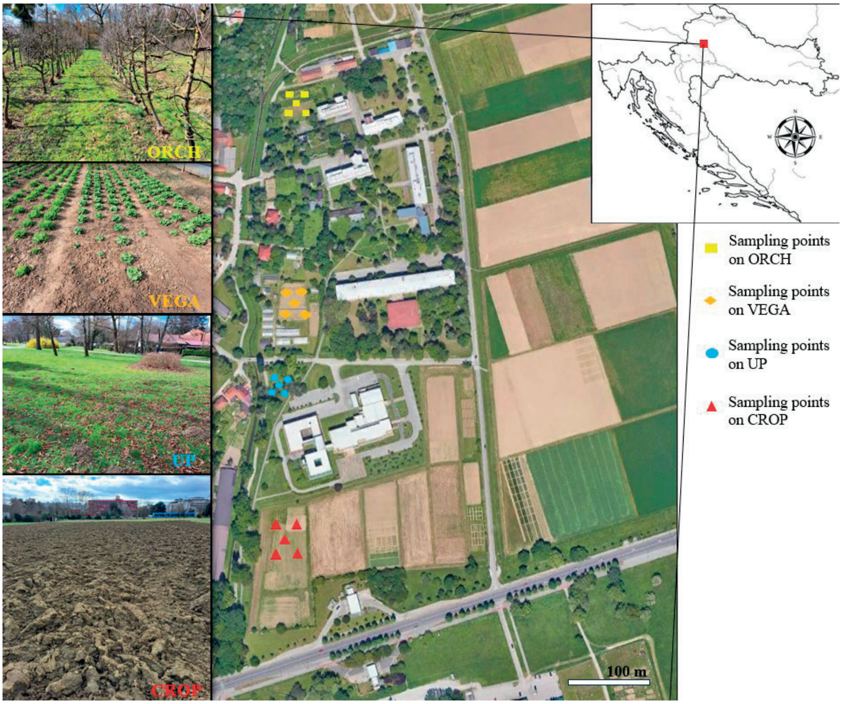

Figure 1. The position of study area in Croatia and study sites (CROP, ORCH, VEGA, and UP) with sampling points

According to the Köppen classification (Šegota and Filipčić, 2003), the study area has a moderately warm, humid climate with hot summers (Cfb). All study sites are located on a Holocene terrace near the Bliznec stream and have the same geomorphological features, namely flat terrain in the lowlands at an altitude of about 128 m above sea level. Soil type according to Croatian classification is Humofluvisol (Škorić et al., 1985). According to the IUSS Working Group of WRB (2015), the soil type is Endogleyic Fluvisol (Loamic) (Rubinić et al., 2015).

The study sites differ in the long-term (more than 40 years) anthropogenic impact via soil management practices. The cropland (CROP) is intensively managed, including annual primary and secondary tillage, fertilization, and pesticide application. Crops are grown in a typical crop rotation that includes maize, winter wheat, barley, corn, soybeans, and canola. The amounts of mineral fertilizers applied each year were adapted to the culture grown and ranged from 30-150 kg/ha N, 60-150 kg/ha P_2O_5, and 40-200 kg/ha K_2O. The apple orchard (ORCH) is grass-covered. The orchard was planted in 2003, and before the planting of the orchard, deep plowing was done at a depth of 50-60 cm. On the investigated plot, before the establishment of apple orchards, a 30-year-old cherry orchard was uprooted. Annual plantation maintenance includes mowing the grass, and protecting plantations with permitted pesticides for preventive control of diseases and pests. Every year, in autumn, mineral fertilizers are applied in the area around the trees in the amount of 100 kg/ha N, 230 kg/ha P_2O_5, and 300 kg/ha K_2O. The vegetable garden (VEGA) is characterized by regular annual fertilizing with mineral (80-310 kg/ha N; 30-100 kg/ha P_2O_5; 150-400 kg/ha K_2O) and organic fertilizers adapted to the different vegetable crops (lettuce, peppers, beans, tomatoes, potatoes, and onions). Chemical protection is commonly used. Vegetation cover in an urban park (UP) comprises of grasslands and ornamental trees such as Silver birch (*Betula pendula*) and Black poplar (*Populus nigra*) without anthropogenic influence regarding tillage, fertilization, and plant protection. During the year, grass is mowed and collected in the park, and fallen leaves are collected in autumn.

