Research Article

Solubility and availability of copper, zinc lead and iron in technosols under the effect of increasing copper levels

Abstract

Soluble (H_2O and 0.01M $CaCl_2$) and bioavailable (0.05M EDTA) forms of copper, zinc, lead and iron in Technosols from the industrial area of a steel producing plant were assessed following addition of increasing Cu levels (500 and 1000mg kg^{-1}). A natural, uncontaminated leached Cinnamonic forest soil from a rural area outside the steel plant was chosen as a control. The aim of the study was to assess the effect of high copper concentrations on the soluble (H_2O and 0.01M $CaCl_2$) and available (0.05M EDTA) fractions of Cu and other heavy metals (Zn, Pb, Fe) in the technogenic soils and to analyze the statistical relationships with the plant (*Eruca sativa*) concentrations. Higher fixation of copper was observed in the technogenic soils, compared with the control soil, both before and after the addition of Cu. Regarding Cu, Zn, and Pb a significant linear correlation between EDTA-extractable and pseudo-total (aqua regia) forms of heavy metals were found (R_{Cu}=0.838, R_{Zn}=0.698 and R_{Pb}=0.664). Concentrations of soluble forms of heavy metals obtained by extraction with 0.01M $CaCl_2$ and H_2O did not significantly predict bioavailability to plants. The increase of copper concentration in plants is related to the decrease of the concentrations of Zn and Pb in the biomass. In Technosols, Pb concentrations in plants exceeded permissible levels for food safety.

Keywords: bioavailability, copper, extraction, heavy metals, soil contamination

Volume 2 Issue 3 - 2018

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Received: June 04, 2018 | **Published:** June 18, 2018

Introduction

Contamination of soil by anthropogenic sources is a problem of a great interest. Close to the existing and already closed metallurgical plants, the pollution of soil by heavy metals is widespread and is a subject of intensive investigation.[1–5] Heavy metals are very persistent and difficult to remove from soil and unlike the organic contaminants they can't be transformed to non-toxic compounds.[6,7] The mobility and bioavailability of heavy metals to plants depends on their different chemical forms.[8–10] The labile form of the element is that amount which is in equilibrium with the form in solution "for a certain period of time", making it the best indicator of "chemically reactive form" compared to the "total load" of the metal in soil.[11] The quantification of labile forms of heavy metals makes it possible to evaluate, the potential leaching to ground or surface water as well as their entry into the food chain. The water soluble fraction is the most available fraction to the living organisms in soil. This phase contains the most mobile and potentially available metal species at very low concentrations.[12] Extraction of heavy metals from soil, using non-buffered salt solutions, e.g. 0.01M $CaCl_2$, 1M $MgCl_2$ or 1M NH_4NO_3, which mainly dissolve soluble and cation-exchange fractions are popular methods used for the evaluation of soil contamination and the availability of heavy metals to plants.[9,12,13] Another method to assess heavy metal availability is using synthetic chelating agents, such as EDTA, mostly because of its ability to form very stable, water soluble and well defined complexes with a wide range of multivalent cations.[12,14] As a disadvantage of this method is stated EDTA's ability to dissolve the hard soil phase, mainly carbonates and Fe- and Al-oxides. Chelating agents such as EDTA or DPTA extract a greater proportion of total forms of heavy metals from the solid phase of soil and are assumed to be suitable for predicting the availability to plants under specific conditions.[15,16]

The site under investigation is situated near the city of Sofia, in the industrial area of "Kremikovtsi" metallurgical smelter (production was discontinued in 2009). The region around the smelter including several villages was found to be polluted by heavy metals.[17,18] The soils from the area were affected by significant anthropogenic input of Pb and Zn as atmospheric contamination. Other authors have found that concentrations of lead, zinc, cadmium, copper, nickel and arsenic in the agricultural soils around "Kremikovtsi" exceed sanitary guidelines, due to dust emissions on the one hand and geogenic enrichment on the other.[4] A scrap spoil and tailing ponds from the industrial area of the "Kremikovtsi" steel works are reported to cause contamination of drainage waters and are characterized with high contents of Fe, Pb, Zn, Cd, Cu and As.[19] The aims of the present study were:

I. To assess the effect of high copper concentrations on the soluble (H_2O and 0.01M $CaCl_2$) and available (0.05M EDTA) fractions of copper and other heavy metals (Zn, Pb and Fe) in the investigated soils;

II. To determine the risk of metal mobilization in the event of high input of copper in technogenic soils possessing slightly alkaline pH and higher organic matter content;

III. To assess if labile and most reactive metal forms can predict plant concentrations in the Technosols. Copper was chosen as a model contaminant because at lower concentrations it has high "specific sorption" in soils and ability to form surface and labile complexes with soil organic matter[20, 21] and at high levels of added metal the binding strength of the metal ions with the soil results in increased mobilization.[22,23]

Experimental section

The study site was represented by: Technosols,[24] affected by heavy metals and coke dust from the industrial area of "Kremikovtsi" steel works. A natural, uncontaminated leached Cinnamonic forest soil from a rural area outside the steel works was studied as a control. Soil was sampled from the upper 0-30 cm layer of the studied profiles, from an area of 9m^2, in three replicates. Main physico-chemical properties and heavy metal contents of the investigated soils before copper addition are presented in Table 1. The soil pH values vary between 6.7 and 7.7, which define them as neutral to slightly alkaline. Cation exchange capacity of the Technosols is close to that of the control, and the organic matter content varies from 2.5% in the control to 17.5% in Technosols (P6), due to the presence of coal impurities and coke dust. Clay content of Technosols is several times lower than that of the control soil. Heavy metal contents of Technosols are elevated compared to the control, but only lead contents exceeds maximum permissible levels for arable and grasslands according Bulgarian standard.[25]

Table 1 Soil physico-chemical properties and heavy metal contents;[26] and new data from this study

