Contents, distribution, and fractionation of soil organic carbon and trace elements in soils under a green manure application

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Abstract: We quantified the soluble fractions of the soil organic carbon (SOC) concentrations and the total and water-soluble trace elements in soils contaminated by household waste and remediated via the addition of green manure over 13 years and identified the main factors controlling the vertical distribution and accumulation of the trace elements. Green manure favoured the active formation of soil organic matter. The SOC of the examined soils was characterised by the active stabilisation by mineral soil compounds, but by a low degree of humification. The soils showed increased concentrations of Cr and Ni ions. The SOC and different soil compounds enriched by Si, Ca, and Mn ions were the important determinant for the distribution of Sr, V and Cu ions, as well as for the distribution of Pb and Cr ions bound to the water-soluble components of the soils. The low degree of SOC humification may be one of the main reasons of the high concentrations of Cu and Pb ions in the composition of the water-soluble soil compounds. The nickel ions were mainly associated with compounds enriched by the Al and Fe ions. The extremely high percentage concentration of the Ni ions in the water-soluble components of the soils may be result of the absence of the Ni ions adsorption by humic substances.

Keywords: Anthrosols; contamination of soils; element-pollutants; fulvic acids; humic acids; organic amendment

The application of different organic amendments has been widely used in contaminated soils to reduce the mobility and bioavailability of trace elements and to increase plant productivity. The soluble fractions of soil organic matter (humic acids and fulvic acids) play an important role in the immobilisation of trace elements, possibly due to the intensive formation of ion-humic complexes (Wiszniewska et al. 2016). The system of humic and fulvic acids is dynamic and can be variable under the influence of different organic amendments.

Green manures are one of the most commonly used organic amendments. Many studies have focused on the effects of green manures in terms of increasing the supply of nutrients available to the plants and the biological activity as well as in improving the soil structure and reducing pest and disease problems, but little attention has been paid to the long-term dynamics of the soluble fractions of soil organic matter and how the interactions between the organic matter and the trace elements vary under the long-term influence of the green manure addition.

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In this frame, we realised research focused on the concentration and distribution of soluble fractions of soil organic matter, the accumulation of trace elements in soils, and the association of trace elements with the reactive phase-carriers of soils. We examined soils formed on the territory of a large agricultural array from the west coast of the Pacific Ocean (the Primorye Region of the Russian Far East). A 13-year field experiment was conducted using Capillaric Uterquic Anthrosol (Humic, Bathyclauic), which is contaminated with household waste. The remediation in the area consisted of the removal of the contaminated upper part of the soil profiles with the use of green manure (mostly legumes) over a period of 13 years.

The objectives of this study are as follows: (i) to quantify the soluble fractions of the soil organic carbon concentrations and the total and water-soluble trace element contents in the soil profiles; (ii) to identify the main factors controlling the vertical distribution and accumulation of the trace elements in the soil. We present data about the influence of the long-term addition of green manures on the qualitative and quantitative characteristics of the soil organic carbon and show that despite the removal of the contaminated upper layer, the vertical distribution of the trace elements reflects the previous contamination.

MATERIAL AND METHODS

A field experiment was conducted over 13 years at the agrochemical station of the Federal Research Center of Agricultural Biotechnology of the Far East named after A.K. Chaiki (Figure 1). The station is located in the southern part of the coast of the Russian Far East (43°51'N latitude; 131°57'E longitude). It has a monsoon climate, with a mean annual precipitation of 700 mm. The mean annual total solar radiation and radiation balance is 118.9 and 52.2 kcal/cm², respectively (Purtova & Kostenkov 2009).

