

Comparison of chromium mobility at naturally enriched and anthropogenically polluted sites: A column leaching experiment

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Citation: Dajčl J., Tejnecký V., Němeček K., Borůvka L., Drahota P., Drábek O. (2022): Comparison of chromium mobility at naturally enriched and anthropogenically polluted sites: A column leaching experiment. *Soil & Water Res.*, 17: 100–112.

Abstract: This study aims to compare the chromium (Cr) mobility in two soils with different Cr sources. The first one is an anthropogenically contaminated soil from an area of a piston ring production factory, and the second one is a serpentine soil with a naturally increased Cr level from the National Nature Reserve Mohelno serpentine steppe in the Czech Republic. To assess the influence of naturally occurring environmental factors on the Cr mobility, two sets of column leaching experiments were constructed, namely an acidified water treatment (AW) and a simulated root exudate treatment (SRE). It was found that the anthropogenically contaminated soil leached out many times more Cr for both (the AW and SRE) treatments in comparison with the serpentine soil. Generally, all the samples showed enhanced leaching from the bottom layer, respectively the horizon, for both treatments. Only the anthropogenic soil showed some differences in the bottom layer, which was more susceptible to the AW treatment than to the SRE one. These findings show the high dependence of the leachability of Cr on the Cr content origin. It has been proven that naturally enriched sites where elevated levels of Cr originate from the bedrock are more resistant to Cr leaching than anthropogenically contaminated soils. Feasible causes of these differences are discussed in this study.

Keywords: anthropogenic contamination; BCR fractionation; leachability; risk elements; serpentine soils

Chromium (Cr) is a natural component of the Earth's crust (> 200 mg/kg), found in a variety of rock materials, especially ultramafic rocks and their derived soils (Mandal et al. 2011; Farkaš et al. 2013). The behaviour, toxicity and mobility of Cr strongly depends on its oxidation state, which, in the environment, occurs mostly as trivalent Cr(III), hexavalent Cr(VI), or as

elemental Cr(0) (Ščančar & Milačič 2014). Elemental Cr was discovered in 1797 by French chemist Louis Vauquelin in the mineral crocoite (PbCrO₄) in a Siberian gold mine (Nriagu & Nieboer 1988).

Sources of Cr in soils may originate from naturally Cr-enriched bedrock or from anthropogenic activity. Serpentine soils formed from ultramafic rocks or ser-

Supported by the European Structural and Investment Funds, Operational Programme Research Development and Education Project NutRisk Centre (No. CZ.02.1.01/0.0/0.0/16_019/0000845) and Internal Grant Agency of the Czech University of Life Sciences, FAPPZ, Prague SV21-8-21130.

<https://doi.org/10.17221/129/2021-SWR>

pentinite belong to the primary natural sources of Cr with typically elevated Cr concentrations exceeding 200 mg/kg and reaching up to 10 000 mg/kg. These soils have a typically high Mg and Fe content and Ni, Cd, Co, Cu, and Mn trace elements and significantly low levels of plant nutrients, such as Ca, K, N, P and S (Baumeister et al. 2015; Choppala et al. 2015). Elevated levels of Cr and Ni especially pose an environmental risk, as well as high concentrations of oxidised Mn forms, have significant potential for Cr(III) oxidation (Oze et al. 2007).

In case of anthropogenic activity, there are a number of Cr-containing pollution sources such as: metallurgical industry, production, fungicides, corrosion inhibitors, sewage treatment, electroplating, chemical manufacturing, wood treatment, cement production, etc. (EPA 1998; ATSDR 2012).

In an oxic environment, Cr exists as Cr(VI), while in an anoxic environment Cr(VI) is readily reduced to Cr(III) by ferrous oxides and ferric oxyhydroxides as ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$), goethite (FeOOH) and hematite (Fe_2O_3) due to their abundant occurrence and large surface area. Besides ferrous oxides, Cr(VI) can be naturally reduced to Cr(III) by various other reducing agents such as S^{2-} ions, organic matter, and by microbial communities (Banks et al. 2006; Cheng et al. 2011). The oxidation of Cr in the soil can be caused by low molecular mass organic acids (citric acid, gallic acid, etc.) and Mn(IV) oxides, the only known naturally occurring oxidants of Cr(III) to Cr(VI) (Nriagu & Nieboer 1988; Guha et al. 2001).

Due to the known toxic effects of Cr, especially Cr(VI), control measurements of the Cr levels in water, soil and food are performed. The national threshold values and international recommended values assume the total measured Cr to be Cr(VI). This is because Cr is known as being very unstable in its forms converting back and forth from one stage to another ($\text{Cr(III)} \leftrightarrow \text{Cr(VI)}$), which is strongly dependent on the environmental conditions. The maximum contaminant level goal for the total Cr in drinking-water set by EPA is 100 $\mu\text{g/L}$ (EPA 2017). The provisional guideline value for the total Cr concentration according to the WHO is 50 $\mu\text{g/L}$ (WHO 2008). This limit was also embraced by the European Union and the Czech Republic (Council Directive 98/83/EC 1998; Decree 252/2004 Coll.).