Soil sampling and laboratory analysis

Composite soil samples (0-30 cm) were taken in March 2023 with a pedological probe. They consisted of five sub-samples taken at a distance of 1 m in a cross arrangement. Five soil samples were taken at each study site: CROP, ORCH, VEGA, and UP. The disturbed soil samples were prepared for analysis according to ISO 11464:2006. The laboratory analysis included soil pH (ISO 10390:2005), physiologically available phosphorus (P_2O_5) and potassium (K_2O) (Egner et al., 1960), and humus content (JDPZ, 1966). The SOC content was calculated by dividing the humus content by the Van Bemmelen factor (1.724). The total concentrations of PTEs (As, Cu, Pb, and Zn) were determined by the portable X-ray fluorescence method using the Vanta handheld XRF analyser C Series (Olympus, Waltham, MA, USA, 2019). The measurement was conducted according to the loose powder method (Takahashi, 2015). The quality control of the data was performed by analysing certified (SRM 2711) and reference soil samples (ISE 989).

Statistical analysis

Obtained data of soil properties were processed at the level of descriptive statistics (minimum, maximum, mean, standard deviation, skewness). A statistical comparison of soil properties between the study sites (land use types) was carried out using a one-way analysis of variance (ANOVA). In cases where the ANOVA revealed significant differences, a post hoc test (Fisher's LSD test) was performed. The statistical analysis was performed with MS Excel.

RESULTS AND DISCUSSIONS

Basic chemical soil properties

The mean pH values for the studied soils of ORCH and CROP (4.84 and 6.46, respectively) (Table 1), showed an acidic and weakly acidic soil reaction. The soils of UP and VEGA had a neutral reaction (6.95 and 6.97, respectively). The SOC content in agricultural soils (CROP, ORCH, and VEGA) varied in narrow ranges, with mean values below 2%, which is considered low content. The soils of UP had a medium SOC content (2.13-2.99%) (Table 1). The ORCH had a moderately skewed data distribution for SOC (skew 0.64), while other soil types had a highly positively skewed data distribution (skew > 1) (Table 1). The mean P_2O_5 concentrations in UP and ORCH (7.7 and 10.1 mg/100 g of soil, respectively) pointed to a poor supply of P_2O_5 (Table 1). The soils of CROP and VEGA were richly supplied with P_2O_5 (mean values of 20.7 and 22.7 mg/100 g of soil, respectively). Data distribution for P_2O_5 concentration was highly positively skewed in CROP (skew 1.48), while other land use types had symmetrical data distribution (Table 1). This indicated uneven fertilization in CROP and the need for a site-specific approach to fertilization. The lowest mean concentrations of K_2O were found in UP (12.0 mg/100 g of soil), indicating a poor supply of soils with K_2O. Other land use types (VEGA, CROP, and ORCH) were well supplied with K_2O (mean values of 17.7, 18.7, and 22.7 mg/100 g of soil, respectively) (Table 1).

Table 1. Descriptive statistics for basic chemical properties of the studied soil samples

Statistical parameter	CROP	ORCH	VEGA	UP
		$pH_{(KCl)}$		
Min.-Max.	5.72-6.89	4.51-5.29	6.87-7.06	6.85-7.00
Mean ± SD	6.46 ± 0.42	4.84 ± 0.36	6.97 ± 0.08	6.95 ± 0.06
Skew	-1.22	0.48	-0.17	-0.89
		SOC (%)		
Min.-Max.	1.33-1.50	1.44-1.62	1.70-1.95	2.13-2.99
Mean ± SD	1.39 ± 0.07	1.52 ± 0.06	1.78 ± 0.09	2.39 ± 0.32
Skew	1.62	0.64	1.75	1.62
		P_2O_5 (mg/100 g of soil)		
Min.-Max.	17.5-26.2	9.0-11.1	19.8-26.5	3.8-11.6
Mean ± SD	20.7 ± 2.99	10.1 ± 0.89	22.7 ± 2.78	7.7 ± 2.82
Skew	1.48	0.12	0.56	0.12
		K_2O (mg/100 g of soil)		
Min.-Max.	16.8-21.5	20.5-25.5	16.0-19.8	7.6-17.5
Mean ± SD	18.7 ± 1.66	22.7 ± 1.69	17.7 ± 1.33	12.0 ± 3.86
Skew	0.96	0.70	0.54	0.41

Min.-Max. – minimum-maximum; Mean ± SD – mean value ± standard devaiation; Skew - skewness

Effect of land use type on basic chemical soil properties

The one-way ANOVA revealed statistically significant differences ($P<0.05$) in basic chemical properties between the soils of CROP, ORCH, VEGA, and UP (Table 2). To find out which mean values differ from each other, a post hoc test was conducted for every soil property (Tables 3-6).

Table 2. Summary statistics of the ANOVA for $pH_{(KCl)}$, SOC, P_2O_5 and K_2O in four different land use types

Soil property	SS	df	MS	F_{exp}	p value	F_{crit}
$pH_{(KCl)}$	15.1	3	5.02	51.7	1.87E-08	3.24
SOC	2.97	3	0.990	27.3	1.59E-06	3.24
P_2O_5	842.9	3	280.9	35.5	2.68E-07	3.24
K_2O	292.5	3	97.5	14.1	9.65E-05	3.24

SS - sum of squares, df - degrees of freedom, MS - mean square.