Soils were collected from two soil profiles. After the careful removal of roots and stones, the soil samples were ground to a powder. The powders were sieved through a 0.25-mm mesh. The soil pH, clay content and bulk density were analysed using Pansu and Gautheyrou's (2006) recommendations. The content of the soil organic carbon (SOC) was determined by the wet combustion method of Tyurin, which is very close to the Walkey-Black method (Minkina et al. 2018). This method is included into the register of methods approved for the determination of organic matter in soils of the Russian Federation (GOST 26213-91). According to the GOST 26213-91 guidelines, the SOC was extracted with a mixture of K2Cr2O2 and concentrated H2SO4, followed by titration with 0.2 mol/l of Mohr's salt. The different

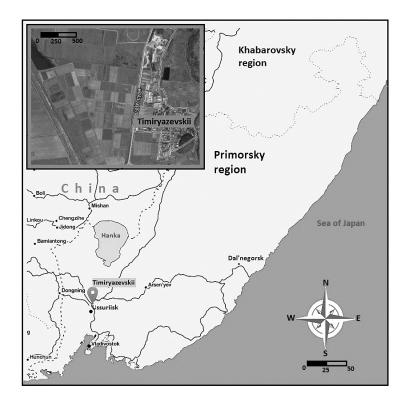


Figure 1. Map showing the sampling locations

SOC fractions were determined using the method of Tyurin modified by Ponomareva and Plotnikova as described by Vorob'eva (2006). The SOC fractionation for humic acids and fulvic acids was employed using a sequential extraction that consisted of the following extraction solutions:

- (a) Fraction 1 of the "free" (colloidal form) humic acids and the labile Fe/Al oxyhydrate-bound humic acids ($C_{\rm HAI}$) and fulvic acids ($C_{\rm FAI}$) was extracted with a 0.1 mol/l NaOH solution;
- (b) Fraction 2 of the Ca-bound humic acids (C_{HA2}) and fulvic acids (C_{FA2}) was extracted with a 0.1 mol/l NaOH solution after acid treatment (0.1 mol/l H_2SO_4) to remove the carbonates;
- (c) Fraction 3 of the clay mineral and the stable Fe/Al oxyhydrate-bound humic acids ($C_{\rm HA3}$) and fulvic acids ($C_{\rm FA3}$) was extracted with a 0.02 mol/l NaOH solution after 6 h of heating (100 °C) in a water bath;
- (d) Fraction 1a of the «aggressive» free fulvic acids $(C_{\rm FA1a})$ was extracted with 0.1 mol/ l of $\rm H_2SO_4$. The humic acids were precipitated from each extraction solution by adding 1N of $\rm H_2SO_4$. The concentrations of the selected fractions of the fulvic acids were calculated as the difference between the SOC content of each extraction solution and the concentration of the humic acids in each solution, respectively (Vorob'eva 2006). A saturated $\rm Na_2SO_4$ solution was added to coagulate the silt particles and accelerate the filtration in each extraction solution.

The total macro element contents of the soils were determined via energy dispersive X-ray fluorescence spectroscopy (EDX), using a Shimadzu EDX-800HS-P instrument as described by Timofeeva et al. (2018). For the measurement of the total trace element contents, the soil samples were completely dissolved in HF and HNO $_3$ based on Pansu and Gautheyrou (2006). The trace element concentrations in the soil watersoluble components (WSC) obtained at a 1:10 soil to water ratio. The trace element concentrations in the suspensions were analysed by atomic absorption spectrometry (Atomic Absorption Spectrophotometer AA-7000, Shimadzu).

Each chemical analysis was performed with three parallel probes to identify the adequate iteration number. The data were processed statistically (median value and regression analyses) using the software packages Microsoft Excel and SPSS (SPSS Inc., Ver. 16, 2007). An analysis of variance was used to determine the significant differences and correlation matrices for the trace elements, selected soil properties, and

different fractions of humic acids and fluvic acids. The significance level (*P*) did not exceed 0.05.

RESULTS AND DISCUSSION

Soil characterisation. The soil used in this study is classified as Capillaric Uterquic Anthrosol (Humic, Bathyclauic) according to the World Reference Base for Soil Resources (2006). The studied soils are constituted by four horizons (Ap - Bt - Btg - Cg) (Figure 2). The characterisation of some of the morphological features and chemical, physico-chemical, and physical properties of the studied soils are given in Table S1 in the Electronic Supplementary Material (ESM) (according to the authors' results). The soils are characterised by significant weathering processes which increase the accumulation of the clay fraction in the middle and lower parts of the soil profiles. The soil texture varied from heavy loam and light clay in the upper soil horizons to medium and heavy clay in the middle and lower horizons. The soil bulk density varied from 1.00 to 1.46 g/cm³, with maximum levels in the lower horizon. The soils were slightly acidic, with levels of the pH_{H_2O} ranging from 5.92 to 6.77. The soil was dark-coloured in the middle part of the soil profiles as a result of the migration of the soluble fractions of the soil organic carbon from the upper parts of the soil profiles.