The aim of this work was to assess the contamination risk of water sources by Cr originating from anthropogenic activity, namely the metallurgical industry and production of piston rings, and Cr

from a naturally enriched serpentine soil. The hypothesis is that there are environmental risks related to changes in the fractionation and mobility of Cr in soils depending on the external conditions, which may enhance the Cr leaching from the soil, specifically by acidic precipitation and root exudates.

MATERIAL AND METHODS

Study area and sampling. The anthropogenically polluted soil used in this study was collected from a waste deposit, which belongs to a Czech manufacturer of piston rings. Due to the site's proximity to a local stream, it has been monitored for a long time due to the possible water contamination.

The sampling area is located 388 meters above sea level with an average total rainfall of 550 to 600 mm per year (CHMI 2020). The infiltration and permeability rate are up to 0.05 mm/min with a low water holding capacity (up to 100 L/m^3), the local soil is more prone to water erosion with a high risk of acidification (VUMOP 2019).

Naturally, any acidic rain water and root exudates are assumed to especially affect the leaching of elements (risk elements and nutrients) from the upper layers of the soil.

Samples from the anthropogenically polluted site were collected at two different spots (K1, K2, Figure 1) in two different depths (upper layer 0–15 cm; lower layer 15–30 cm). After preliminary analyses, a spot with an elevated Cr content was selected for the leaching experiment. Any spots with a relatively low Cr contamination (less than ~ 50 mg/kg) was discarded. The soil can be classified as Technosol (IUSS Working Group WRB 2015).

Naturally enriched soil samples were taken from the National Nature Reserve Mohelno serpentine steppe in Southern Moravia, near the village Mohelno, Czech Republic, where Cr is one of the components of the parent rock and mineral part of the derived soil (Chytrý 2012). The bedrock is predominantly a serpentinite one accompanied by coarse gabbro. Most of the soil in the area is a grainy light soil, weakly acidic, with a very high pseudo-total N content. In addition to Cr, high levels of Co and Ni have been measured in the soils due to the presence of these potentially toxic elements (PTEs) in the serpentinite (Fiala et al. 2017). The possible risk of transferring high Co, Cr and Ni concentrations into the above-ground plant biomass and, thus, into the food chain due to sheep and goat grazing in this area, lead to

an interest in studying this location (Veselý et al. 2011; Veselý 2014; Fiala et al. 2017).

Samples from the Mohelno serpentine steppe were collected from a forested site, with respect to the soil horizons (A, B, C), marked as SA, SB, SC. The sampling spots are at 49°6'0.206"N, 16°10'0.800"E, about 12 m above the surface of the Mohelno reservoir and about 40 m from the reservoir's dam. The average total rainfall is 450 to 550 mm per year (CHMI 2020). The infiltration and permeability rate are 0.15 to 0.20 mm/min with a water holding capacity of 100 to 160 L/m³ (VUMOP 2019).

The soil type is modal Cambisol, magnesian in variety, according to the Czech Taxonomic Classification System of Soils (Němeček & Kozák 2001), or a haplic magnesian Cambisol according to the World Reference Base of Soil Resources (IUSS Working Group WRB 2015). The soil profile is composed from an organic horizon O to 2 cm in depth (mixture of fermenta-

tion F and humified H horizons), an organo-mineral horizon Ah to 6 cm in depth, cambic brown horizon Bv from 6 to 17 cm in depth, and a weathered Cr soil horizon below 17 cm in depth. Both localities have the influence of forest stands and nearby water resources (stream, dam) in common.

To compare the Cr leachability with the anthropogenically contaminated soil, only its upper (0–15 cm) and lower (15–30 cm) layers, Ah (SA) and Bv (SB) horizons, were selected. In the laboratory, the samples were dried in an oven (~40 °C) to a constant weight and crushed and sieved through a 2 mm sieve.

Determination of soil properties. The active soil pH (pH_{H₂O}) was measured by preparing a 1 : 4 soil : liquid (w : v) ratio using deionised water, then the mixture was measured using a calibrated UB-5 pH meter (Denver Instrument, USA) after agitation for 5 min. The particle size distribution, the percentage share of the clay, silt, and sand fractions, were obtained by the hydrometer method according to Gee and Or (2002). The organic oxidisable carbon content (C_{ox}) was measured by a modified Tyurin's oxidimetric method according to the methodology by Pospíšil (1964). The exchangeable Mn, Fe, Al, Na, K, Mg and Ca cations were determined according to the Cools and De Vos method (2010) by adding 30 mL of 0.1 M BaCl₂ to 2.5 g of a soil sample, shaken for 2 h, and centrifuged at 3 000 rpm for 10 min; the cation exchange capacity (CEC) was calculated as the sum of the exchangeable cations, determined by means of inductively coupled plasma-optical emission spectroscopy (ICP-OES, Thermo Scientific iCAP 7 000, USA). Also, the amount of H⁺ was potentiometrically determined in the same extract (pH meter). The mineralogical analysis of the soil samples was performed by means of an X-ray diffraction (XRD) phase analysis (X'Pert Pro, PANalytical B.V., Almelo, the Netherlands) after agate ball mill grinding (Vibratory Micro Mill PULVERISETTE 0, Fritsch, Germany). The mineralogical analysis by means of XRD was also performed for the separated heavy fractions of the samples. Approximately 0.2 g of the sample was weighed and a 10 mL of a heavy liquid (sodium metatungstate, Na₆[H₂W₁₂O₄₀], density of 2.82 g per cm³, Acros Organics, Germany) were added, centrifuged at 9 000 rpm for 10 min, where the light fraction was first separated. The heavy fraction was filtered, washed by deionised water and ethanol. The clean samples of the heavy fraction were dried at 30 to 40 °C in an oven to a constant weight. The heavy fraction samples prepared by cutting and