The ORCH had a significantly ($P<0.05$) lower mean pH_{KCl} value (4.84) compared to the other study sites (Table 3). No significant differences were found between mean pH_{KCl} values for CROP, VEGA, and UP (6.46, 6.97, and 6.95, respectively) (Table 3). Changes in soil reaction in agricultural soils can be attributed to fertilization (Grieve, 2001; Butorac et al., 2005; Karalić, 2010). It can be assumed that the long-term use of "acid" mineral fertilizers in ORCH leads to lower pH values, as shown in the study by Ge et al. (2018). The authors reported a decrease in pH values of 1.4 units after long-term use of mineral fertilizers. The pH values in CROP, VEGA, and UP are consistent with the usual pH values for Humofluvisols in Croatia reported by Vukadinović and Vukadinović (2011), Husnjak (2014), and Rubinić et al. (2015).

Table 3. Multiple comparison post hoc test for the significant differences between land use types in the $pH_{(KCl)}$ values

Land use type (mean value)	CROP	ORCH	VEGA
CROP (6.46)			
ORCH (4.84)	**1.62***		
VEGA (6.97)	0.51	**2.13***	
UP (6.95)	0.48	**2.10***	0.02

*difference is significant at p <0.05 (LSD = 0.53)

The mean SOC content was significantly higher (2.39%) in UP than in other land use types (Table 4).

Table 4. Multiple comparison post hoc test for the significant differences between land use types in the SOC content (%)

Land use type (mean value)	CROP	ORCH	VEGA
CROP (1.39)			
ORCH (1.52)	0.13		
VEGA (1.78)	0.39	0.26	
UP (2.39)	**1.00***	**0.87***	**0.61***

*difference is significant at $P < 0.05$ (LSD = 0.41)

The mean SOC content in agricultural soils decreased in the following order: VEGA > ORCH > CROP (1.78, 1.52, and 1.39%, respectively) (Table 4). The highest SOC content in agricultural soils established in VEGA can be attributed to the application of organic fertilizers. However, no significant differences in SOC content were found between the agricultural soils (Table 4). Loveland and Webb (2003) pointed out an important threshold of 2% SOC in agricultural soils in temperate regions below which a potentially serious decline in soil quality will occur. Numerous authors have shown that agricultural production reduces the SOC content in soil (Celik et al., 2005; Lehtinen et al., 2014; Barančikova et al., 2016; Bogunović et al., 2020). Soil tillage enhances the mineralization of soil organic matter (Kizilkaya and Dengiz, 2010; Haghighi et al., 2010; Jiang et al., 2006). The removal of crop residue (Raffa et al., 2015) and the avoidance of animal "green" manuring also affect the decrease in SOC content in agricultural soils (Maltas et al., 2018).

The UP and ORCH had significantly lower mean P_2O_5 concentrations (7.7 and 10.1 mg/100 g of soil, respectively) compared to the CROP and VEGA (20.7 and 22.7 mg/100 g of soil, respectively) (Table 5). Differences in the mean P_2O_5 concentrations between UP and ORCH and between CROP and VEGA were not statistically significant. A low P_2O_5 concentration in UP is expected given the absence of fertilization. The low supply of soils in ORCH with plant available phosphorus can be linked to acid soil reaction (mean pH value 4.84, Table 1).

Table 5. Multiple comparison post hoc test for the significant differences between land use types in the P_2O_5 concentration (mg/100 g of soil)

Land use type (mean value)	CROP	ORCH	VEGA
CROP (20.7)			
ORCH (10.1)	**10.6***		
VEGA (22.7)	2.07	**12.7***	
UP (7.7)	**12.9***	2.36	**15.0***

*difference is significant at $P < 0.05$ (LSD = 4.75)

It is well known that pH is the main factor that determines the phytoavailability of phosphorus. Many authors (Kisić et al., 2002; Mesić, 2001; Bogunović et al., 2017; Margenot et al., 2018) reported low P_2O_5 concentrations in acid soils. Higher P_2O_5 concentrations in CROP and VEGA can be attributed to higher pH values (mean 6.46 and 6.97, respectively, Table 1) and larger amounts of phosphate fertilizers applied.

The UP had a significantly lower mean K_2O concentration (12.0 mg/100 g of soil) compared to other land use types (Table 6).

Table 6. Multiple comparison post hoc test for the significant differences between land use types in the K_2O concentration (mg/100 g of soil)

Land use type (mean value)	CROP	ORCH	VEGA
CROP (18.7)			
ORCH (22.7)	3.98		
VEGA (17.7)	1.00	**4.98***	
UP (12.0)	**6.72***	**10.7***	**5.72***

*difference is significant at $P < 0.05$ (LSD = 4.45)

It was expected due to the lack of mineral fertilization. The ORCH had the highest K_2O concentration (22.7 mg/100 g of soil), which was significantly higher than the VEGA (17.7 mg/100 g of soil). Differences in K_2O concentrations between other land uses were not statistically significant. It is well known that fruit production requires high concentrations of potassium in soil due to its profound influence on fruit quality (Kumar et al., 2024).