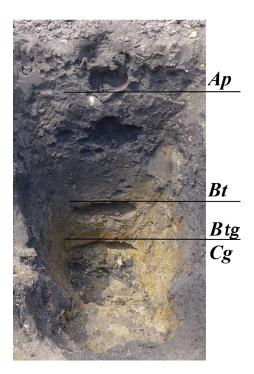


Figure 2. View of the Capillaric Uterquic Anthrosols profile

The upper parts of the soil profiles had the highest contents of CaO (1.54%) and MnO (0.24%). The maximum level of SiO_2 was also found in the Ap horizon (72.23%), but the vertical distribution of SiO_2 was not typical for the studied soil type. The highest content of SiO_2 in the Ap horizon might be related to the fact that the upper part of the soil profile was removed prior to the experiment, and the compounds enriched by the Si ions were inherited from the mineral horizon of the soil. The contents of $\mathrm{Al}_2\mathrm{O}_3$ and $\mathrm{Fe}_2\mathrm{O}_3$ increased in the middle soil horizons (15.80% for $\mathrm{Al}_2\mathrm{O}_3$; 7.44% for $\mathrm{Fe}_2\mathrm{O}_3$).

Soil organic carbon. The SOC contents decreased sharply with the soil depth, with a minimum value of 0.46 g/kg at a depth of 133–152 cm (Table 1). The divergence in the SOC levels at the depths of 0–36 and 36–94 cm confirmed the differentiation of the soil profiles and the correct allocation of the soil horizons. Compared with the SOC contents in the topsoil layers of agricultural soils with similar main soil-forming processes, the SOC levels in the upper part of the studied Capillaric Uterquic Anthrosol profiles could be characterised as medium.

Based on the results of the fractional composition of the SOC from the studied soils, fulvic acid is the predominant extractable SOC fraction (25.00% to 30.42% of the SOC content). This is also supported by the $C_{\rm HA}$: $C_{\rm FA}$ ratio, which characterises the humatefulvate type of the organic matter, with the exception of the Bt horizon, where the concentration of the

humic acid was slightly higher than that of the fulvic acid. The Ca-bound and clay mineral and stable Fe/Al oxyhydrate-bound fractions of the fulvic acids represented the major part of the fulvic acids in the studied soils. The fractions of the "aggressive" fulvic acids and labile Fe/Al oxyhydrate-bound fulvic acids were the minor fractions of all the fulvic acids, accounting for 0.15% to 5.37% of the SOC content. The distribution of the fulvic acids throughout the soil profiles showed an accumulation of all the studied fractions in the topsoil layer.

The percentages of the humic acid fractions varied from 6.73% to 27.46% of the SOC content throughout all the profiles. The concentrations of the individual humic acid fractions decreased in the order $C_{\rm HA3} > C_{\rm HA2} > C_{\rm HA1}$. The highest concentrations of all the studied fractions of the humic acids were found in the Ap.

Humin accounted for more than 40% of the SOC content in the studied soils. The distribution of the humin concentration throughout the studied soil profiles showed a decrease with the soil depth. In contrast, humin was the main part of the SOC in the Cg horizon (69.7% of the SOC).