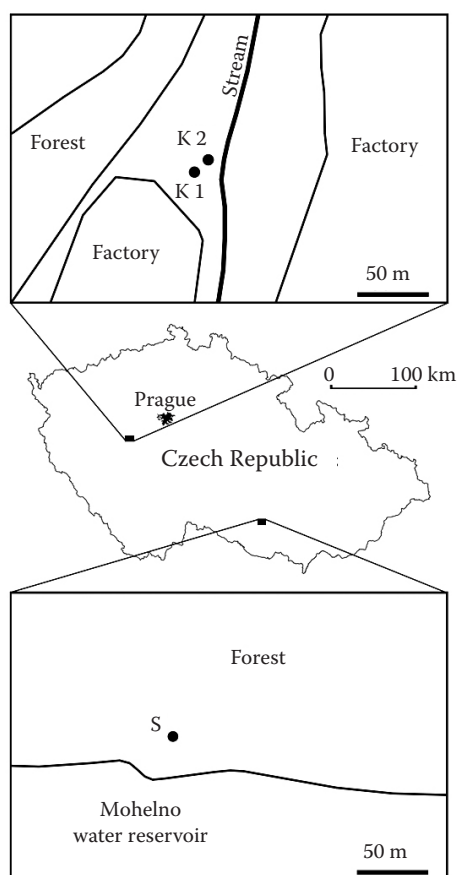


Figure 1. Anthropogenically polluted site (upper part), with two sampling spots (K1 and K2) and naturally enriched Mohelno serpentine steppe (bottom part) with sampling spot S; sampling area and the local water

<https://doi.org/10.17221/129/2021-SWR>

polishing were analysed in more detail by a scanning electron microscope (SEM) (TESCAN VEGA3XMU, TESCAN Ltd., Czech Republic) equipped with detectors of an energy-dispersive spectrometer (EDS) (Bruker QUANTAX 200, Bruker Nano GmbH, Germany) to assess the specific Cr-bearing minerals.

Analysis of potentially toxic elements in soils. The pseudo-total contents of the Cr and other elements were determined by means of *Aqua regia* extraction according to UNECE (2006). The solution was diluted 10 times with deionised water (conductivity 18.2 M Ω) and filtered through 0.45 μm nylon disc filters (Cronus, UK) prior to analysis. The extract was analysed for the PTE content by ICP-OES (Thermo Scientific iCAP 7000, USA). The analysis was performed in triplicate at least and procedural blanks were included. A three step Community Bureau of Reference (BCR) sequential extraction was performed according to a method described by Tokalioglu et al. (2003). The target metal forms were extracted from the soil samples in these stages: weakly bound metals (exchangeable) released into 0.11 mol/L of acetic acid, metals bound to Fe/Mn oxides (reducible) extracted using 0.1 mol/L of hydroxylammonium chloride, metals bound to organic matter and sulfides (oxidisable) liberated by oxidising the sample in 8.8 mol/L of hydrogen peroxide, followed by dissolution into 1.0 mol/L of ammonium acetate. The extracts were diluted and filtered as stated above. The PTE content in the extracts was also determined by ICP-OES. The detection limits of selected elements by means of ICP-OES were as follows (mg/L): 0.0386 (Al), 0.0079 (Ca), 0.0007 (Cr), 0.0060 (Cu),

0.0184 (Fe), 0.0934 (K), 0.0029 (Mg), 0.0001 (Mn), 0.0258 (Na), 0.0004 (Ni), 0.0067 (P), 0.0015 (Pb), 0.0121 (S), 0.0521 (Si), and 0.0060 (Zn).

The elemental composition of the parent rocks was assessed by means of X-ray fluorescence spectroscopy (XRF) (Delta Premium XPD 6000, OLYMPUS INNOV-X, USA) after agate ball mill grinding (Vibratory Micro Mill PULVERISETTE 0, Fritsch, Germany).

Leaching experiment. This study focuses on the potential leachability of Cr from the contaminated soil in relation to the simulated environmental mobilising agents, namely the acidified water and simulated root exudates. The influence of the acidified water and root exudate soil washing on the Cr mobility and fractionation was simulated in a laboratory column leaching experiment in order to assess its potential Cr transport in the studied localities or possible accumulation in local waters.

The acidified water was prepared as an acidified deionised water (DIW) solution (adjusted to pH 4.6 using HNO_3) (Ash et al. 2016). The simulated root exudates were mixed according to a modified method by Feng et al. (2005) from acetic acid (60.05 g/mol), lactic acid (90.08 g/mol), citric acid (192.13 g/mol), malic acid (134.09 g/mol) and formic acid (46.03 g per mol) in a ratio of 4 : 2 : 1 : 1 : 1 into a 0.001 M solution (average pH \sim 3.45) and two drops of toluene were added as a biocidal agent.

