

Original Research

Possible Influence of Agriculture on an Unsaturated Zone in Croatia

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Received: 30 April 2018

Accepted: 30 October 2018

Abstract

Soil contamination in the agricultural areas developed on open aquifer systems can be environmental problem. The subject of this study is the Cambisol soil developed in the area of the Velika Gorica well field. The aim of this research was to determine possible agricultural influence on the unsaturated zone of the Zagreb aquifer area where Cambisol soil is developed. Concentrations of potentially toxic metals (Cu, Cd and Zn) and major cations and anions (Na^+ , K^+ , NH_4^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , and SO_4^{2-}) were determined in soil horizons. Correlations between physical and chemical soil properties, analysed ions and potentially toxic metals were made. Samples that were closer to the surface showed increased element concentrations, indicating the increased impact of agricultural activities in the research area. All analysed potentially toxic metals showed highest concentrations in residual fraction, which indicates the possible influence of agricultural activities such as usage of fertilizers, manure, sludge as soil fertilizer and fungicides, or point sources of contamination, uncontrolled, active or untended waste dumps and aerodeposition. Statistical analysis showed strong correlations between the concentrations of the studied potentially toxic metals and some soil properties such as soil texture, pH and organic matter. In addition, correlation results between nitrates and some potentially toxic metals such as Cu and Zn indicate that these elements come from the same source of contamination, in this case probably agricultural activity. Even though the influence of agricultural activities is recognized, all results show that the impact is decreasing after approximately 0.8 m depth.

Keywords: agricultural activities, unsaturated zone, potentially toxic metals, cations and anions, Cambisol

Introduction

Increased concentrations of anions and cations, as well as potentially toxic metals in the agricultural soils developed in the area of water field Velika Gorica, can present environmental risk. One of the sources for contamination by potentially toxic metals are agricultural inputs. Agricultural inputs can be from animal manure and artificial fertilizers, which are enriched with potentially toxic metals. Triple super phosphates and calcium/magnesium phosphate contain varying concentrations of cadmium [1], while copper and zinc are substantially added to soils by agricultural practices [2]. Both elements are used widely as fertilizers and stimulants of animal growth [3]. Considering agricultural soils, the accumulation of potentially toxic metals may have different effects, either directly endangering the natural soil functions, or indirectly endangering the biosphere by bioaccumulation and inclusion in the food chain. Many previous studies were made to get information about soil accumulation of potentially toxic metals from agriculture. Medunić et al. [4] studied the fractionation of copper and zinc in apple orchard soil using sequential extraction procedure. They concluded that copper and zinc are bounded to residual and reducible fractions and their total values do not exceed maximal permissible concentrations (MAC) in agricultural land.

Apart from potentially toxic metals, a load of cations and anions from agricultural sources can also present risks for groundwater pollution. Agriculture presents one

of the most prevalent diffuse nitrogen sources. Inorganic nitrogen fertilizers are applied to increase the immediate availability of nitrogen for plant growth [1]. Bubalo et al. [5] studied agricultural impact on groundwater vulnerability using nitrates. The authors concluded that the study area is highly vulnerable to nitrate, especially those from agricultural origin. Potassium is an essential and major nutrient for crop production [6]. Manure has potassium in its compounds, and an excessive load of this product to agricultural soil may result in very high concentrations of this element in soils and groundwater.

Therefore, the goal of this research was to determine the main soil properties and soil accumulation of potentially toxic metals and cations/anions under long cultivation in Cambisol located in the vicinity of the Velika Gorica well field.

Material and Methods

Study Site Description

The study area is in the immediate vicinity of the well field Velika Gorica, which is located in the SE part of the Zagreb aquifer (Fig. 1). The well field Velika Gorica is situated in the western part of the city of Velika Gorica.