According to the studied soil use history, the SOC partly consisted of the initial SOC formed under natural conditions and partly of the SOC formed by the intensive long-term inputs of grass litter. The content of the initial SOC is related to the SOC content in the subsoil layers of the native soils and is not significant because the upper organo-accumulative horizon with

Table 1. Content and fractional composition of the soil organic carbon in the Capillaric Uterquic Anthrosols (in g/kg)

D .	Horizons (depth, cm)					
Parameter	Ap (0-36)	Bt (36-94)	Btg (94–133)	Cg (133–152)		
SOC	26.46 ± 0.94	13.64 ± 0.75	4.71 ± 0.17	0.46 ± 0.01		
C_{HA1}	0.43 ± 0.03	0.19 ± 0.01	0.07 ± 0.01	ND		
C_{HA2}	3.08 ± 0.22	1.87 ± 0.06	0.07 ± 0.01	0.005 ± 0.001		
C_{HA3}	3.57 ± 0.26	1.68 ± 0.07	0.38 ± 0.02	0.03 ± 0.01		
C_{FA1a}	0.50 ± 0.03	0.02 ± 0.01	0.03 ± 0.01	ND		
C_{FA1}	1.42 ± 0.08	0.19 ± 0.01	0.05 ± 0.01	0.005 ± 0.001		
C_{FA2}	4.80 ± 0.17	2.70 ± 0.09	0.57 ± 0.03	0.04 ± 0.01		
C_{FA3}	1.20 ± 0.06	0.51 ± 0.02	0.80 ± 0.03	0.07 ± 0.01		
$C_{HA}:C_{FA}$	0.89 ± 0.05	1.07 ± 0.06	0.36 ± 0.01	0.22 ± 0.01		
Humin	11.45 ± 0.82	11.17 ± 0.77	2.76 ± 0.11	0.35 ± 0.01		

SOC – soil organic carbon; $C_{\rm HA1}$ – "free" (colloidal form) humic acids and labile Fe/Al oxyhydrate-bound humic acids; $C_{\rm HA2}$ – Ca-bound humic acids; $C_{\rm HA3}$ – clay mineral-bound and stable Fe/Al oxyhydrate-bound humic acids; $C_{\rm FA1}$ – "aggressive" free fulvic acids; $C_{\rm FA1}$ – labile Fe/Al oxyhydrate-bound fulvic acids; $C_{\rm FA2}$ – Ca-bound fulvic acids; $C_{\rm FA3}$ – clay mineral-bound and stable Fe/Al oxyhydrate-bound fulvic acids; $C_{\rm HA}$: $C_{\rm FA}$ – proportions of humic acids and fulvic acids; ND – not detected; the values are the means (n=6), with standard deviations

a maximum SOC content was removed. Our results indicate that adding green manure over a period of 13 years, combined with the high decomposition rates of the "fresh" grass litter at a high level of radiation balance and slightly acidic pH levels, is favourable for the active transformation of grass litter into soil organic matter. The predominance of the Ca-bound and clay mineral and the stable Fe/Al oxyhydratebound acid fraction in the SOC indicated the active removal of SOC from the solution and the transfer to a solid phase and, thus, the stabilisation of the SOC in the soil. However, the low humic acid concentrations in the composition of the SOC indicated a low degree of SOC humification, which was related to the significant formation of high-turnover fulvic acids. The migration of humic substances through the profiles resulted in a black colour up to a depth of 94 cm, which can be attributed to the long-term contribution of the "fresh" grass litter to the surface soil, causing a dilution effect of the organic material. Most likely, to increase the SOC humification in soil, a period longer than years is needed.

Trace element. The studied trace elements were selected as the most widespread environmental pollutants. The total trace element contents in the studied soils were compared with the mean background contents of the elements in surface soils around the world, as reported by Kabata-Pendias (2011).

Strontium and vanadium. The mean total contents of Sr and V ions were below the background

values for the surface soils (Table 2). After the water extractions, the Sr and V ions accounted for 4.81% and 2.59% (median values) of the total Sr and V ion content, respectively (Table 2). The contents of the Sr and V ions were highest at the Ap horizon. Several reports have suggested the accumulation of Sr and V ions in organic-rich soil layers in areas with an anthropogenic element input (Kabata-Pendias 2011).