Into each column, 20 g of the sieved (< 2 mm) soil samples were weighed and placed on filter paper placed over a layer of glass marbles (Figure 2). Vertical glass columns (18 cm long, 3 cm in diameter) were

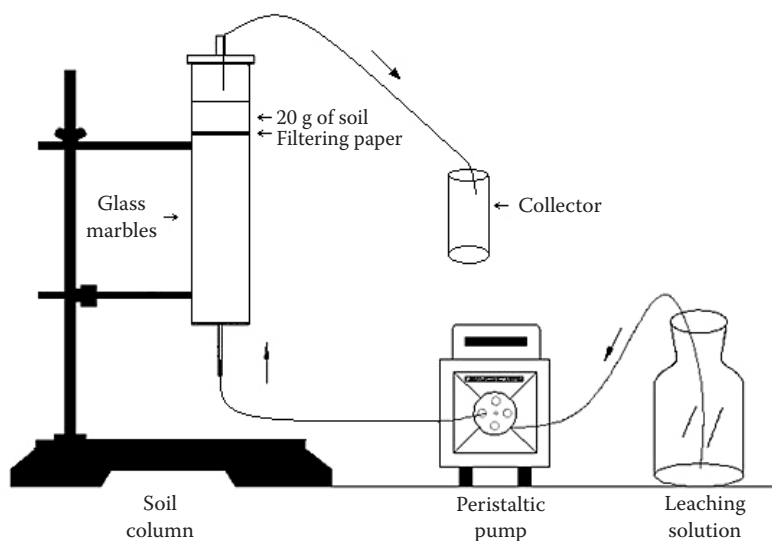


Figure 2. Column leaching experiment (picture adapted from Zhou et al. 2017)

used. Experimental solutions were pumped vertically upward through the columns; the solution mobility was provided by a peristaltic pump (Kouřil PCD 83.4S) set to flow at 50 mL per hour, giving an hourly soil:solution ratio of 2:5. The methodology of the leaching experiments was modified according to Ash et al. (2015). The leaching experiments ran continuously for 48 h. The leaching experiment settings simulated a hydrodynamic event of 40 mm precipitation, representing the average situation at the studied localities during rainfall. The leachates were collected after each hour of the first 12 h, and after 24 h and 48 h. The collected solutions were immediately measured for the pH and redox potential by a digital portable multi-meter (Multi 3620 IDS SET C 2, WTW Wissenschaftlich, Germany), filtered through nylon 0.45 mm syringe filters, and the target elements were determined using ICP-OES. The redox potential was recalculated according to the correction value $+207 U_{\text{Ref}}$ (mV) SenTix ORP 900 for temperature ($T = 25\text{ }^{\circ}\text{C}$). All the measurements were undertaken in four replications.

To estimate the levels of the Cr leached between 12th and 24th h and between the 24th and 48th h, the measured values were graphed and then a trendline was added using Statgraphics (Ver. 17). The corresponding equations were used to find the missing values. The data were used to create the cumulative graphs.

After the leaching experiment, the soil samples were dried in an oven ($\sim 40\text{ }^{\circ}\text{C}$) to a constant weight and the *Aqua regia* and BCR extractions and the XRF analysis were performed.

RESULTS AND DISCUSSION

Basic soil properties. All the soil samples were slightly acidic ($\text{pH}_{\text{H}_2\text{O}}$ ranges from 5.72 to 6.95),

which, in the case of serpentine soil, corresponds to the most common pH values of serpentine soils (Oze et al. 2004). The pH of the mineral horizon (B, respectively layer 15–30 cm K 1/2) is lower than the one for the overlaying organic horizon (A, respectively layer 0–15 cm K 1/1). The greatest CEC values occur in the A horizon of the serpentine soil and in the upper layer (0–15 cm) of sample K 1. The organic matter content in the serpentine soil reflects the particular soil horizons, with a significant accumulation of organic matter in the A horizon (3.47%). In the case of the anthropogenically polluted soil, no differences in the organic matter content between both layers were observed (Table 1). According to the World Reference Base for Soil Resources, serpentine samples (SA) with 9% clay, 53.5% silt and 37.5% sand belong to a silt texture class and the anthropogenic soil (K 1/1) with 1.6% clay, 19.3% silt and 79.1% sand belong to a loamy sand texture class. All the samples were classified as light soils.

All the horizons, respectively layers, at the examined localities contain very high amount of Cr. The anthropogenically contaminated soil upper (K 1/1) and lower (K 1/2) layers contain 2 767 mg/kg (XRF), 846 mg/kg (*Aqua regia*) and 3 967 mg/kg (XRF), 1 351 mg/kg (*Aqua regia*) of Cr, respectively. The serpentine soil, A and B horizons contain 637 mg/kg (XRF), 59.6 mg/kg (*Aqua regia*) and 791 mg/kg (XRF), 94.4 mg/kg (*Aqua regia*), respectively.