Variable lithology, pedological characteristics and land use characterize the study site. The study area consists of a large alluvial plain that has two marked

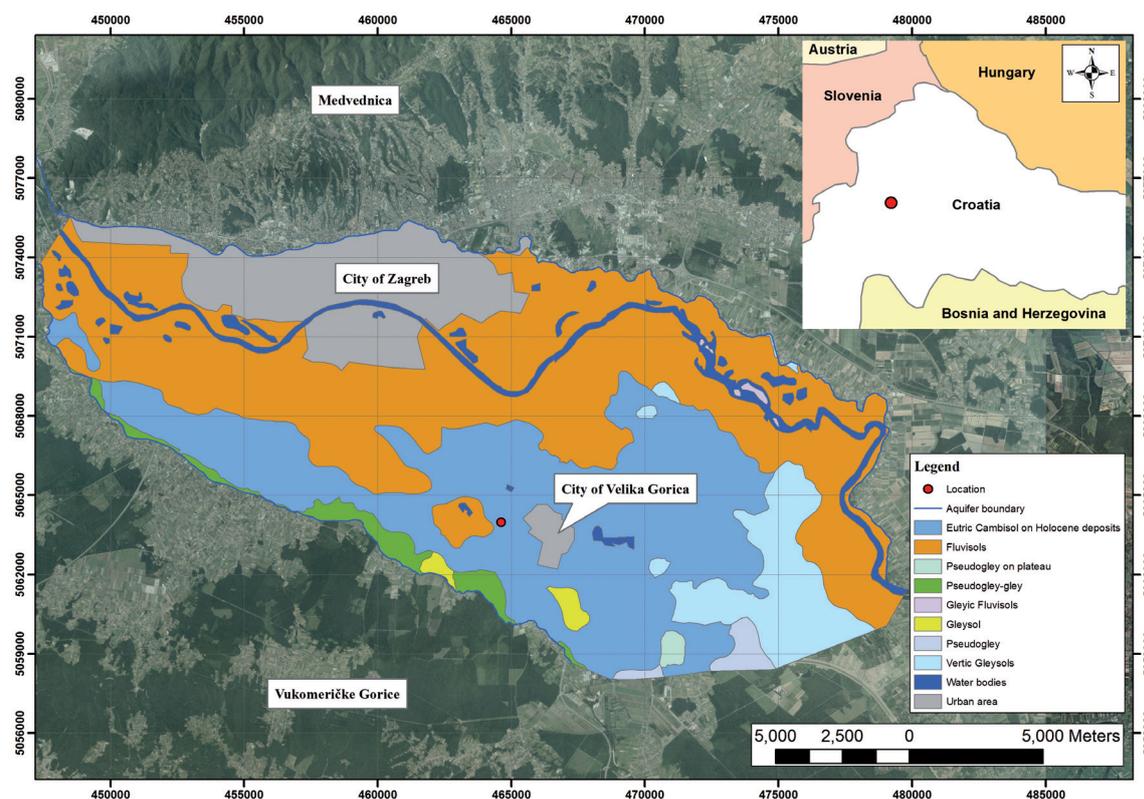


Fig. 1. Pedological map of Zagreb aquifer system with location of soil profile.

geomorphological features: the raised sealed terrace of the Sava River (varying in width down the river's length), and a Holocene terrace [7]. Numerous meanders of the Sava River inundated fluvial cones, and numerous bowl-shaped depressions abound in the alluvial plain. The climate of the Velika Gorica is classified as a moderately continental climate (Cfwbx in the Köppen climate classification system) with four separate seasons. Summers are warm, and winters are cold, without a discernible dry season.

The study area consists mainly of Quaternary deposits made of Pleistocene non-carbonate loess, Holocene alluvium of the first terrace of the Sava River, flooding sediments and alluvium splay sediments [8]. There are two different water-bearing layers: first water-bearing layer with the dominantly alluvial sediments of the Sava River and second water-bearing layer with predominantly lake-pond deposits. The first layer contains Holocene alluvial deposits [9], which are in direct contact with the Sava River, which is very pronounced in the vicinity of the Sava [10]. According to Velić and Durn [9], the second water-bearing layer contains Pleistocene lacustrine-marshy deposits. Even though they present one hydrogeological unit, geochemical stratification along the depth is recognized [11]. The thickness of the unsaturated zone in the Zagreb area generally varies from 8 m in the NW part to 2 m in the SE part [12].