Soils	pH (H_2O)	OM (%)	CEC cmol+/kg	Clay, %	Cu	Zn	Pb	Fe
					mg kg^{-1}			
1. Control soil (Leached Cinnamonic forest soil)	6.7	2.5	26.9	40	30	69	50	35400
2. Technosol (P6)	7.7	17.5	26.6	0.4	260	360	586	55200
3. Technosol (P7)	7.7	11.8	26.7	19.1	64	335	322	46200
4. Technosol (P8)	7.6	5.2	20.3	11.3	78	348	334	52800
MPC* (soil pH is 6.0–7.4)					150	320	100	-
MPC* soil pH is >7.4					300	400	120	-

*Maximum permissible concentrations of heavy metals for arable land and grasslands, according Bulgarian standard.[25]

The levels of added copper - 500 and 1000 mg kg^{-1} soil (under the form of Cupric acetate solution) were consistent with the national law and represented maximum and intervention concentrations of copper for industrial and production sites respectively.[25] A total of 12 variants were tested: Control, P6, P7, P8 without added Cu; Control Cu_{500}, P6 Cu_{500}, P7 Cu_{500}, P8 Cu_{500} with 500mg kg^{-1} added Cu; Control Cu_{1000}, P6 Cu_{1000}, P7 Cu_{1000}, P8 Cu_{1000} with 1000mg kg^{-1} added Cu. In a previous study,[26] pseudo-total (PT) forms of heavy metals, extracted by aqua regia and bioavailable forms, extracted by 1M NH_4NO_3 were assessed and reported. Statistically significant correlation between bioavailable forms of Cu extracted by 1M NH_4NO_3 and Cu concentration in plants (R=0.798) was obtained. A pot experiment was carried out with the investigated soils in a greenhouse, using 1 kg containers in three replications with test plants (*Eruca sativa*). Plant biomass was harvested 21 days after sowing and heavy metal concentrations in plants were analyzed. Plant samples were digested by concentrated HNO_3 and H_2O_2 on a sand bath until clarification of the solution and after that heavy metal concentrations were analyzed by AAS.[27] Soils from the greenhouse experiment were used for further chemical analyses. Soils were sieved through 1 mm sieve (non-rhizosphere soil) and major soil properties were analyzed. The cation exchange capacity was determined by the method of Ganev and Arsova.[28] Soil reaction was measured in 1:2.5 – soil: water suspensions. Soil organic matter was analyzed by the method of Tyurin.[29] Heavy metals in soils were determined by the following methods: water soluble forms in soil water (ratio 1:10) and shaking for 1 hour;[30] 0.01M $CaCl_2$ extractable forms in soil:sollution ratio (1:10) and shaking for 2 hours;[13] EDTA extractable forms in 0.05M EDTA (pH 7), soil:sollution ratio of 1:5 and 30 minutes of shaking.[31] Pseudo-total forms of metals (PT) were analyzed by aqua-regia digestion.[32]

Heavy metal analyses were performed with a high resolution radial viewing ICP - OES system - HORIBA JY ULTIMA 2 (Jobin Yvon, Longjumeau, France). The European standard EN ISO 11885 "Water quality determination of selected elements by inductively coupled plasma optical emission spectroscopy (ICP-OES)" was used as a method for the determination of Cu, Fe, Pb and Zn in soil extracts. Reagents of highest purity grade were used: 30 % HCl and 65 % HNO_3 (Suprapur, Merck) and deionized water. The stock solutions of the elements of interest Cu, Zn, Pb, and Fe (1mg mL^{-1}) were prepared by using Merck mono – element standard solutions, traceable to SRM from NIST 1000 mg L^{-1} Certipur®. The accuracy and the precision of the analytical results were experimentally demonstrated by certified reference material TMDA-51.2 from National Water Research Institute - fortified water for trace elements, prepared from Lake Ontario water, filtered, diluted, and preserved with 0.2 % nitric acid. Statistical processing of data - correlation and regression analysis were performed by STATGRAPHICS Centurion.

Results and discussion

Soil pseudo-total (PT) and EDTA-extractable contents of copper, before and after the addition of 500 and 1000 mg kg^{-1} of copper are presented in Figure 1. Adding copper to the soils regularly increased Cu pseudo-total contents (Figure 1), with the exception of some variants, Control Cu_{500}, Control Cu_{1000} and P7 Cu_{500} where lower concentrations of copper than expected were obtained. The reason of that could be the specific sorption of copper with the mineral components of the soil, e.g. CaO, Fe_2O_3, MnO_2, largely present in the soils from the vicinity of the smelter.[4] The concentrations of EDTA-extractable forms of copper varied depending on the type, the

Citation: Nenova L, Zgorelec Z, Benkova M, et al. Solubility and availability of copper, zinc lead and iron in technosols under the effect of increasing copper levels. *Int J Hydro.* 2018;2(3):379–386. DOI: 10.15406/ijh.2018.02.00100

physico-chemical properties of the soil, and the copper loadings, and ranged between 2.9 and 405.9mg kg^{-1} (Figure 1). When comparing pseudo-total and EDTA extractable forms of Cu, the percentage of EDTA extractable forms from the pseud-total forms is higher in the control soil then in Thechnosols. Before the addition of copper in the Control variant, EDTA extracts ~ 18 % of pseudo-total forms of copper, and after that about 64% and 49% in the variants Control Cu_{500} and Control $Cu_{1000,}$ respectively. In thechnogenic soils (P6, P7 and P8) before copper addition EDTA extracts ~4-5% of pseudo-total contents and after that - about 32- 48% of copper. The copper fixation in Technosols is due from one hand to the elevated organic matter content (coal impurities and coke dust) and from the other hand to the higher pH values of these soils compared to the Control. Despite the differences in the extracted concentrations of copper, depending on the soil and its loading, there was a good correlation between pseudo-total and EDTA-extractable copper concentrations-R=0.838 (Table 2). Similar results for such a relationship were obtained by Hornburg and Brümmer.[33] A negative correlation was obtained between soil pH values and EDTA-extractable Cu concentrations (equation 1). With increasing pH values, EDTA-extractable Cu decreased, because of increased Cu specific sorption by the mineral soil components at higher pH. In particular, 70.2 % of the total variability in the $Cu_{(EDTA)}$ concentrations was explained by a linear regression model with pseudo-total Cu content as predictor variable (Table 2). An improved relationship was obtained when pH was included as independent variable, explaining 75.7 % of the total variability in $Cu_{(EDTA)}$.