Therefore, higher doses of potassium fertilizers applied in ORCH are reason for higher K_2O concentrations in soil. Uzoko and Ekeh (2014) also found differences in potassium status in soils under different land use types and attributed it to different fertilization.

Potentially toxic elements (PTE) in soil

The As, Cu, Pb, and Zn concentrations in the studied soils are presented in Figure 2 a-d. The As concentrations ranged from 14 (UP) to 20 mg/kg (CROP and ORCH), Figure 2 a, and exceeded the mean value of As for Croatia (13 mg/kg) according to the Geochemical Atlas of Croatia (Halamić and Miko, 2009). The Cu concentrations varied in a wider range (32-59 mg/kg), see Figure 2 b. They were above the mean value of 29.7 mg/kg established for the top-soil of Croatia (Halamić and Miko, 2009). However, Pb concentrations (23-31 mg/kg), Figure 2 c, were lower than the mean values for Croatian soils (38 mg/kg; Halamić and Miko, 2009). The Zn concentrations varied in the widest range (92-132 mg/kg), as shown in Figure 2 d. In agricultural soils (CROP, ORCH, and VEGA), they were above the mean value for Croatian soils of 99 mg/kg (Halamić and Miko, 2009).

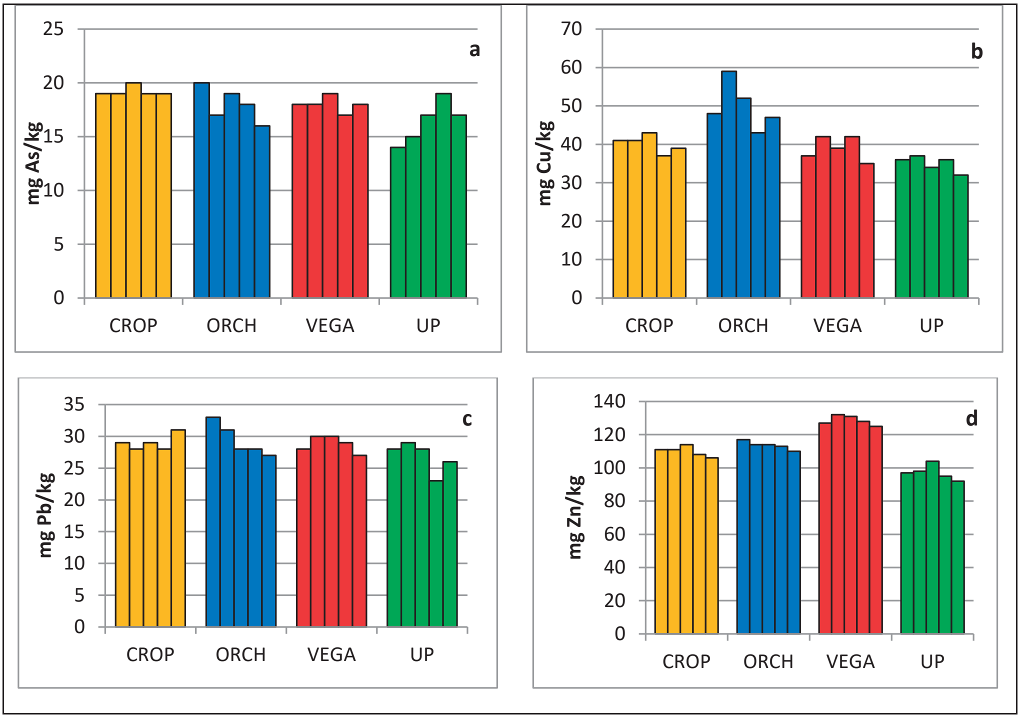

Figure 2. The concentrations of As (a), Cu (b), Pb (c) and Zn (d) in soils of studied land use types

To examine the effect of land use type on concentrations of PTEs in the studied soils, a one-way analysis of variance was performed (Table 7). Statistically significant differences ($P<0.05$) in PTE concentrations in soils between studied land use types were established for As, Cu, and Zn.