The study area is generally made from three main pedological units, Fluvisols, Pseudogley on plateau and Eutric Cambisols developed on the Holocene deposits [13]. The investigated pedological profile is situated in Eutric Cambisols on the Holocene deposits. The following soil horizons were recognized: A-Bw-C-2C-3C. The texture of these soils is silty clay loam. Soil structure is mainly granular. The presence of the clayey cambic horizon with the structure of pedological profile A-(B) w-C is characteristic for the specified soil. The upper part of this soil profile is generally permeable, which enables the infiltration of water and potential contaminants into the aquifer [14]. In the area of Zagreb aquifer Cambisols were developed at fluvial loamy deposits where groundwater reaches the 1 m depth [13].

Field and Laboratory Work

Field research was conducted in the area of the Velika Gorica well field, which is located west of Velika Gorica. The field research consisted of borehole drilling, sampling, a description of the pedological profile and recognition of the soil horizons (A-Bw-C-2C-3C).

Five disturbed soil samples for laboratory analysis were collected from soil horizons. Soil samples were air-dried and passed through a 2 mm sieve for laboratory analysis. Particle size distribution was determined by sieving and pipette methods. Mineral composition of <2 mm and <2 μm fractions of the analysed soils was determined by X-ray powder diffraction (XRD) using a Philips diffractometer (graphite monochromator, $\text{CuK}\alpha$ radiation, proportional counter). The identification of clay minerals was generally based on the methods outlined by Moore and Reynolds [15]. Carbonate content was determined by the volumetric method [16], iron and manganese extractable with Na dithionite-citrate bicarbonate were obtained by the method of Mehra and Jackson [17], while organic matter was determined using a hydrogen peroxide solution. Cation exchange capacity (CEC) was determined using barium chloride solution [18]. Determination of anions and cations on the previously frozen soil samples was performed using the method of ion chromatography (ICS-90).

Ion chromatography is a part of liquid chromatographic techniques with which the ions can be separated and detected. This method was used to determine the concentrations of sodium (Na^+), potassium (K^+), ammonium (NH_4^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), chlorides (Cl^-), nitrates (NO_3^-) and sulphates (SO_4^{2-}) in each soil horizon. The steps of sample preparation for ions determination are described in detail. Each soil sample (10 g) was put in 100 mL glass and diluted with ultra-pure water (conductivity less than 1 $\mu\text{S}/\text{cm}$) to stay overnight. After that, samples were put on a shaker for 1 hour. Suspensions were then centrifuged at 3000 rpm for 20 min and filtrated. Geochemical fractionation of potentially toxic metals in selected soils were analysed using sequential extraction. A series of reagents was used to extract operationally defined metal species (the selectivity depends on such

Table 1. Sequential extraction procedure applied in this study.

Step	Fraction	Label	Reagent/concentration/volume	Conditions
1.	Acid	CARB	Acetic acid (CH_3COOH)/0.11 mol/l/40ml	pH 2.9, 16 h agitation at 20°C
2.	Reducible	FEMN	Hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$)/0.5 mol/l/40ml	pH 2 (regulated with HNO_3), 16 h agitation at 20°C
3.	Oxidisable	OM	Hydrogen peroxide (H_2O_2)/ 8.8 mol/l/10 ml + 10 ml Ammonium acetate ($\text{NH}_4\text{OOCCH}_3$), 1 mol/l/50 ml	1 h at 20°C, occasional shaking, 2 h water bath at 85°C, pH 2 (regulated with HNO_3) 16 h agitation at 20°C
4.	Total	RES	Hydrochloric acid (HCl)/ 37%/7 ml Nitric acid (HNO_3)/65%/ 2.3 ml	2h water bath at 100°C, cooling at room temperature

Table 2. Physical and chemical characteristics of studied soil profile.