$$Cu_{(EDTA)} = 134.5 + 0.40 * Cu_{(PT)} - 18.14 * pH; (R^2 = 0.757,\ p < 0.000) \quad (1)$$

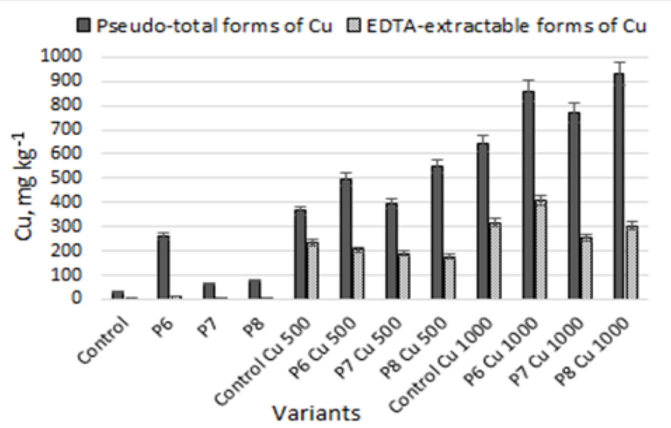

Figure 1 Soil pseudo-total and EDTA extractable forms of Cu, mg kg^{-1}.

Cu labile forms, extracted by 0.01M $CaCl_2$ were very low, because of the strong fixation in the natural soil (pH>6) and the Technosols (pH~7.7) and ranged from 0.10 to 0.36 mgkg^{-1} (Figure 2). Significant differences between the variants were observed only when 1000mg kg^{-1} of copper were added. Very similar were the data from the water extracts, i.e. 0.1-0.45mg kg^{-1} Cu (Figure 2). Adding copper in high concentrations (1000mg kg^{-1}) to the natural Cinnamonic soil from the region may lead to a risk of surface water contamination (~ 0.09mg L^{-1}).[34] There was a significant positive correlation between Cu concentrations in H_2O and 0.01M $CaCl_2$ extracts (R=0.824; R^2=0.679) (Table 2) which indicates that 0.01M $CaCl_2$ can successfully mimic heavy metal concentrations in the soil liquid phase. Similar results were reported by Ure[12] who has named these extractants "soil solution". The influence of pseudo-total content is significantly less pronounced for $Cu_{(CaCl2)}$ explaining 30.5% of the variance (Table 2) but still indicates that pseudo-total pool can significantly predict Cu mobilization as assessed by 0.01M $CaCl_2$ in the soils studied. Our results are in conformity with the study of McBride et al.[35] who treated large sets of data on soluble and high total Cu loadings in soil and found that the most important soil property for predicting Cu solubility was the total Cu (acid digestion). After copper addition in soil, it's concentration in plant biomass increased significantly from 4mg kg^{-1} in the Control variant to 34.0mg kg^{-1} in Profile 8 Cu_{500} (Table 3). There was no significant difference between copper concentrations in plants at the two levels of copper addition.

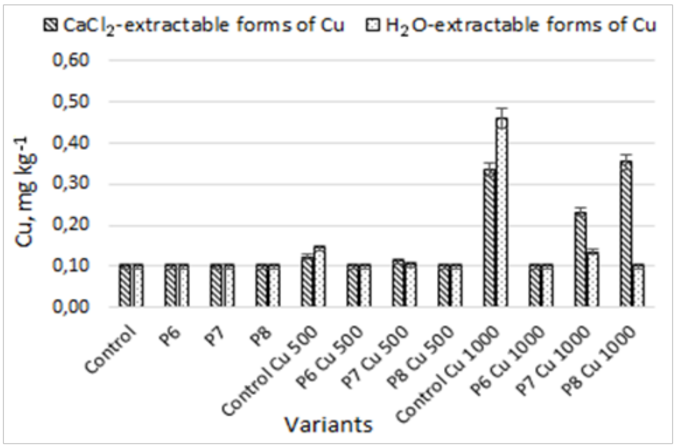

Figure 2 Soil 0.01M $CaCl_2$ and H_2O-extractable forms of copper.

According to Kabata-Pendias[8] concentrations of copper in plants ranging between 20 and 100mg kg^{-1} indicate contamination of soil. In a previous investigation, using similar soil from the region of "Kremikovtzi", ameliorated with organo-mineral amendments a negative correlation between Cu in soil solution and Cu in plant biomass was found, due to the formation of unavailable metal-organic complexes of copper in soil.[38] In the present study, plant concentrations could be significantly predicted by pseudo-total and EDTA-extractable forms of copper, but not by water or 0.01M $CaCl_2$ extractions (desorptions), due to bioavailability of specific copper species but not the total soluble forms of copper. The explained variance in plant copper concentrations reached 76.6 %, based on the $Cu_{(PT)}$ fraction and 73.4% based on the $Cu_{(EDTA)}$ fraction (Table 4).