The mean European threshold, lower and higher guideline values (100, 200 and 300 mg/kg) are defined on the basis of Cr ecological risks by the Ministry of the Environment, Finland (2007). The preventive limits of Cr in soils for agricultural production are 90 mg/kg for normal loamy to clayey soils and 55 mg/kg for light sandy soils by means of *Aqua Regia* extraction (Czech Ministry of En-

Table 1. Basic soil properties: active pH ($\text{pH}_{\text{H}_2\text{O}}$), pH of 0.1 M BaCl_2 extracts ($\text{pH}_{\text{BaCl}_2}$), cation exchange capacity (CEC), organic oxidisable carbon content (C_{ox}) and humus content

		$\text{pH}_{\text{H}_2\text{O}}$	$\text{pH}_{\text{BaCl}_2}$	CEC (meq(+)/kg)	C_{ox}	Humus (%)
Serpentine soil	SA	7.0	4.5 ± 0.05	196 ± 6.79	3.5 ± 0.06	6.0 ± 0.1
	SB	6.7	4.3 ± 0.12	138 ± 1.66	1.4 ± 0.03	2.5 ± 0.6
	SC	6.9	4.8 ± 0.15	189 ± 0.15	0.6 ± 0.02	1.1 ± 0.03
Anthropogenically polluted soil	K 1/1 (0–15 cm)	6.0	4.4 ± 0.04	208 ± 4.87	6.0 ± 0.01	10.3 ± 0.01
	K 1/2 (> 15 cm)	5.7	4.1	139 ± 4.79	6.0 ± 0.01	3.0 ± 0.01

SA – serpentine soil (horizon A); SB – serpentine soil (horizon B); SC – serpentine soil (horizon C); K 1/1, K1/2 – anthropogenically polluted sites; 3 replicates, mean and standard deviation (unlisted values of standard deviation are less than 0.005)

<https://doi.org/10.17221/129/2021-SWR>

vironment, Decree No. 153/2016 Coll.). All the studied samples significantly exceed the Czech preventive values.

Mineralogy of samples. The dominant component of the SA and SB samples is quartz, followed by major components of plagioclase, K-feldspar, muscovite/illite, and minor phases of amphibole, vermiculite, kaolinite and pyroxene. The SC sample showed pyroxene as the dominant component, olivine, antigorite/lizardite and chlorite as the major components, and had minor phases of amphibole and K-feldspar. The distribution of minerals corresponds to the weathering of the main original minerals. The dominant part of the anthropogenically polluted soil was quartz, the major component was mullite, with minor phases of maghemite/magnesioferrite and calcite.

The dominant component according to the X-ray diffraction analysis of the heavy fraction of SA and SB was also quartz, followed by the major components of enstatite and albite and minor phases of cosmochlor, muscovite, chlorite and amphibole. A questionable component of SA was goethite (Table 2). The mineralogy of the heavy fraction of the anthropogenically contaminated soil revealed an amorphous phase, mullite and quartz as the dominant components, major phase of magnetite, minor phases of rutile and plagioclase, and the questionable presence of crocoite (PbCrO_4) (Table 2).

The heavy fraction analysis by SEM-EDS confirmed crocoite as the main Cr-bearing mineral in the anthropogenically contaminated soil (Figure 3). In the serpentine soil, chromian spinels which are a petrogenetic indicator in basic and ultrabasic systems created from MgAl_2O_4 spinel and Cr-chromite were found as the main Cr-bearing mineral (Irvine 1967; Suzuki et al. 2007) (Figure 3).

Mineral Cr-chromite (trivalent Cr; $\text{Fe}(\text{Fe},\text{Cr})_2\text{O}_4$) and Cr-magnetite (hexavalent Cr; $\text{Fe}(\text{Fe},\text{Cr})_2\text{O}_4$) phases (Becquer et al. 2003; Baumeister et al. 2015),

are typical in serpentines. Phyllosilicates (serpentines and chlorites) and the most common clays, such as smectites and vermiculites, are also common mineral phases in serpentine soils (Oze et al. 2004).

Column leaching experiment results. The results suggest that the serpentine soil is significantly less prone to Cr leaching than the anthropogenic material. All the samples showed enhanced leaching from the bottom layer, respectively the horizon, after both treatments (acidified water – AW, simulated root exudate – SRE). The upper layer of the anthropogenically contaminated soil (K 1/1) leached out 21 times more Cr (4.20 mg/kg Cr/48 h) during the leaching experiment with the AW treatment than the serpentine A (SA) horizon (0.20 mg/kg Cr/48 h) and 12.6 times more Cr (5.02 mg/kg Cr/48 h) during the leaching experiment with the SRE treatment than the SA horizon (0.40 mg/kg Cr/48 h).

Also, the lower layer of the anthropogenically contaminated soil (K 1/2) released many times more Cr than the serpentine B horizon (SB). Sample K 1/2 released 46.4 times more Cr (16.7 mg/kg Cr/48 h) during the leaching experiment with the AW treatment than the SB sample (0.36 mg/kg Cr/48 h) and 25.3 times more Cr (12.6 mg/kg Cr/48 h) during the leaching experiment with the SRE treatment than the SB sample (0.50 mg/kg Cr/48 h).

These differences should be caused mainly by the geogenic origin of the serpentine soil, the age and advanced degree of weathering, when the primary and secondary minerals are relatively stable in a natural environment. This makes the serpentine soil much less sensitive to leaching than the anthropogenic material. The present Cr occurs mostly in its trivalent Cr(III) state, strongly bound in Cr-spinels. Instead, Cr-bearing silicates including clay minerals and Cr-chlorite are more involved in the potential Cr transfer into the soil solution, vegetation and waters (Baumeister et al.