Soil horizons	Soil Depth (m)	Colour	pH (KCl)	Sand (%)	Silt (%)	Clay (%)	OM (%)	Carbonate (mass.%)	CEC (meq/100)
A	0-0.2	5Y/4/2	6.36	16	60	24	8.98	16.77	34.43
Bw	0.2-0.4	5Y/4/2	6.57	5	58	37	10.18	15.90	31.74
C	0.4-0.6	5Y/4/3	7.05	5	55	40	9.19	22.94	37.48
2C	0.6-0.8	5Y/4/3	6.93	7	54	39	7.97	21.25	24.63
3C	0.8-1.1	5Y/3/2	6.47	9	50	41	7.16	6.73	19.55

factors as chemicals employed, the time and nature of contact, and the sample-to-volume ratio) in a defined sequence from 1 g of the sample. Sequential extraction scheme (Table 1) was used according to Rauret et al. [19] and it gave four fractions: acid (bound to carbonates-CARB), reducible (bound to iron and manganese oxides, hydroxides and oxyhydroxides-FEMN), oxidizable (bound to organic matter and/or sulphides-OR/SUL) and residual (total dissolving using aquaregia-RES). Sequential extraction was conducted in centrifuge tubes (polyethylene, 50 ml). Between each successive extraction step, the liquid phase was separated by centrifuge at 3000 rpm for 10 minutes. All the reagents used in the extraction procedures were of analytical grade. The resulting solutions were analysed by flame atomic absorption spectrometry (AAnalyst 700, Perkin Elmer). The correlation between analysed soil properties and elements was estimated by Pearson correlation coefficient. This statistical analysis was done using Statistica 64 [20].

Results and Discussion

Table 2 presents physical and chemical characteristics of studied soil profile. The texture of analysed soil is silty clay loam. The highest proportion of sand is determined in A horizon and the smallest in C horizon, which is in correlation with the highest CEC value for this depth. The smallest CEC value is determined in 3C horizon, which is not in correlation with the proportion of clay, but it correlates with OM. Values of pH are varied from 6.36 to 7.05, which represent uniformity by changing the depth. Deviation of pH values has a sample taken from C horizon showing neutral conditions. Change in pH values along the soil profile can be associated with a change of carbonates, while alkalinity of the soil with the presence of magnesium and calcium carbonates [21]. Similar chemical characteristics (pH and CEC) of Cambisol were reported by Ružičić et al. [22].

The highest percentages of organic matter were determined in A, Bw and C horizons, and with increasing depth these values gradually fall. Organic matter generally has very high CEC values. In this study, organic matter showed similar distribution characteristics with CEC values.

The sequential chemical analysis presented diverse distribution in sequenced fractions of investigated soil. The average proportion of Cu fraction in soil horizons was arranged in the following decreasing orders: RES (72-81%) > OR/SUL (19-26%) > FEMN (0-2%) > CARB (0%) (Fig. 2). A similar order in Cambisol type of soil was reported by Leśniewska et al. [23]; Nogueirol and Alleoni [24]; Ružičić et al. [25]; and Pakuła and Kalembasa [26]. The highest concentration (81%) of Cu in the analysed soil was detected in the residual fraction in A horizon (Fig. 2). The highest copper concentration in the top soil horizon of our study soil profile can be from agricultural agents such as fungicides. In addition, most of the copper concentration accumulated in leaves and soil by spraying can be retained in topsoil through the biological cycle and tillage [27]. Although a higher concentration of copper in soils can be from agricultural practices, it can be from other sources. Romić and Romić [28] in this study area found higher concentrations of copper, which are a consequence of point sources of contamination, uncontrolled, active or untended waste dumps. The second highest enrichment of Cu is in OR/SUL or oxidizable fraction.