Relationships between heavy metals on soil and plant level as influenced by copper addition

Zinc

The addition of copper has not influenced significantly Zn pseudo-total concentrations in soils (Figure 3). They ranged between 52.0 and 360 mg kg^{-1} and in Technosols they are very close to the maximum permissible levels (400mg kg^{-1}), according to the national regulations for soils with pH>7.4[25] (Table 1) (Figure 3). The percentage of $Zn_{(EDTA)}$ forms of pseudo-total forms are low and ranged between 1.8 and 8.6%. It was higher in the control soil (Control, Control Cu_{500} and Control Cu_{1000}) because of the lower initial concentration of zinc in the studied natural soil. A large percentage of zinc in the soil is often retained in the residual soil fraction and the proportion of the bioavailable forms, extracted by Tessier's procedure is smaller compared to the other heavy metals (Cu, Pb and Ni) even in highly contaminated soils.[9] In the present study for $Zn_{(CaCl2)}$ concentrations there was no significant variability between the variants (Figure 4). Only two of the variants had higher concentrations of Zn compared with the control, e.g. P6 Cu_{500} and P8 Cu_{1000}. The addition of 1000mg kg^{-1} Cu in soils increased Zn mobility in all the variants assessed by the H_2O extraction (Figure 4), without exceeding permissible levels for surface waters (3.0mg L^{-1}).[34] The addition of high amounts of copper probably leads to replacement of zinc from soil compartments due to competitive sorption effect at soil organic matter and soil oxides. The statistical analysis has demonstrated that there was moderately strong but significant relationship between EDTA-extractable and pseudo-total forms of Zn (R=0.698; R^2=0.487) (Table 2). Zinc concentrations in soil extracted by H_2O and 0.01M $CaCl_2$ were not significantly correlated with the pseudo-total forms. Zn concentrations in *Eruca sativa* plants varied between 21.0 and 70.0mg kg^{-1} (Table 3). In the variants from the natural soil, Zn concentrations in plants were lower compared to the Technosols. In some of the variants (marked with bold in) (Table 3) Zn concentrations in plants exceeded highest levels assessed in foodstuff by Rose et al.[36] There was an antagonistic effect between Cu and Zn uptake by plants - the addition of copper to the soil in some variants has diminished Zn concentrations in plant biomass. Copper and zinc are elements absorbed by a similar mechanism by plants, therefore each of them could competitively inhibit root absorption of the other.[8] A significant correlation was recorded between pseudo-total zinc concentration in soil and plant uptake (R= 0.742; R^2=0.551) similarly to copper (Table 4). These results correspond with the study of Lombi et al.[39] who found that correlation coefficients between the amounts extracted with aqua-regia and the concentration in sunflower plants from a pot experiment are positive and significant for Cd and Zn.

Table 2 Linear regression models between Cu, Zn, Pb and Fe concentrations in soil, extracted with different reagents: aqua regia (PT), EDTA, H_2O and 0.01M $CaCl_2$

Relationship between:	p-Value	R	R^2	Equation of the fitted model
Cu				
$Cu_{(EDTA)}$ and $Cu_{(PT)}$	0.000	0.838	0.702	$Cu_{(EDTA)}=21.9 + 0.36*Cu_{(PT)}$
$Cu_{(CaCl2)}$ and $Cu_{(PT)}$	0.012	0.552	0.305	$Cu_{(CaCl2)}=0.05 + 0.0002*Cu_{(PT)}$
$Cu_{(H2O)}$ and $Cu_{(CaCl2)}$	0.001	0.824	0.679	$Cu_{(H2O)=}0.02 + 0.70*Cu_{(CaCl2)}$
Zn				
$Zn_{(EDTA)}$ and $Zn_{(PT)}$	0.012	0.698	0.487	$Zn_{(EDTA)}=2.70 + 0.02*Zn_{(PT)}$
Pb				
$Pb_{(EDTA)}$ and $Pb_{(PT)}$	0.019	0.664	0.441	$Pb_{(EDTA)=}-14.12 + 0.0008*Pb_{(PT)}$
Fe				
$Fe_{(EDTA)}$ and $Fe_{(H2O)}$	0,000	0.875	0.766	$Fe_{(H2O)=}-0.37 + 0.029*Fe_{(EDTA)}$

Table 3 Heavy metal concentrations in *Eruca sativa* plants, mg kg^{-1}±StDev (data were presented in)[26]

Variants	Cu, mg kg^{-1}	Zn, mg kg^{-1}	Pb, mg kg^{-1}	Fe, mg kg^{-1}
Control	4.0±0.2	32.0±1.6	1.7±0.1	156.0±7.8
P6	6.0±0.3	63.0±3.2	6.0±0.3	280.0±14.0
P7*	-	-	-	-
P8	6.0±0.3	58.0±2.9	15.0±0.8	880.0±44.0
Control Cu_{500}	14.0±0.7	23.0±1.2	2.5±0.1	190.0±9.5
P6 Cu_{500}	19.0±1.0	48.0±2.4	5.0±0.3	412.0±20.6
P7 Cu_{500}	22.0±1.1	70.0±3.5	8.0±0.4	1210.0±60.5
P8 Cu_{500}	34.0±1.7	39.0±2.0	12.0±0.6	1100.0±55.0
Control Cu_{1000} P6 Cu_{1000}	19.0±1.1 32.0±1.6	21.0±1.1 54.0±2.7	1.0±0.1 4.0±0.2	226.0±11.3 755.0±37.8
P6 Cu_{1000}	32.0±1.6	54.0±2.7	4.0±0.2	755.0±37.8
P7 Cu_{1000}	24.0±1.2	36.0±1.8	12.0±0.6	1015.0±50.8
P8 Cu_{1000}	29.0±1.5	31.0±1.6	3.0±0.2	385.0±19.3
Maximum level	~40.0**	~60.0**	3.0***	-

*In variant P7 not enough biomass was collected to analyze heavy metal content

**Dietary exposure to metals and other elements in the 2006 UK[36]

***Maximum levels of Pb in foodstuffs: according European Commission.[37]

Table 4 Linear regression models between heavy metal concentrations in soils, extracted by different reagents and heavy metal concentrations in plants