In the present study, the distributions of the Sr and V ions in the soil profiles are mainly controlled by their strong affinities for the SOC and soil compounds enriched by the Mn, Si, and Ca-ions (Table S2 in ESM, Figure 3). The Sr and V ion contents significantly correlated with all the fractions of the SOC (Table S3 in ESM, Figure 4). The positive correlation of the Sr and V ions bound to the WSC with the acidic fractions of the SOC showed that the fixation of the Sr and V ions by the soil organic substances led to the formation of unstable complexes, without a significant Sr and V retention. The highly positive correlation between the Sr and V contents and the soil compounds enriched by the Mn, Si, and Ca ions is related to the presence of the Sr and V ions in the soil minerals (Timofeeva et al. 2018). The Sr and V ion values showed a negative correlation with the clay and Fe ion contents.

Our results point out that despite the low total of the Sr and V ion contents, the retention of these elements by the secondary soil minerals during natural soil weathering had no significant influence on the

Table 2. Trace element compositions of the Capillaric Uterquic Anthrosols and comparison of the trace element contents in the Capillaric Uterquic Anthrosols with other published mean background element contents in the soils (in mg/kg)

Element	Element fraction	Horizons (depth, cm)				Mean background contents
		Ap (0–36)	Bt (36–94)	Btg (94–133)	Cg (133–152)	of the elements in the soils around the world (Kabata-Pendias 2011)
Cu	total WSC*	44.36 ± 3.16 5.06 ± 0.38	37.67 ± 2.20 2.53 ± 0.16	38.35 ± 2.51 2.61 ± 0.17	34.42 ± 2.84 1.04 ± 0.08	38.9
Ni	total WSC	19.93 ± 1.38 1.38 ± 0.06	43.34 ± 3.26 3.03 ± 0.17	48.15 ± 3.60 2.96 ± 0.14	29.41 ± 2.08 1.69 ± 0.08	29.0
Pb	total WSC	25.74 ± 1.96 2.98 ± 0.16	37.66 ± 2.39 3.42 ± 0.25	25.35 ± 1.30 1.01 ± 0.07	19.52 ± 1.24 1.24 ± 0.05	27.0
Cr	total WSC	97.80 ± 7.93 4.27 ± 0.32	115.41 ± 8.60 3.33 ± 0.25	89.67 ± 7.13 1.12 ± 0.06	$106.33 \pm 8.28 \\ 0.98 \pm 0.04$	59.5
V	total WSC	112.62 ± 9.28 4.13 ± 0.22	87.64 ± 6.03 2.18 ± 0.11	89.25 ± 6.58 2.22 ± 0.13	91.33 ± 7.07 1.59 ± 0.08	129.0
Sr	total WSC	166.24 ± 10.61 8.96 ± 0.62	134.80 ± 9.92 6.63 ± 0.39	128.71 ± 8.03 6.65 ± 0.48	132.83 ± 10.20 5.03 ± 0.31	175.0

^{*}WSC – element concentrations in the soil water-soluble components; the values are the means (n = 6), with standard deviations

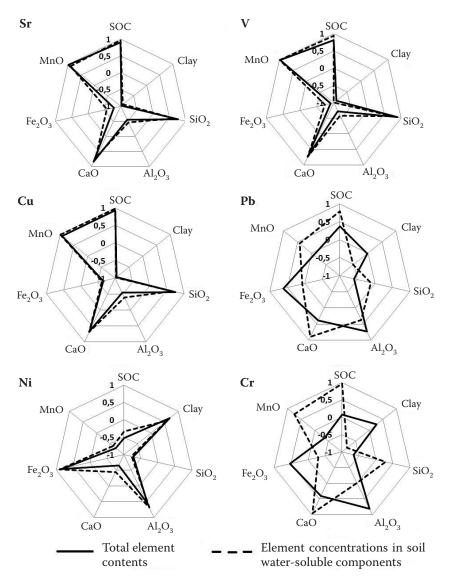


Figure 3. Correlation coefficients between the contents of the trace elements and the chemical and physical properties of the soils

vertical distribution of the Sr and V ions in the soils. This is partially evidenced by the additional input of the Sr and V ions in the studied soils, which might be a result of previous anthropogenic emissions, such as the decomposition of household waste.