Table 2. Mineralogy of the heavy fraction according to the X-ray diffraction analysis

SA	SB	SC	K 1/1	K 1/2
Quartz	quartz	lizardite	amorphous phase, mullite, quartz	amorphous phase, mullite, quartz
Enstatite, albite	enstatite, albite	quartz, enstatite, chlorite	magnetite	magnetite
Cosmochlor, muscovite, chlorite, amphibole	amphibole, cosmochlor, chlorite	magnetite, forsterite, amphibole	rutile, plagioclase	rutile, plagioclase
Goethite		cosmochlor	crocoite	crocoite

SA – serpentine soil (horizon A); SB – serpentine soil (horizon B); SC – serpentine soil (horizon C); K 1/1, K1/2 – anthropogenically polluted sites

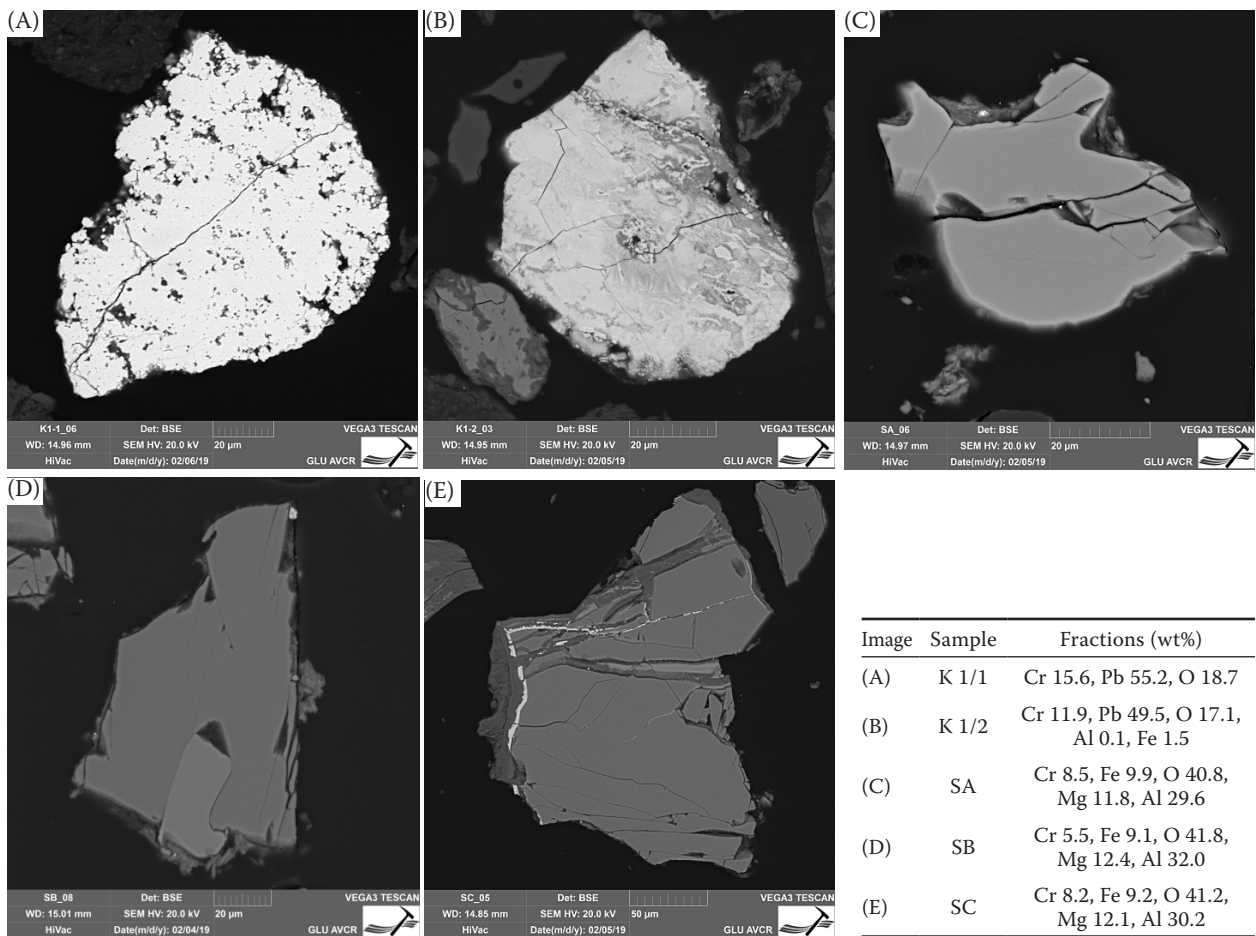


Figure 3. Scanning electron microscope (SEM) images of the heavy mineral fractions separated from the anthropogenically contaminated soil upper (K 1/1) and lower layer (K 1/2) and the serpentine soil horizons A, B, C (SA, SB, SC)

2015; Jeřábková et. al. 2018). However, high-valent Mn-oxides, which can be released from the present chlorites, pose a risk of Cr(III) oxidation and subsequently Cr(VI) leaching from the Cr-spinels into serpentine soil solutions (Oze et al. 2004).

The serpentine soil showed higher susceptibility to the SRE treatment in both the A and B horizons compared to the SWR treatment. The higher Cr content in the B horizon corresponds to a slightly higher Cr leaching from this horizon by both leach-

ing solutions (Table 3). These findings correspond to the experiment of Andjelković et al. (2012), who observed that more Cr was leached during treatment with acidic rainwater (2.01%) than with non-acidified rainwater (1.44%).