The average proportion of Zn fraction in soil horizons was distributed in the following decreasing orders: RES (61-80%) > OR/SUL (11-14%) > FEMN (5-9%) > CARB (0-20%) (Fig. 3). Medunić et al. [4]; Dabiri et al. [29]; Ružičić et al. [25]; Bakircioglu et al. [30]; and Liu et al. [31] found the same orders of Zn fractioning in Cambisol. In soil, zinc forms complexes with organic matter quite quickly, and this has a holding-

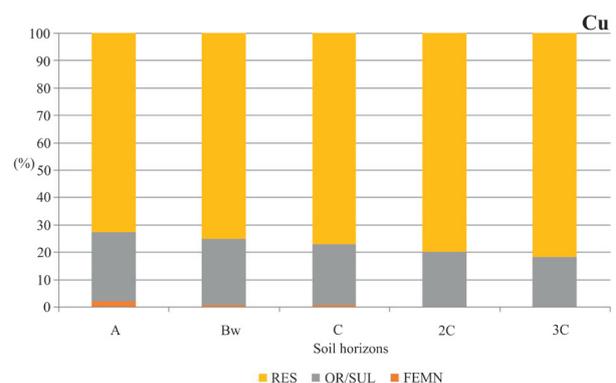


Fig. 2. Distribution of copper in fractions in soil profile.

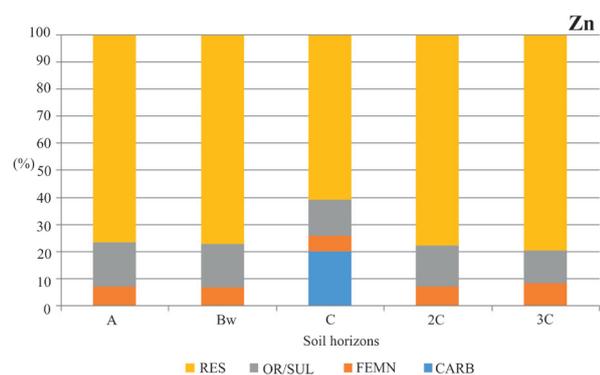


Fig. 3. Distribution of zinc in fractions in soil profile.

back effect on the activity of Zn in the soil solution [32]. Although copper shows generally much higher affinity to OM as compared to zinc, it is possible that zinc is also bound with organic matter, which can be seen in Table 4.

The average proportion of Cd fraction in soil horizons was distributed in the following decreasing orders: RES (15-80%) > FEMN (10-100%) > CARB (0-15%) > OR/SUL (0%) (Fig. 4). The proportion of FEMN-extractable Cd in A horizon is 100%. The percentage of FEMN fraction decreased with depth. Ahmadipour et al. [33] found that FEMN fraction makes approximately 90% of the Cd in subsurface soil. The amounts of organic and sulphide-bound cadmium (OR/SUL) are not detected in all soil horizons (Fig. 4). Cadmium is mostly bound to RES fraction, which can be related to anthropogenic sources such as the application of fertilizers.

Even goethite is present as a minor mineral phase according to mineralogical analysis, and it can be related to FEMN fraction in analysed soil. Zhang et al. (2013) [34] showed that Cd variations in arable soil are greatly influenced by parent material and soil properties, as well as human activities, such as industrial production, traffic and the application of fertilizers.