Copper and lead. The mean values of the total Cu and Pb ions were similar in the studied soils and in the global surface soils (Table 2). The deeper profiles showed a relatively distinct peak for the total Cu ion content in the Ap and a peak for the total Pb ion content in the Bt horizon. The highest concentrations of the Cu and Pb ions bound to the WSC were found in the upper soil horizon. In general, the Pb ions showed the highest mobilisation after the water extraction with a mean percentage of 7.75% of the total Pb ion content.

The mean percentage of the Cu ions bound to the WSC accounted for 6.99% of the total Cu content.

The compounds enriched by Mn ions and the SOC were the soil factors that best explained the distribution and accumulation of the Cu ions (Table S2 in ESM, Figure 3). The $C_{\rm HA1}$, $C_{\rm HA3}$, $C_{\rm FA1a}$, $C_{\rm FA1}$, and $C_{\rm FA3}$ fractions were most important for the Cu (Table S3 in ESM, Figure 4). Likewise, significant correlations were found between Si and Ca and Cu ion contents. The soil compounds enriched by the Al and Fe ions affected total Pb ion content. The Pb ions bound to the WSC were only associated with the compounds enriched by the Ca ions and the SOC. The concentration of the Pb ions bound to the WSC was largely associated with humin and with $C_{\rm HA2}$, $C_{\rm fA2}$ (Figure 4).

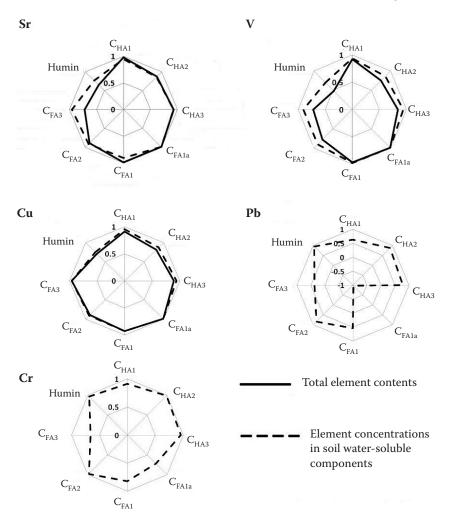


Figure 4. Correlation coefficients between the contents of the selected trace elements and the concentrations of the soil organic carbon fractions

The ability of the soil compounds enriched by the Al and Fe ions that bonded with the Pb ions in stable forms may be explained by the formation of innersphere complexes with a stronger binding (Caporale & Violante 2016). In the studied soils, the relationships between the Pb and Ca ions and the SOC shows that Pb ions are predominantly retained by exchange reactions and were effectively removed by the water solution as a result of cation exchange with the Ca²⁺ and with the ligand exchange sites of the SOC. These results are in good agreement with prior studies reporting a formation of soluble Pb complexes with the organic matter in soils with an increased organic matter content (Silvetti et al. 2014). The commonly accepted theory of the formation of soluble Pb complexes with low-molecular weight soil organic compounds was not confirmed in this study because a significant association between the Pb ions and all the studied fulvic acid fractions was not observed.

The clear accumulation of the Cu ions in the topsoil should be considered as evidence of past contamination by household waste associated with the corrosion of the Cu-containing materials. The relationship between Cu ion concentration and the soil properties indicates that the interaction of the Cu ions with the soil compounds enriched by the Si and Ca ions - mainly occurs as an inner sphere complexation with the formation of strong chemical bonds between these compounds and less so as an outer sphere complexation, which prevents the direct sorption of the Cu ions to compounds enriched by the Si and Ca ions by the water molecules. The association of the WS fraction of the Cu ions bound to the WSC with the soil compounds enriched by the Mn ions evidence the predominance of the outer sphere complexation. Previous studies have demonstrated that organic matter is a key factor in predicting the behaviour of the Cu in the soil in the

way that increasing the soil organic matter contents decrease the mobility compounds containing the Cu ions (Ruqia et al. 2015). Our results showed that Cu had a strong affinity with the SOC (Figure 4). In our case, all the SOC fractions were capable of bonding with the Cu ions in both the stable and unstable complexes.

Nickel. The mean total Ni ion concentration was 1.21 times greater than the global background. The highest content of the Ni ions was found in the middle part of the soil profiles (Table 2). The concentrations of the Ni ions bound to the WSC varied between 5.74 and 6.99% of the total Ni ion content.