The anthropogenically contaminated soil showed a slightly different trend. Also, the lower layer that was richer in Cr leached out more Cr than the upper layer. However, the lower layer showed higher susceptibility to the AW treatment (Table 3).

Table 3. Cumulative values of the leached Cr mg/kg/48 h, 2 replicates, mean

Solution	Sample	Cr	Solution	Sample	Cr
AW	SA	0.20	SRE	SA	0.40
AW	SB	0.36	SRE	SB	0.50
AW	K 1/1	4.20	SRE	K 1/1	5.02
AW	K 1/2	16.7	SRE	K 1/2	12.6

AW – acidified water; SRE – simulated root exudates treatments; SA – serpentine soil (horizon A); SB – serpentine soil (horizon B); K 1/1, K 1/2 – anthropogenically polluted sites

<https://doi.org/10.17221/129/2021-SWR>

These cumulative values from the 48-hour leaching experiment (Table 3) are not negligible, especially in regards to a long-term view. Pei et al. (2008) observed the leaching of Cr from an AOD slag (Argon Oxygen Decarburized slag, a by-product of the stainless-steel refining process) in their 20-year experiment where the total Cr concentrations reached up to 137 mg/L. These values represent a threat, especially in the case of continuously enhanced Cr levels during the leaching experiment (K 1/2) (Table 4) (Liu et al. 2016).

Under the SRE treatment, the pH of the leachates from the serpentine horizons (SA and SB) decreased during the experiment from 6.77 and 6.12 at the initial time to 4.72 and 4.26 at the end point, respectively. The changes after the AW treatment were negligible. This may be attributed to the fast washout of the buffer ions from the sorption complex during the experiment. For Ca and K, their independence on the pH and high solubility in an aqueous environment are typical. On the other hand, Mg, as well as Mn and Ni are cations decreasing their leachability with an increasing pH due to the adsorption on aluminosilicate and Fe-oxide phases and the precipitation of hydroxide and carbonates (Zandi & Russell 2006).

An opposite trend was shown in the anthropogenically contaminated soil (K 1/1; K 1/2) treated with AW, when the pH slightly increased during the whole experiment from an initial 6.41 to 6.61 (K 1/1) at the end point, and more markedly from 5.99 to 6.42 in the case of the bottom layer (K 1/2). This may be caused by the dissolution of the present calcite and the related Ca-minerals and continuous washing out of other buffer ions from the sorption complex during the experiment, as the highest values in the leachates had major elements such as Ca, K

and Mg (Table 4). A similar increase in the pH due to the dissolution of the Ca-silicate mineral larnite during the Cr leaching experiment was observed by Liu et al. (2016), who tested the effect of ultra-pure water of pH 7.00 as a neutral leachant on an argon oxygen decarburisation slag. Also, Oravec and Eštoková (2017) described the enhanced pH of leachates due to the dissolution of the alkali compounds from Zeolite- and Slag-based concrete samples, treated with distilled water (pH 6.54) and rain water (pH 6.24).

Generally, all the samples except the bottom layer of the anthropogenic soil showed positive correlations between the leached Cr and most of the other elements after the AW and SRE treatments. On the contrary, the bottom layer of the anthropogenic soil showed a large number of negatively correlated elements with the leached Cr after both treatments, as K 1/2 was the only sample which kept the Cr concentration in the leachates during the leaching experiment increasing.

Both the upper layers of the examined soils (SA and K 1/1) after the SRE treatment showed a negative correlation of the leached Al with Cr, in the case of the anthropogenic soil, also Fe and Cu with Cr, which indicates that these elements (Al, Fe, Cu) increased their solubility during the leaching experiment.

The only positive correlations of the leached Cr in the bottom layer of the anthropogenic soil were revealed as Ca after the AW treatment and Al and Fe after the SRE treatment. These findings correspond with the chromium binding on the present Fe-, Mn- and Al- oxides, which are susceptible to dissolution by organic acids (Lee et al. 2007; Bolanos et al. 2018), and also correspond with the changes in the BCR fractions as listed below (Tables 5 and 6).

Table 4. Cumulative values of the other elements, mg/kg/12 h, 4 replicates, mean

	Al	Ca	Cu	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Si	Zn
SA AW	1.68	80.5	0.29	2.50	64.6	29.1	0.15	28.6	0.58	5.63	0.04	9.18	23.8	0.15
SB AW	8.15	30.8	0.20	12.1	18.0	39.3	0.22	54.5	2.02	2.90	0.02	13.1	66.2	0.12
SA SRE	3.47	442	0.16	12.2	93.6	157	2.50	30.0	1.44	4.38	0.04	9.63	34.6	0.33
SB SRE	13.4	171	0.19	27.1	38.2	262	1.83	66.0	6.68	2.87	0.06	17.7	61.3	0.31
K 1/1 AW	6.88	279	0.67	2.66	285	40.2	1.83	18.2	0.50	3.74	0.71	62.7	66.3	0.80
K 1/2 AW	8.10	132	0.37	1.70	193	23.4	1.60	16.1	0.55	1.75	0.77	63.7	59.5	0.52
K 1/1 SRE	73.4	680	1.08	33.7	300	97.7	4.14	16.7	0.63	4.52	0.98	74.2	80.5	1.68
K 1/2 SRE	92.5	472	0.84	40.1	307	84.0	4.99	16.8	0.88	2.33	0.96	83.7	79.3	1.17