The highest concentrations of cations in studied soil were determined in 2C horizon, with the exception of ammonium (Fig. 5). The lowest concentrations of cations

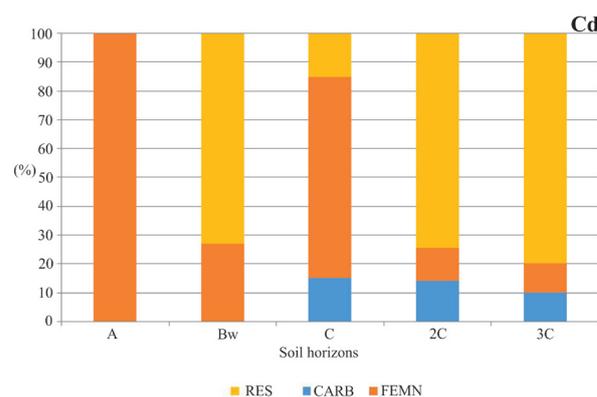


Fig. 4. Distribution of cadmium in fractions in soil profile.

were determined in A horizon, with the exception of sodium. The potassium concentration in analysed soil varied from 42 mg/kg to 119 mg/kg (Fig. 5). Mocanu et al. [35] reported similar concentrations of potassium in Cambisol. The calcium varied from 1164 mg/kg to 2326 mg/kg (Fig. 5). Sedlář et al. [36] determined approximately 1743 mg/kg of calcium concentrations in Cambisol. Magnesium varied from 428 mg/kg to 864 mg/kg (Fig. 5). Ammonium content in analysed soil varied between 24 mg/kg to 55 mg/kg (Fig. 5). Bakšić et al. [37] got similar concentrations of ammonium in A horizon of Cambisol.

The highest concentrations of anions in studied soil were determined in A, C and 2C horizons (Fig. 6). Sulphates varied from 57 mg/kg (3C horizon) to 90 mg/kg (C horizon). The highest chloride concentrations (3027 mg/kg) were determined in 2C horizon, which correspond to calcium concentrations. Nitrates varied from 59 mg/kg (C horizon) to 307 mg/kg (A horizon) (Fig. 6). The lowest chloride and nitrate concentrations were determined in C horizon. Nitrate concentration generally decreased from the surface to the end of investigated soil profile, which is probably controlled with soil texture and human activities in surface horizons (Fig. 6). Bubalo et al. [5] reported the same trend during their research of nitrate concentration through soil depth. These results

Table 3. Mineral content of soil samples; legend: +++ -dominant mineral phase; ++ - significantly present mineral phase; + - minor mineral phase; ? – mineral in the sample is not reliably determined (due to its small share and/or due to overlapping of its diffraction pattern with diffraction pattern of another minerals); MM- mixed clay minerals; Chl-Vrm- chlorite-vermiculite; Vrm- vermiculite.

Depth (m)	Quartz	Plagioclase	Goethite	Illitic material	Kaolinite	Chlorite	14Å mineral	MM	Dolomite
0-0.2	+	+	+	+++	++	++/+++	+ /+++ (Vrm? and/or Chl-Vrm?)	+	+
0.2-0.4	+	?	+	+++	++	++/+++	++ (Vrm)	+	+
0.4-0.6	+	?	+	+++	++	++/+++	++ (Vrm)	+	+
0.6-0.8	+	?	+	++/+++	++	++/+++	?	+	+
0.8-1.1	+	?	+	+++	++	++ (and Chl-Vrm?)	++	+ /+++	+

Table 4. Correlation coefficients of main soil properties and analysed chemical components in a Cambisol (*statistically significant correlation is marked bold; $\alpha = 0.05$).