Relationship between:	p-Value	R	R^2	Equation of the fitted model
Cu				
$Cu_{(plant)}$ and Soil_$Cu_{(PT)}$	0.001	0.875	0.766	$Cu_{(plant)}$ =4.96 + 0.025*Soil_$Cu_{(PT)}$
$Cu_{(plant)}$ and Soil_$Cu_{(EDTA)}$	0.001	0.857	0.734	$Cu_{(plant)}$ =5.36+ 0.06*Soil_$Cu_{(EDTA)}$
Zn				
$Zn_{(plant)}$ and Soil_$Zn_{(PT)}$	0.002	0.742	0.551	$Zn_{(plant)}$ =18.91 + 0.09*Soil_$Zn_{(PT)}$
$Zn_{(plant)}$ and Soil_$Zn_{(H2O)}$	0.043	-0.618	0.382	$Zn_{(plant)}$ =54.5–26.7*Soil_$Zn_{(H2O)}$
Fe				
$Fe_{(plant)}$ and Soil_$Fe_{(H2O)}$	0.020	-0.684	0.468	$Fe_{(plant)}$=796.31–542.78*Soil_$Fe_{(H2O)}$
$Fe_{(plant)}$ and Soil_$Fe_{(EDTA)}$	0.011	-0.731	0.534	$Fe_{(plant)}$=1081.26–18.88*Soil_$Fe_{(EDTA)}$

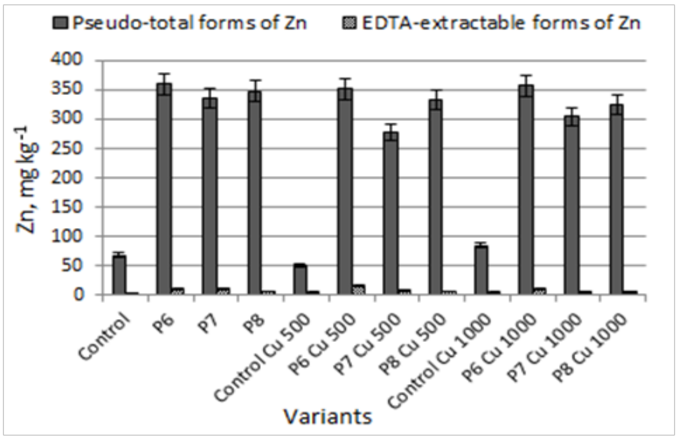

Figure 3 Soil pseudo-total and EDTA-extractable forms of Zn.

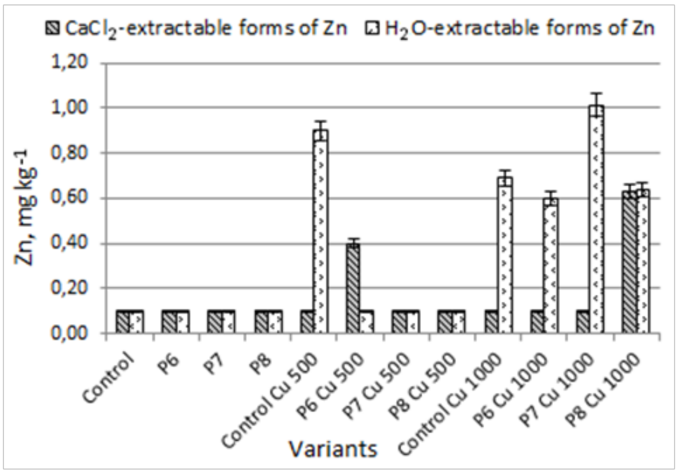

Figure 4 Soil 0.01M $CaCl_2$ and H_2O-extractable forms of zinc.

Lead

Pseudo-total forms of lead ranged between 46.5 and 586mg kg^{-1} (Figure 5). The level of lead in Technosols (P6, P7 and P8) exceeded two, three times maximum permissible concentrations for arable and grasslands (120mg kg^{-1}) (Table 1). The addition of copper diminished the pseudo-total concentrations of lead assessed by aqua regia digestion most probably due to redistribution of the residual pool and therefore a decreased ability to extract Pb (Figure 5). The range of $Pb_{(EDTA)}$ forms is between 7.3 and 36.6mg kg^{-1} (Figure 5). It is known that at alkaline conditions (pH>7) lead is less mobile in soil than other heavy metals.[21] Lead, solubilized by 0.01M $CaCl_2$ and H_2O was below the detection limit of ICP-AES. There was a moderately strong but significant relationship between pseudo-total and EDTA-extractable forms of Pb in soil (R=0.664; R^2=0.441) (Table 2). At high initial copper concentrations in Technosols (P6), the mobility of lead assessed by EDTA-extraction increased mostly due to competitive sorption effect Cu-Pb. According to European Commission[37] the limit value of Pb in plants is 3.0mg kg^{-1} (Table 3). The normal range of lead for cabbage plants is about 1.7–2.4mg kg^{-1}.[8] Our results showed that Pb concentrations in *Eruca sativa* biomass, collected from Technosols exceeded significantly (in some variants four-five times) permissible levels (Table 3). This could pose a real health risk if these plants are grown and consumed from the population in the area. The addition of high levels of copper has affected the lead uptake by plants and again has diminished Pb concentrations. There was no significant relationship between Pb concentrations in plants and Pb extracted from soil.