Table 7. Summary statistics of the ANOVA for As, Cu, Pb and Zn in different land use types

PTE	SS	df	MS	F_{exp}	p value	F_{crit}
As	17.7	3	5.9	3.69	0.034	3.24
Cu	588.5	3	196.2	14.8	6.97E-0.5	3.24
Pb	15.4	3	5.1	1.83	0.181	3.24
Zn	2503.4	3	834.5	76.2	1.09E-09	3.24

SS - sum of squares, df - degrees of freedom, MS - mean square

The land use type had no significant effects on the concentration of Pb in the studied soil. It was expected since agricultural production does not contribute to the introduction of Pb into soils. Furthermore, the studied soils were exposed to uniform atmospheric pollution due to the small spatial distance between study locations (Figure 1). Ivezić et al. (2001) also found no significant differences between Pb concentration in soils under agricultural land uses and natural vegetation in the Danube basin in Croatia on 74 studied sites. Since ANOVA revealed significant differences in As, Cu, and Zn concentrations between the studied soils, we conducted post-hoc tests (Tables 8-10). The lowest mean As concentration (16.5 mg/kg) was established in UP, Table 8.

Table 8. Multiple comparison post hoc test for the significant differences between land use types in the As concentration (mg/kg)

Land use type (mean value)	CROP	ORCH	VEGA
CROP (19.1)			
ORCH (17.9)	1.14		
VEGA (17.9)	1.14	0.00	
UP (16.5)	**2.65***	1.51	1.51

*difference is significant at P <0.05 (LSD = 2.13)

It was significantly (P<0.05) lower than in CROP (19.1 mg/kg). Differences between As concentrations in soils of other land use types were not statistically significant (Table 8). The enrichment of agricultural soil by arsenic was proven in the study of Alexakis et al. (2021), conducted in north-west Greece. The authors reported a mean value of 19.8 mg/kg for 102 samples from soils under agricultural land use. Kobza (2021) reported a mean value of As concentration of 10.2 mg/kg for agricultural soil in Slovakia based on 318 top-soil samples, while one region (soils on alluvial deposits) had a mean value 24.5 mg/kg. According to Kabata Pendias and Mukherjee (2007) agricultural practices, especially the application of nitrogen and phosphate fertilizers, may be a significant source of As in agricultural soils. Perčin et al. (2023) reported variable concentrations of As (2-8 mg/kg) in nitrogen fertilizers.

The highest Cu concentration (49.7 mg/kg) was established in ORCH (Table 9). It was significantly higher (P>0.05) than the mean Cu concentrations in CROP, VEGA, and UP (40.3, 38.9, and 34.9 mg/kg, respectively). Differences in Cu concentrations among other land use types were not statistically significant. The determined Cu concentrations in soils of the studied land use types are in agreement with data reported by Ballabio et al. (2018) based on the LUCAS database for 21682 top-soil samples from EU countries. They established a higher Cu concentration in orchards (27.3 mg/kg) in comparison to cropland and vegetable gardens (16.1 and 13.0 mg/kg, respectively).

Table 9. Multiple comparison post hoc test for the significant differences between land use types in the Cu concentration (mg/kg)

Land use type (mean value)	CROP	ORCH	VEGA
CROP (40.3)			
ORCH (49.7)	**9.36***		
VEGA (38.9)	1.43	**10.8***	
UP (34.9)	5.44	**14.8***	4.01

*difference is significant at P <0.05 (LSD = 6.13)

Elevated Cu concentrations in orchards were reported in many studies (Li et al., 2005; Wang et al., 2015; Brunetto et al., 2017; Fu et al., 2020). Anthropogenic influence on Cu concentrations in orchards depends on the quantity, frequency, and period of application of plant protection agents (Li et. al., 2005; Park et al., 2011). Therefore, the Cu concentrations in ORCH in the current study (43-59 mg/kg), Figure 2b, were lower compared to some studies with longer and more intense application of plant protection agents, e.g., 85.8 mg/kg (Fu et. al., 2020) and 147.9 mg/kg (Wang et al., 2015).

The lowest Zn concentration was determined in UP (97.2 mg/kg), Table 10. In agricultural soils, Zn concentration increased in the following order: CROP< ORCH<VEGA (110.0, 113.6, and 128.6 mg/kg, respectively). All differences in mean Zn concentration were statistically significant, except the one between CROP and ORCH (Table 10).

Table 10. Multiple comparison post hoc test for the significant differences between land use types in the Zn concentration (mg/kg)

Land use type (mean value)	CROP	ORCH	VEGA
CROP (110.0)			
ORCH (113.6)	3.6		
VEGA (128.6)	**18.6***	**15.0***	
UP (97.2)	**12.8***	**16.4***	**31.4***

*difference is significant at P <0.05 (LSD = 5.58)

Significantly lower Zn concentrations in UP compared to agricultural soils can be explained by the lack of fertilization and application of plant protective agents. Agricultural practices may significantly contribute to Zn concentrations in soils (Kabata Pendias and Mukherjee, 2007). Park et al. (2011) reported higher Zn concentrations in orchards in comparison to non-agricultural soils and an increase in Zn concentrations with the age of the orchard due to the accumulation in soil.