In general, the percentage of the Ni ions bound to the WSC in the studied soils was higher when compared to the of the Ni content available to the plants in the contaminated soils. For example, Mehes-Smith et al. (2013) indicate that the level of bioavailable Ni ions was only 3% of the total element content in the soils from a mining region in Canada. A similar Ni behaviour was observed in soils from a greenhouse in Turkey, where the total Ni was the most threatening metal, but the mobility of the compounds containing Ni ions was extremely low (Topcuoglu 2016). This is likely partly attributable to the declining mobility of the compounds containing Ni by the adsorption of the Ni ions onto the ligand exchange sites of the humic substances and the binding to solid organic matter in these soils. In the studied soil, the Ni ion content showed a negative correlation with the SOC (Table S2 in ESM).

Significant correlations were observed between contents of the Ni ions and the soil compounds enriched by the Fe ions (Table S2 in ESM, Figure 3). Positive correlations were observed between the total Ni ion content and the clay contents, while the concentration of the Ni ions bound to the WSC was largely dependent on the Al ion content. This suggests the formation of mainly labile complexes of Ni ions with colloids of Al, which were formed via the weathering of primary minerals (Kabata-Pendias 2011). Nickel associated with clay represented less available for remobilisation form of element.

Chromium. The mean level of the total Cr ion content was 1.71 times higher than the global background value (Table 2). The highest levels were found in the middle and lower soil horizons. The mean concentration of the Cr ions bound to the WSC was 2.36% of the total Cr ion content, with the highest concentration in the Ap (4.36% of total Cr ion content).

The total Cr ion content indicated a great affinity for compounds enriched by Al ions, which re-

tain Cr ions in stable unavailable forms (Table S2 in ESM, Figure 3). The combination of the SOC and soil compounds enriched by Ca and Mn ions is best explained the variability of the Cr ions in the WSC. The concentration of the Cr ions in the WSC mostly depended on the humic acid concentrations, the Ca-bound fractions of the fulvic acids, and the humin (Table S3 in the ESM, Figure 4).

The enrichment of the studied soils with the Cr ions throughout all the soil horizons was direct evidence of a past contamination. This is supported by the increased amounts of Cr-containing compounds both in industrial and municipal wastes (Bavaresko et al. 2017).

The affinity of the Cr ions to the SOC and soil compounds enriched by the Mn ions has a significant ecological aspect. Manganese oxides and hydroxides have high redox activities and can oxidise significant amounts of Cr³⁺, which has a relatively low toxicity and mobility, to Cr5+, which is highly toxic and mobile (Leita et al. 2009). Studies in soils with different organic matter contents have shown that organic compounds promote the dissolution of easily reducible Mn oxides and form stable complexes with Cr³⁺ (Bavaresko et al. 2017). Our results point to the formation of unstable Cr ion complexes with the SOC in the studied soil, most likely due to the electrostatic interaction of the Cr ions with the negatively charged functional groups of the organic matter. The speciation of the Cr ions with the SOC suggests that the distribution of the Cr ions is mainly controlled by the fractions of the SOC with a higher molecular weight and by the extent of the polymerisation.

CONCLUSION

The addition of green manure over 13 years to contaminated soils by household waste with the removed upper part of the soil profiles increased the SOC content to a level that corresponded to the mean values of the SOC for the undisturbed soils of the studied region. The SOC of the examined soils was characterised by the active stabilisation by the Ca, clay minerals, and stable Fe/Al oxyhydrates, but by a low degree of humification. The fractional composition of the SOC showed that high-turnover of fulvic acids were the dominant extractable fraction of the SOC in the soil.