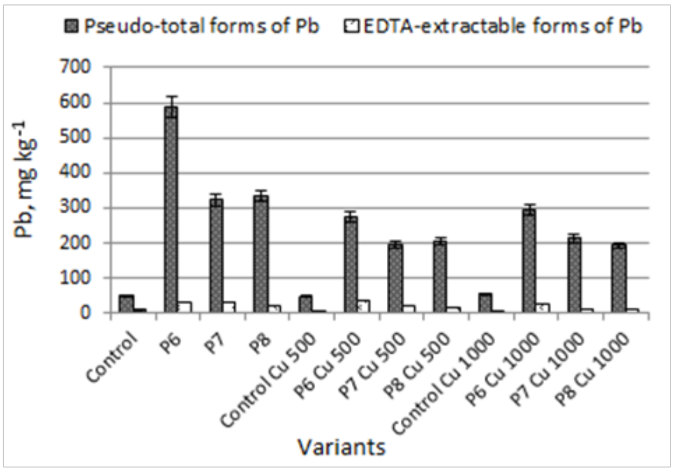

Figure 5 Soil pseudo-total and EDTA-extractable forms of Pb.

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Iron

Pseudo-total forms of iron in the Control variant (Figure 6) were close to the average values in soils worldwide 35 400mg kg^{-1} (~3.5%).[8] In the Technosols (P6, P7 and P8) pseudo-total forms of Fe were considerably higher, 5 – 5.5 %, due to the activity of the steel works. The addition of copper, similarly to lead has again caused a decrease in pseudo-total forms of Fe in Technosols (Figure 6). A similar trend, as for Cu was observed for Fe, regarding the proportion of EDTA extractable forms (7.8 and 57.5mg kg^{-1}) (Figure 7) from pseudo-total contents, *i.e.* higher proportions were found in the control soil than in Technosols. Soluble forms of Fe extracted by $CaCl_2$ and H_2O (0.08 - 1.35 mg kg^{-1} are presented in Figure 8). Only in the control soils (Control, Control Cu_{500}, Control Cu_{1000}), apart from Cu addition, H_2O extracted more Fe than in the other variants. As regards Fe, a significant positive correlation between EDTA and H_2O extractable forms was observed ($R=0.875$; $R^2=0.766$), (Table 2). At the conditions of the Technosols (pH=7.6 - 7.7) iron is weakly extracted by EDTA, $CaCl_2$ and H_2O extractants. This could be due to the fact that in alkaline conditions the precipitation of iron is possible.[8] As an essential element for plant growth and development, concentrations of Fe in food are not regulated. In our study Fe concentrations in plants ranged from 156mg kg^{-1} in the control variant to 1210mg kg^{-1} in the P7 Cu_{500} variant (Table 3) pointing at contamination by the activity of the metallurgical smelter and accumulation of iron in plant biomass. The content of Fe in plant biomass was negatively correlated with the contents in water and EDTA-extracts ($R=-0.684$ and $R=-0.731$), (Table 4), making those extractants unsuitable for predicting Fe uptake by *Eruca sativa* plants at the conditions of increasing Cu loadings. The reason could again be the speciation of Fe into different complexes in solution and unavailability of the specific Fe-organic complexes extracted by 0.05M EDTA in the soils studied.

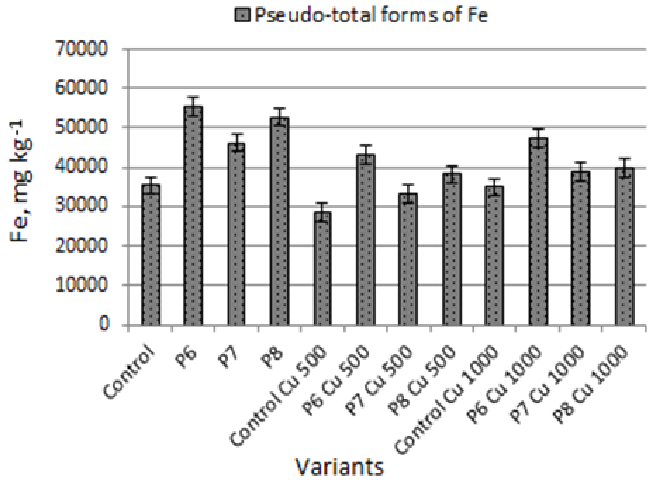

Figure 6 Soil pseudo-total forms of Fe, mg kg^{-1}.

Conclusion

Availability and extractability of Cu, Zn, Pb and Fe at increasing Cu levels was studied in three Technosols and a control soil from the vicinity of a ferrous metallurgical plant, by making use of H_2O, 0.01M $CaCl_2$ and 0.05M EDTA extractants. As a result of the additional copper contamination of the studied soils, the availability of copper to *Eruca sativa* plants increased significantly, without exceeding average levels for foodstuffs. The increase of copper concentration in plant biomass was related with the decrease of the concentrations of Zn and Pb. In some variants of Technosols, Pb in plants exceeded over four times permissible levels for food. The proportions of EDTA extractable forms of pseudo-total forms of copper were lower in the Technosols than in the control soil, due to specific sorption of copper at slightly alkaline pH. Similar tendency was observed for the proportions of $Fe_{(EDTA)}$ of the pseudo-total contents. The addition of copper at high concentrations has caused mobilization of Zn labile forms, determined by the methods used. Regarding Cu, Zn, and Pb a significant linear correlation between EDTA-extractable and pseudo-total forms of metals was found. The weak soil extractants (desorbents) such as H_2O and 0.01M $CaCl_2$ could not significantly predict the bioavailability to plants at the conditions of the pot experiment in Figure 9.

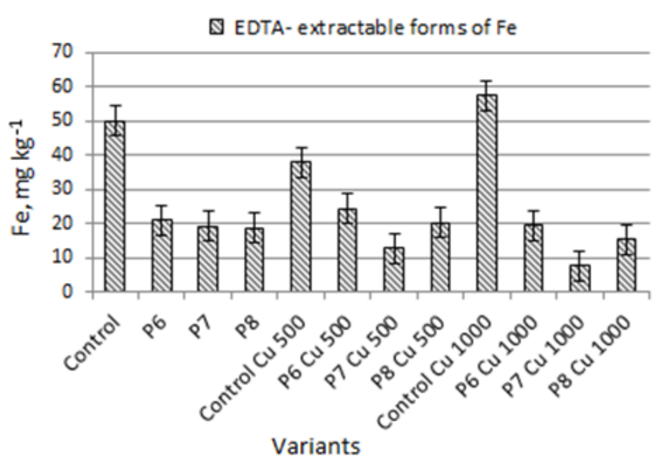

Figure 7 Soil EDTA-extractable forms of Fe, mg kg^{-1}.