The variations in Zn concentrations found in the agricultural soils in the current study may be attributed to different types and amounts of fertilizers (mineral and organic), and plant protective agents used. Perčin et al. (2023) reported a very wide range of Zn concentrations (1.4-166 mg/kg) in different formulations of mineral nitrogen fertilizers.

Soil contamination by PTEs

The maximum permissible concentrations (MPC) of PTEs in agricultural soils in Croatia (Table 11) are prescribed taking into account pH_{KCl} values (Official Gazette 71/19). The concentrations of Cu and Pb (Figure 2 b and 2 c) were below MPC in all soil samples. The As and Zn concentrations in the soils of UP, CROP, and VEGA (Figure 2 a and 2 d) were also below MPC. However, As and Zn concentrations in three soil samples from ORCH (with pH_{KCl} <5) exceeded the MPC of 15 and 60 mg/kg, respectively.

Table 11. Maximum permissible concentrations (MPC) (mg/kg) of PTEs in agricultural soils in Croatia (Official Gazette 71/19)

Element	pH_{KCl}		
	< 5	5-6	> 6
As	15	25	30
Cu	60	90	120
Pb	50	100	150
Zn	60	150	200

European countries had different approaches to define risk levels associated with different concentrations of heavy metals in soils (Toth et al., 2016). The Finish standard values (MEF, 2007) represent a good approximation of mean values from different national systems (Carlon et al., 2007) that have been widely applied. This legislation sets different values (Table 12) indicating the need for different actions if exceeded. The threshold value indicates the need for further area assessment, and the guideline value indicates the contamination level that represent ecological or health risk.

Table 12. Threshold and guideline values for heavy metals in soils (MEF, 2007)

Element	Threshold value	Guideline value
As	5	50
Cu	100	150
Pb	60	200
Zn	200	250

The Cu, Pb, and Zn concentrations in the studied soils (Figures 2 b-d) were below threshold values according to this criterion. However, As concentrations (14-20 mg/kg; Figure 2 a) were above threshold values. Therefore, all studied soils require further assessment regarding As concentrations.

CONCLUSIONS

The basic chemical properties and PTE concentrations of the studied soils were significantly affected by land use type. Long-term agricultural practices decreased SOC content but increased concentrations of physiologically available nutrients. The pH was significantly decreased in ORCH compared to the other land use types. The As, Cu, Pb, and Zn concentrations were lowest in UP. Significantly higher Cu concentrations were found in ORCH compared to other agricultural soils. The soils of UP, CROP, and VEGA had PTE concentrations below MPC. Only three soil samples from ORCH were contaminated by As and Zn. Long-term tillage, fertilization and application of pesticides altered chemical soil properties and reduced soil quality of studied agricultural soils.

REFERENCES

Alexakis, D. E., Bathrellos, G. D., Skilodimou, H. D., Gamvroula, D.E. (2021). Spatial distribution and evaluation of arsenic and zinc content in the soil of a karst landscape. *Sustainability*, 13. 6976.

Assefa, F., Elas, E., Soromessa, T., Ayele, G. T. (2020). Effect of changes in land–use management practices on soil physicochemical properties in Kabe watershed, Ethiopia. *Air, Soil, Water Research*, 13(1). 1–16.

Ballabio, C., Panagos, P., Lugato, E., Huang, J. H., Orgiazzi, A., Jones, A., Fernandez-Ugalde, O., Borelli, P., Montanarella, N. (2018). Copper distribution in European topsoils: An assessment based on LUCAS soil survey. *Science of the Total Environment*, 636. 282-298.

Barančikova, G., Makovnikova, J., Halas, J. (2016). Effect of land use change on soil organic carbon. *Agriculture*, 62(1). 10–18.

Boente, C., Matanzas, N., Garcia-Gonzales, N., Rodriguez- Valdes, E., GFallego, J.R. (2017). Trace elements of concern affecting urban agriculture in industrialized areas: A multivariate approach. *Chemosphere*, 183. 546–556.

Bogunović, I., Trevisani S., Šeput, M., Juzbašić, D., Đurđević, B. (2017). Short-range and regional spatial variability of soil chemical properties in an agro-ecosystem in eastern Croatia. *Catena*, 154. 50–62.

Bogunović, I., Viduka, A., Magdić, I., Telak, L.J., Francos, M., Pereira, P. (2020) Agricultural and forest land-use impact on soil properties in Zagreb periurban area (Croatia). *Agronomy*, 10.1331.

Brinkley, C. (2012) Evaluating the benefits of peri-urban agriculture. Journal of Planning Literature, 27(3). 259–269.

Brunetto, G., Avellar Ferreira, P., A., Melo, G., W., Ceretta, C., A., Tosseli, M. (2017). Heavy metals in vineyards and orchard soils. *Revista Brasiliera de Fruticulture*, 39(2). 1-12.