	pH (CaCl)	pH (KCl)	Sand	Silt	Clay	OM	Carbonate	CEC	Cu	Cd	Zn	Na	K	Mg	N-NH ₄ ⁺	Ca	S-SO ₄ ²⁻	Cl	N-NO ₃ ⁻	
pH (CaCl)	1.00																			
Sand	-0.90		1.00																	
Silt	-0.30		0.10	1.00																
Clay	0.40		-0.30	-0.90	1.00															
OM	0.30		-0.60	0.70	-0.50	1.00														
Carbonate	0.70		-0.50	0.20	-0.10	0.30	1.00													
CEC	0.30		-0.40	0.70	-0.40	0.70	0.70	1.00												
Cu	-0.20		0.00	0.80	-0.90	0.70	0.00	0.30	1.00											
Cd	0.10		0.00	-0.90	0.70	-0.60	-0.50	-0.90	-0.50	1.00										
Zn	-0.40		0.30	0.90	-1.00	0.50	0.10	0.40	0.90	-0.70	1.00									
Na	0.50		-0.10	-0.20	0.10	-0.30	0.80	0.20	-0.30	-0.10	-0.10	1.00								
K	0.90		-0.70	-0.40	0.30	0.10	0.60	0.00	-0.10	0.30	-0.30	0.60	1.00							
Mg	0.90		-0.70	-0.40	0.30	0.10	0.60	0.00	-0.10	0.30	-0.30	0.60	1.00	1.00						
N-NH ₄ ⁺	0.70		-0.90	0.00	0.10	0.70	0.20	0.20	0.30	0.10	-0.10	-0.20	0.60	0.60	1.00					
Ca	0.80		-0.50	-0.70	0.60	-0.30	0.50	-0.20	-0.50	0.50	-0.60	0.70	0.90	0.90	0.30	1.00				
S-SO ₄ ²⁻	0.40		-0.30	0.50	-0.30	0.40	0.90	0.90	0.10	-0.80	0.30	0.60	0.20	0.20	0.00	0.10	1.00			
Cl	-0.10		0.30	-0.60	0.20	-0.60	-0.40	-0.90	-0.10	0.80	-0.20	0.10	0.30	0.30	-0.10	0.40	-0.70	1.00		
N-NO ₃ ⁻	-0.60		0.70	0.50	-0.80	-0.10	-0.10	-0.10	0.60	-0.30	0.80	0.10	-0.30	-0.30	-0.50	-0.40	0.00	0.30	1.00	

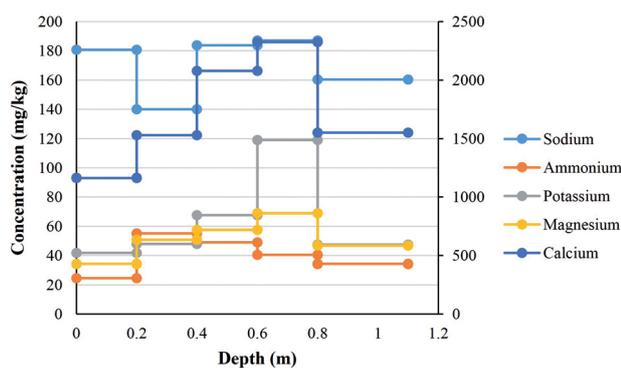


Fig. 5. Distribution of cations in soil profile.

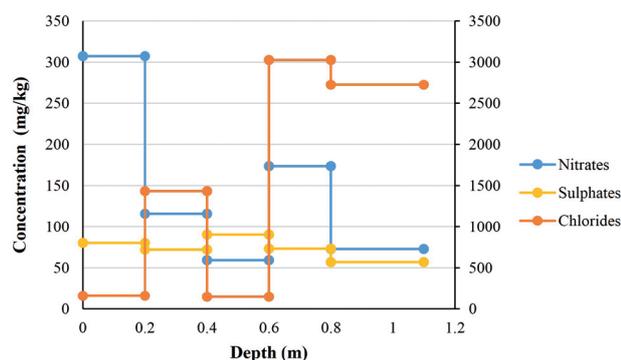


Fig. 6. Distribution of anions in soil profile.

are consistent with nitrate concentrations, which were measured in the groundwater of the Zagreb aquifer [38, 39] and are generally lower than those observed in the investigated soil profile.