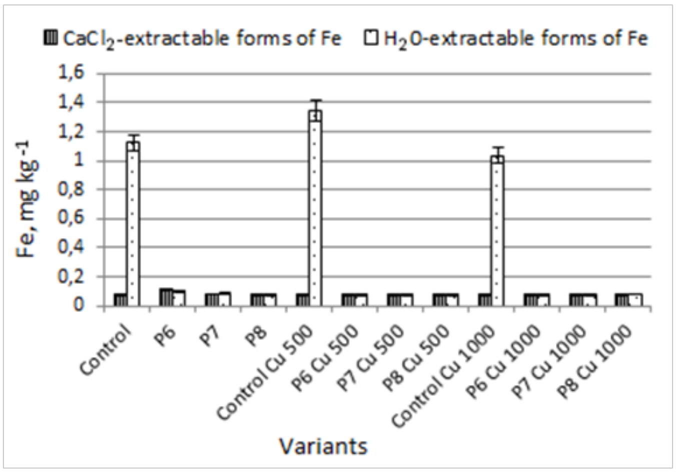

Figure 8 Soil 0.01M $CaCl_2$ and H_2O-extractable forms of Fe, mg kg^{-1}.

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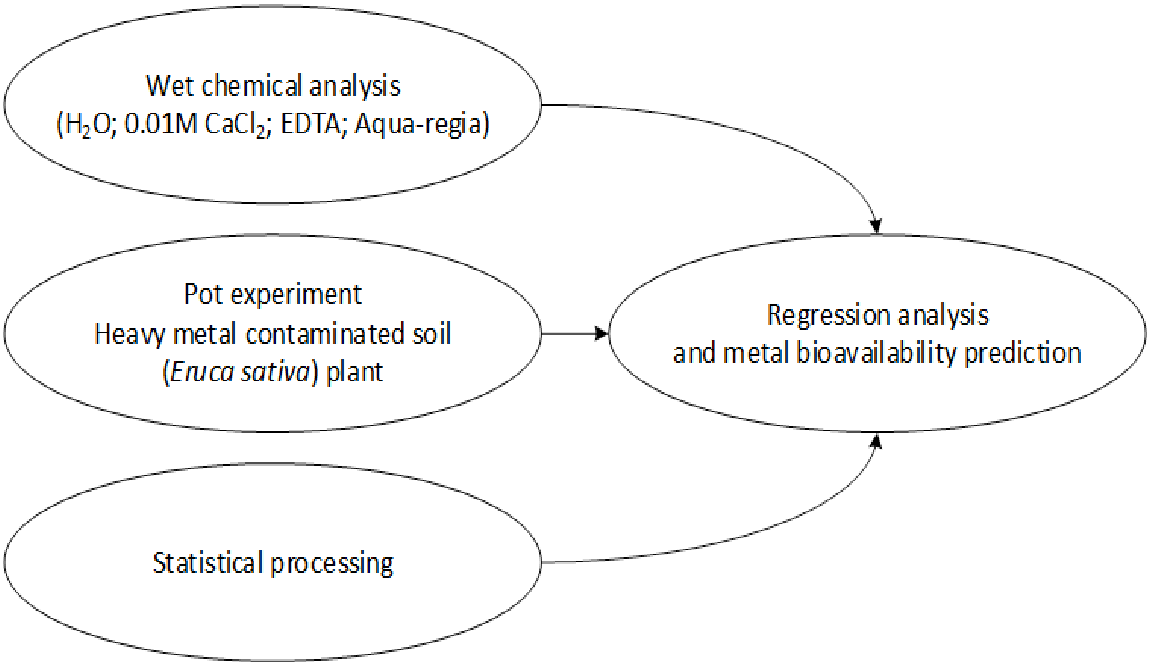

Figure 9 Graphical abstract.

Acknowledgements

This study was funded by the Project DN 06/1 (2016–2019) of the National Science Fund, Ministry of Education and Science, Bulgaria.

Conflict of interest

The author declares there is no conflict of interest.