Despite the removal of the contaminated upper part of the soil profiles, the studied soils continued to have

increased concentrations of Cr and Ni ions compared to the global contents. The Sr, V and Cu ions, as well as the Pb and Cr ions bound to the water-soluble components of soils were strongly positively related to the SOC contents and the different soil compounds enriched by the Si, Ca, and Mn ions. Significant differences between the associations of these elements with the humic acids or with the fulvic acids were not observed. Surprisingly, despite the presence of an organic-rich topsoil layer, Ni ions occur mainly in bound inorganic forms. The results of this study indicate that only small portions of the total Cr ion content is available to the plants. The percentage concentrations of the Cu and Pb ions bound to the water-soluble components of the soils pointed to the more easily desorption of the ions of these elements into the soil solution. The low degree of SOC humification may be one of the main reasons for the high concentrations of these element ions bound to the water-soluble components in the studied soils. The percentage of the Ni ions bound to the water-soluble components of the soil fraction was extremely high.

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REFERENCES

- Bavaresco J., Fink J.R., Rodrigues M.L.K., Gianello C., Barron V., Torrent J. (2017): Chromium adsorption in different mineralogical fractions from Subtropical Soils. Pedosphere, 27: 106–111.
- Caporale A.G., Violante A. (2016): Chemical processes affecting the mobility of heavy metals and metalloids in soil environments. Current Pollution Reports, 2: 15–27.
- Kabata-Pendias A. (2011): Trace Elements in Soils and Plants. 4rd Ed. Boca Raton, CRC Press.
- Leita L., Margon A., Pastrello A., Arcon I., Contin M., Mosetti D. (2009): Soil humic acids may favour the persistence of hexavalent chromium in soil. Environmental Pollution, 157: 1862–1866.
- Mehes-Smith M., Nkongolo K.K., Narendrula R., Cholewa E. (2013): Mobility of heavy metals in plants and soil: a case study from a mining region in Canada. American Journal of Environmental Science, 9: 483–493.

- Minkina T., Pinskii D., Zamulina I., Nevidomskaya D., Gusler C., Mandzhieva S., Bauer T., Morozov I., Sushkova S., Kizilkaya R. (2018): Chemical contamination in upper horizon of Haplic Chermozem as a transformation factor of its physicochemical properties. Journal of Soils and Sediments, 18: 2418–2430.
- Pansu M., Gautheyrou J. (2006): Handbook of Soil Analysis Mineralogical, Organic and Inorganic Methods. Heidelberg, Springer-Verlag, Berlin.
- Purtova L.N., Kostenkov N.M. (2009): Organic Carbon Content and Energy Reserves in Soils of Natural and Agrogenic Landscapes of the South of the Russian Far East. Vladivostok, Dal'nauka. (in Russian)
- Ruqia N., Khan M., Masab M., Ur Rehman H., Ur Rauf N., Shahab S., Ameer N., Sajed M., Ullah M., Rafeeq M., Shaheen Z. (2015): Accumulation of heavy metals (Ni, Cu, Cd, Cr, Pb, Zn, Fe) in the soil, water and plants and analysis of physico-chemical parameters of soil and water collected from Tanda Dam Kohat. International Journal of Pharmaceutical Science and Research, 7: 89–97.
- Silvetti M., Castaldi P., Holm P.E., Deiana S., Lombi E. (2014): Leachability bioaccessibility and plant availability of trace elements in contaminated soils treated with industrial by-products and subjected to oxidative/reductive conditions. Geoderma, 214–215: 204–212.
- Timofeeva Ya.O., Kosheleva Yu.A., Semal V.A., Burdukovskii M.L. (2018): Origin, baseline contents, and vertical distribution of selected trace lithophile elements in soils from nature reserves, Russian Far East. Journal of Soils and Sediments, 18: 968–982.
- Topcuoglu B. (2016): Heavy metal mobility and bioavailability on soil pollution and environmental risks in greenhouse areas. International Journal of Advances in Agricultural & Environmental Engineering, 3: 2349–1531.
- Vorob'eva L.A. (2006): Theory and Practice of the Chemical Analysis of Soils. Moscow, GEOS. (in Russian)
- Wiszniewska A., Hanus-Fajerrska E., Muszynska E., Ciarkowska K. (2016): Natural organic amendments for improved phytoremediation of polluted soils: a review of recent progress. Pedosphere, 26: 1–12.
- World Reference Base for Soil Resources (2006): A Framework for International Classification, Correlation and Communication. International World Soil Resources Reports No. 103. Rome, FAO.

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