According to Table 3, the dominant mineral phase in soil fraction below $2 \mu\text{m}$ is illitic material. The second clay mineral in analysed soil is chlorite. Illite and chlorite have CEC from 15 to 40 meq/100 g [40], which corresponds with mineral determination. Soil horizons were rich in potassium as the result of high contents of clay mineral (illite). Prus et al. [41] found enriched potassium in Cambisol from illite mineral. Magnesium concentration is also enriched in soil horizons and it can be associated with clay minerals (chlorite/vermiculite).

Results of correlation matrix between physical and chemical soil properties and potentially toxic metal and ions contents in Cambisol are shown in Table 4. Soil pH and calcium concentration is in strong positive correlation. Bažon et al. [42] also reported positive strong correlations between these two parameters. Concentrations of Zn and Cu have significant correlations with silty fractions in analysed soil. Shelukindo et al. [43] reported similar positive correlations between these elements and siltous materials. A strong positive correlation between zinc and silt components has been observed, which suggests that Zn is strongly bound in silt component of analysed soil (Table 4). Cadmium concentrations are in negative strong correlation with CEC values.

Correlations between the concentrations of the studied potentially toxic metals and some soil properties, such as soil texture and CEC, may point out the prevalent mode of metals retention in soil. For instance, copper is in good correlation with organic matter in our study. Romić et al. [44] found significant positive correlation between Cu and the content of organic matter in their investigation of similar soils, which is consistent with our research. Copper forms stronger organic complexes and therefore soils rich in organic matter can retain more copper. Correlation results between ions are diverse. However, strong positive correlation of nitrates with sand and strong negative correlation of nitrates with clay have been observed. The higher sand content in the upper part of soil indicate the existence of an oxidative environment profile, which is in line with negative correlation with ammonium. Uzoho et al. [45] reported different correlations between nitrates and clay content in soil. Correlation results suggest that some nitrate concentration is bound to clay particles of studied soil, which is consistent with research of Mohsenipour et al. [46]. In this case, it is possible that some part of nitrate can be adsorbed to clay particles, which results in lower nitrate concentrations in the deeper part of the soil profile, but also in the Zagreb aquifer [38, 39]. In addition, a strong positive correlation between nitrates, copper and zinc has been observed, which may refer to the same origin of those elements, i.e., agricultural activity.

Conclusions

The soil of the study area is silty clay loam with generally decreasing sand and silt content and increasing clay content with depth. Organic matter showed similar distribution characteristics with CEC values, which confirms the existence of a higher percentage of leaves and microorganisms in upper parts of soil. The sequential chemical analysis presented diverse distribution in sequenced fractions of investigated soil. All analysed potentially toxic metals showed highest concentrations in RES fraction, which indicates the possible influence of agricultural activities such as usage of fertilizers, manure, fungicides, sludge as soil fertilizer or point sources of contamination, namely uncontrolled, active or untended waste dumps and aerodeposition. Most of the highest cation concentrations were determined in 2C horizon, while the lowest concentrations were observed in A horizon. The highest concentrations of anions were determined in A, C and 2C horizons. Generally, it can be seen that most of ion concentrations are increasing until 0.8 m depth, while afterward they decrease. This indicates that agricultural activity probably has the highest influence on the first four soil horizons. Statistical analysis showed strong correlations between the concentrations of the studied potentially toxic metals and some soil properties, which may point out the prevalent mode of metals retention

in soil. In addition, correlation results between nitrates and some potentially toxic metals such as Cu and Zn indicate that these elements come from the same source of contamination, in this case probably agricultural activity. Due to results of this research, it can be concluded that anthropogenic influence is evident. Even though results suggest that agriculture has an influence on soil quality, other possible sources of contamination should not be neglected. Implementation of protection measures, for example education of farmers and control and monitoring of application of fertilizer and manure, should be done. Also, detailed sampling of percolated water through soil profile in time and determination of basic water ions, as well as determination of concentrations of potentially toxic metals and their sorption parameters, should be of primary interest in future research.

Acknowledgements

I want to change it to: Publication process is supported by the Development Fund of the Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb.

Conflict of Interest

The authors declare no conflict of interest.

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