References

1. Kočevar N, Djiogo S, Ražić S, et al. Accumulation of Heavy Metals From Soil in Medicinal Plants. *Arh Hig Rada Toksikol*. 2017;68(3):236–244.
2. Sallaku F, Fortuzi S, Tota O, et al. Improving participation and cooperation on water management: experience from farmer-managed systems in Albania. *J Food Agric Environ*. 2009;7:132.
3. Kachenko A, Singh B. Heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia. *Water Air Soil Pollut*. 2006;169:101.
4. Schulin R, Curchod F, Mondeshka M, et al. Heavy metal contamination along soil transect in the vicinity of the iron smelter of Kremikovtzi (Bulgaria). *Geoderma*. 2007;140:52–61.
5. Faitondjiev L, Stanislavova S, Thculdjian H. Pollution of plants with toxic elements in the region of Kremikovtzi. *Soil Sci Agrochem Ecol*. 2000;35(5):10–12.
6. Takáč P, Szabová T, Kozáková L, et al. Heavy metals and their bioavailability from soils in the long-term polluted Central Spiš region of SR. *Plant Soil Environ*. 2009;55:167–172.
7. Adriano D. Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability and Risk Assessments. 2nd edition. *Springer-Verlag*. 2001;869.
8. Kabata-Pendias A. *Trace elements in soils and plants*. 4th edition. CRC Press. 2011;505.
9. Ma L, Rao G. Chemical Fractionation of Cadmium, Copper, Nickel, and Zinc in Contaminated Soils. *J Environ Qual*. 1997;26(1):259.
10. Brummer GW. *The importance of chemical "speciation" in the environmental process*. In: Bernhard M, Brickman FE, Sadler PJ, Editors. *The importance of chemical "speciation" in the environmental process*. Berlin, Heidel berg, New York: Springer. 1986;169–192.
11. Degryse F, Waegeneers N, Smolders E. Labile lead in polluted soils measured by stable isotope dilution. *Eur J Soil Sci*. 2007;58:1.
12. Ure AM. Single extraction schemes for soil analysis and related applications. *Sci Total Environ*.1996;178:1–3.
13. Houba V, Lexmond TH, Novozamsky I, et al. State of the art and future developments in soil analysis for bioavailability assessment. Sci Total Environ. 1996;178:21–28.
14. Novozamsky I, Lexmond TH, Houba V. A single extraction procedure of soil for evaluation of uptake of some heavy metals by plants. Intern J Environ Anal Chem. 1993;51:47–58.
15. Feng MH, Shan XQ, Zhang SZ, et al. Comparison of a rhizosphere-based method with other one-step extraction methods for assessing the bioavailability of soil metals to wheat. Chemosphere. 2005;59(7):939–949.
16. Pueyo M, López-Sánchez J, Rauret G. Assessment of $CaCl_2$, $NaNO_3$ and NH4NO_3 extraction procedures for the study of Cd, Cu, Pb and Zn extractability in contaminated soils. *Anal Chim Acta*. 2004;504(2):217–226.
17. Dinev N, Filcheva E, Hristova M, et al. Monitoring of heavy metal contaminated soils and mobility of their organo-mineral copounds. *Soil Sci Agrochem Ecol*. 2011;45:93.

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18. Dimitrova A, Metodiev V, Sidjimov M, et al. Environmental Heavy Metal Pollution and Effects on Child Mental Development – Risk Assessment and Prevention Strategies. *NATO Science for Peace and Security Series-C; Environmental Security*. 2011;245–255.
19. Georgiev P, Grudev S, Bratkova S. God Vissh Minno-Geol. *Inst Sofiya*. 2002;177:44–45.
20. McLaren RG, Hogg DS, Swift RS. Some factors affecting the availability of native and applied soil copper in New Zealand soils. *Forest Ecol Manag*. 1990;37(1-3):131–142.
21. Alloway BJ. *Heavy Metals in Soils*. Blackie Academic and Professional, London. 1995;7–39.
22. Atanassova. Adsorption and desorption of Cu at high equilibrium concentrations by soil and clay samples from Bulgaria. *Environ Pollut*. 1995;87(1):17–21.
23. Atanassova I, Okazaki M. Adsorption-desorption characteristics of high levels of copper in soil clay fractions. *Water Air Soil Pollut*. 1997;98(3-4):213–228.
24. IUSS Working Group WRB. World Reference Base for Soil Resources 2014, update 2015. International soil classification system for naming soils and creating legends for soil maps. *World Soil Resources Reports No. 106. FAO, Rome*. 2015.
25. Decree. State Gazette. *For standards of acceptable content of harmful substances in the soil*. 2008;71.
26. Nenova L, Atanassova I, Simeonova Tz, et al. Mobility and bioavailability of heavy metals on the background of high levels of added copper in technogen-ically affected soils. *Soil Sci Agrochem Ecol*. 2015;48:43.
27. Page AL, Miller RH, Keeney DR. *Methods of Soil Analysis. Part 2. Chemical and microbiological properties.* 2nd edition. ASA and SSSA, Madison, Wisconsin, USA, 1982;1159.
28. Ganev S, Arsova A. Methods of determining the strongly acidic and the slightly acidic cation exchange in soil. *Soil Sci, Agrochem Ecol*. 1980;15(3):22–23.
29. Kononova M. Soil organic matter: Its Nature, Its Role in Soil Formation and in Soil Fertility. *ASUSSR*. 2013;544.
30. Katoh M, Satoshi M, Sato T. Single-Step Extraction to Determine Soluble Lead Levels in Soil. *Int J of GEOMATE*. 2012;3(2):375.
31. Anon. *Analysis of Agricultural Materials*. Ministry of Agriculture Fisheries and Food Reference Book, HMSO, London.1986;427.
32. ISO 11466:1995. *Soil quality-Extraction of trace elements soluble in aqua regia*. International Organization for Standardization. 1995.
33. Hornburg V, Brümmer G. Verhalten von Schwermetallen in Böden 1. Untersuchungen zur Schwermetallmobilität. *Zeitschrift für Pflanzenernährung und Bodenkunde.* 1993:156(6):467–477.
34. Decree 12, State Gazette. *For the quality requirements for surface waters, intended for drinking and domestic water supply*. 2002;63.
35. McBride M, Sauve S, Hendershot W. Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *Eur J Soil Sci*. 1997;48(2):337–346.
36. Rose M, Baxter M, Brereton N, et al. Dietary exposure to metals and other elements in the 2006 UK Total Diet Study and some trends over the last 30 years. *Food Addit Contam*. 2010;27(10):1380.
37. European Commission. Official Journal of the European Commission. COMMISSION REGULATION (EC) No 1881/2006. 2006.
38. Benkova M, Atanassova I. *Effectiveness of lime and glauconite-phosphorite containing organo-mineral ameliorants in heavy metal contaminated soils*. In: Selim M, editor. *Phosphate in Soils. Interaction with Micronutrients, Radionuclides and Heavy Metals.* Francis & Tylor. 2015;291–318.
39. Lombi E, Gerzabek MH, Horak O. Mobility of heavy metals in soil and their uptake by sunflowers grown at different contamination levels. *Agronomie, EDP Sciences*. 1998;18:361–371.

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