Butorac, A., Butorac, J., Bašić, F., Mesić, M., Kisić, I. (2005). The effect of fertilization on phosphorus and potasium stock on suger beet root yield and some soil chemical properties in the corn-soybean-winter wheat- sugar beet root rotation. *Agronomski glasnik,* 1. 3–16.

Carlon, C., D'Alessandro, M., Swartjes, F. (2007) Derivation methods of soil screening values in Europe. A Review and Evaluation of National Procedures Towards Harmonization, Office for Official Publications of the European Communities, Luxembourg

Celik, I. (2005). Land use effects on organic matter and physical properties of soil in a southern Mediterranean high land of Turkey. *Soil and Tillage Research*, 83. 270–277.

Dieleman, H. (2017). Urban agriculture in Mexico City; balancing between ecological, economic, social and symbolic value. *Journal of Cleaner Production*, 163(1). 156–163.

Egner, H., Riehm, H., Domingo, W.R. (1960). Untersuchungen uber die chemische Bodenanalyse als Grundlage fur die Beurteilung des Nahrstoffzustandes der Boden, II: Chemische Extractionsmetoden zu Phosphorund Kaliumbestimmung. *Kungliga Lantbrukshugskolans Annale,*. 26. 199–215.

Fereirra, A., J., D., Guilherme, R., I., M., M., Fereira., C., S., Oliveira., M., D., F. (2018). Urban agriculture, a tool towards more resilient urban communities? *Current Opinion in Environmental Science and Health*, 5. 93–97.

Fu, C., Tu, C., Zhang, H., Li, Y., Zhou, Q., Scheckel, K., G., Luo, Y. (2020). Soil accumulation and chemical fractions of Cu in a large and long-term coastal apple orchard, north China. *Journal of Soils and Sediments*, 20. 3712-3721.

Ge, S., Zhu, Z., Jiang, Y. (2018). Lon-term impact of fertilization on soil pH and fertility in ana apple production system. *Journal of Soil Science and Plant Nutrition,* 18(1). 282–293.

Grieve, I.C. (2001). Human impacts on soil properties and their implications for the sensitivity of soil systems in Scotland. *Catena*, 42(2-4). 361–374.

Haghighi, F., Gorji, M., Shorafa, M. (2010). A study of the effects of land use changes on soil physical properties and organic matter. *Land degradation and development*, 21(5). 496–502.

Halamić, J., Miko, S. (2009). *Geochemical Atlas of the Republic of Croatia.* Zagreb: Croatian Geological Survey.

Huang, S.W. & Jin, J., Y. (2008) Status of heavy metals in agricultural soils as affected by different pattern of land use. *Environment Monitoring and Assessment*, 139. 317–327.

Husnjak, S. (2014). *Croatian soil classification*. Zagreb: Croatian University Press.

ISO (2005) Soil quality. "Determination of pH" (ISO 10390:2005). Geneva: International organization for standardization.

ISO (2006) Soil quality. "Pretreatment of samples for physico-chemical analysis" (ISO 11464:2006). Geneva: International organization for standardization.

IUSS Working group of WRB (2015). World Reference Base for Soil Resources 2014, Update 2015. International soil classification system for naming soils and creating legends for soil maps. In: World Soil Resource Report No. 106, Rome: FAO.

Ivezić, V., Singh, B.R., Almas, A.S., Lončarić, Z. (2011). Water extractable concentrations of Fe, Mn, Ni, Co, Mo, Pb and Cd under different land uses of Danube basin in Croatia. *Acta Agriculturae Scandinavica – Section B- Soil and Plant Science,* 55(2). 1–13.

JDPZ (1966). Priručnik za ispitivanje zemljišta. Knjiga I. Kemijske metode ispitivanja zemljišta, Beograd

Jiang, Y.J., Yuan, D.X., Zhang, C. (2006). Impact of land use change on soil properties in a typical karst agricultural region of southwest China: a case study of Xiaojiang watershed, Yunan. *Environmental Geology,* 50. 911–918.

Kabata-Pendias, A., Mukherjee, A., B. (2007). *Trace elements from soil to human*. Berlin: Springer.

Karalić, K. (2010). Lime requirement determination and liming impact on soil nutrient status. *Poljoprivreda*, 16(1). 77.

Keshavarzi, B., Najmeddin, A., Moore, F., Moghadam, P.A. (2018). Risk based assessment of soil pollution by potentially toxic elements in the industrialized urban and peri-urban areas of Ahvaz metropolis, southwest of Iran. *Ecotoxicology and Environmental Safety*, 167. 365–375.

Kisić, I. (2002) *Remediation of contaminated soils*. Zagreb: Faculty of Agriculture.

Kizilkaya, R. & Dengiz, O. (2010). Variation of land use and land cover effects on some soil physico-chemical properties and soil enzyme activity. *Agriculture*, 97(2). 15–24.

Kobza, J. (2021). Arsenic in agricultural soil of Slovakia. *Polish journal of soil science*, 54(1). 89–101.

Kumar, A., R., Kumar, N., Kavino, M. (2024). Role of potassium in fruit crops – a review. *Agricultural Reviews*, 27(4). 284–291.

Lehtinen, T., Schlatter, N., Baumgarten, A., Bechini, L., Kruger, J., Grignani, C., Zavattaro, L., Costamagna, C., Spiegel, H. (2014). Effect of crop residue incorporation on soil organic carbon and greenhouse gas emissions in European agricultural soils. *Soil use and Management,* 30(4). 524–538.

Li, W., Zhang, M., Shu, H. (2005). Distribution and fractionation of copper in soils of apple orchards. Environmental Science and Pollution Research, 12. 168–172.

Maltas, A., Kebli, H., Oberholzer, H., R., Weisskopf, H., Sinaj, S. (2018). The effects of organic and mineral fertilizers on carbon sequestration, soil properties, and crop yield from long-term field experiment under a Swiss conventional farming systems. *Land Degradation & Development*, 29(4). 926–938.

Margenot, A., J., Sommer, R., Parikh, S.J. (2018). Soil phosphatase activities across a liming gradient under long-term managements in Kenya. *Soil Science Society of America Journal*, 82(4). 850–861.

Mesić, M. (2001) Correction of excessive soil acidity with different liming materials. *Agriculturae Conspectus Scientificus*, 66(2). 75-93.

Ministry of the Environment Finland (MEF) (2007). *Government Decree of the assessment of soil contamination and remediation needs*.

Opitz, I., Berges, R., Piorr, A. (2016). Contributing to food security in urban areas: differences between urban agriculture an peri-urban agriculture in the Global North. *Agriculture Human Values*, 33. 341–358.

Official Gazette (2019). *Ordinance on the protection of agricultural land from pollution* (in Croatian). Zagreb: Government of Republic of Croatia, Ministry of Agriculture and Forestry.

Park., B., J. & Cho, J.Y. (2011). Assessment of copper and zinc in soils and fruit with the age of an apple orchard. *Journal of the Korean Society for Applied Biological Chemistry*, 54. 910–914.

Perčin. A, Zgorelec, Ž., Karažija, T., Kisić, I., Župan, N., Šestak., I. (2023) Metals contained in various formulations of mineral nitrogen fertilizers determined using portable x-ray fluorescence. *Agronomy*, 13.2282.

Raffa, D., W., Bogdanski, A., Tittonell, P. (2015). How does crop residue removal affect soil organic carbon and yield? A hierarchical analysis of management and environmental factors. *Biomass and Bioenergy,* 81. 345–355.

Rashid, A., Schutte, B., J., Ulery, A., Deyholos, M., K., Sanogo, S., Lehnhoff, E., A., Beck., L. (2023) Heavy metal contamination in agricultural soil: Environmental pollutants affecting crop health. *Agronomy*, 13(6). 1521.

Rubinić, V., Pejić, M., Vukoje, I., Bensa, A. (2015) Influence of geomorphology and land use on soil formation – case study Maksimir (Zagre, Croatia). *Agriculturae Conspectus Scientificus*, 80(1). 1–8.

Šegota, T., Filipčić, A. (2003). Köppen classification of climate and Croatian nomenclature. *Geoadria*, 8(1). 17–37.

Škorić, A., Filipovski, G., Ćirić, M. (1985). *Soil classification of Yugoslavia*. Sarajevo: Academy of Science and Art of Bosnia and Herzegovina.

Takahashi, G. (2015). Sample preparation for X- ray fluorescence analysis. *Rigaku Journal*. 31(1). 26-30.

Toth, G., Hermann, T., Da Silva, M.R., Montanarella, L. (2016). Heavy metals in agricultural soils of the European Union with implications for food safety. *Environment International*, 88. 299–309.

Uzoho, B., U. & Ekeh, C. (2014) Potassium status of soils in relation to land use types in Ngor-Okpala, Southeastern Nigeria. *Journal of Natural Sciences Research*, 4(6). 105–114.

Vukadinović, V. & Vukadinović, V. (2011). *Plant nutrition*. Osijek: Faculty of Agriculture.

Zasada, I. (2011). Multifunctional peri-urban agriculture-A review of societal demands and the provision of goods and services by farming. *Land Use Policy*, 28(4). 639–648.

Wang, Q., Y., Liu, J., S., Wang, Y., Yu, H., W. (2015). Accumulation of copper in apple orchard soils: distribution and availability in soil aggregate fractions. *Journal of Soils Sediments*, 15. 1075–1082.

Wilhelm, J., A., & Smith, R.G. (2018). Ecosystem services and land sparing potential of urban and peri-urban agriculture: A review. *Renewable Agriculture and Food Systems*, 33(5). 481–494.