AW – acidified water; SRE – simulated root exudates treatments; SA – serpentine soil (horizon A); SB – serpentine soil (horizon B); K 1/1, K 1/2 – anthropogenically polluted sites

The anthropogenic soil treated with AW revealed the dependence of the Cr concentration on the pH, while the upper horizon showed a negative correlation with the pH and the bottom horizon showed a positive correlation with the pH. On the other hand, the serpentine soil showed a pH dependence on Cr after the SRE treatment; a positive correlation was found in both horizons, and also, in the case of horizon A, after the AW treatment. This may be caused by leaching of basic cations (Ca^{2+} , Mg^{2+} , K^+ etc.) enhancing the pH of the leachates.

Elemental composition and fractionation before and after column leaching experiments. The exchangeable fraction of the Cr in the serpentine soil, compared to the *Aqua regia* data, doubled in the A horizon (1.95 times higher) and B horizon (1.8 times higher) after the SRE leaching experiment, from 7.26% in the original sample to 14.2% and from 3.55% to 6.3%, respectively (Table 5).

Horizon A did not show any other significant changes in dependence on the fraction changes or the AW treatment. A significant increase occurred in the reducible fraction of horizon B in both cases after the SRE (from 16.9 to 27%) and AW (from 16.9 to 24.1%) leaching experiments. The serpentine Cr bound on oxidisable fraction of the B horizon significantly decreased after both leaching experi-

ments from 47.2% to 31.8% (SRE) and from 47.2% to 30.9% (AW) (Table 5).

In general, not more than 14.2% of Cr is bound in an exchangeable fraction. A higher share of Cr is bound on the reducible fraction of the Fe- and Mn- metal oxides (from 16.9% in the original B horizon to 27% in the B horizon after the SRE leaching). The main part of the extractable Cr is bound on the oxidisable fraction ranging from 30.9% (B horizon after the AW leaching) to 47.2% (original B horizon) (Table 5).

This corresponds to a study of the leaching behaviour of Cr derived from chromium ore processing residue undertaken by Weng et al. (1994). They used batch leaching experiments with simulated rainwater (pH 2–12), from where approximately 1% of the total Cr (26 mg/g) was easily leachable. The major Cr form in their soil was chromite ($\text{Fe}(\text{Fe},\text{Cr})_2\text{O}_4$) (Weng et al. 1994).

The anthropogenically contaminated soil showed a moderate decrease in the Cr bound on the exchangeable (from 1.81% to 1.73% and 1.32%), reducible (from 1.56% to 1.36% and 1.07%) and oxidisable fraction (from 55.8% to 50.0% and 40.4%) in the upper layer (0–15 cm depth, K 1/1) after both the SRE and AW leaching experiments, respectively. Also, the lower layer (15–30 cm depth, K 1/2) showed a slightly decreased content of Cr bound on the reducible (from

Table 5. BCR fractionation of the Cr in the serpentine soil, 4 replicates, mean, standard deviation (SD)

Sample	A	SD	B	SD	C	SD	Σ BCR	AQ	SD	XRF	SD
BCR fractionation of Cr (mg/kg) serpentine soil											
Original SA	4.33	0.16	11.9	0.18	23.7	0.95	39.9	59.6	0.46	674	3.67
Original SB	3.35	0.07	16.0	0.43	44.6	0.80	63.9	94.4	1.92	791	0.50
SRE SA	8.72	0.94	12.6	0.88	26.4	0.28	47.7	61.5	1.07	721	19.4
SRE SB	6.00	0.64	25.7	0.04	30.2	0.23	61.9	95.3	0.81	793	53.1
AW SA	3.68	0.00	12.6	0.11	24.1	0.29	40.4	59.9	0.15	714	13.8
AW SB	2.98	0.03	24.0	0.09	30.9	0.28	57.9	99.9	1.41	763	11.6
Sample	A	B	C	AQ tot	A	B	C	XRF tot			
BCR fractionation of Cr (%)											
Original SA	7.26	19.9	39.7	100	0.64	1.76	3.51	100			
Original SB	3.55	16.9	47.2	100	0.42	2.02	5.64	100			
SRE SA	14.2	20.5	42.9	100	1.21	1.74	3.66	100			
SRE SB	6.30	27.0	31.8	100	0.76	3.24	3.81	100			
AW SA	6.15	21.1	40.3	100	0.52	1.77	3.38	100			
AW SB	2.98	24.1	30.9	100	0.39	3.15	4.05	100			

BCR – Community Bureau of Reference; A – BCR exchangeable fraction; B – BCR reducible fraction; C – BCR oxidisable fraction; SRE – simulated root exudates; AW – acidified water; SA – serpentine soil (horizon A); SB – serpentine soil (horizon B); Σ BCR – sum of the BCR fractions; AQ tot – share of the BCR fractions calculated from the pseudo-total content (*Aqua regia*); XRF tot – share of the BCR fractions calculated from the total content (XRF)

<https://doi.org/10.17221/129/2021-SWR>

Table 6. BCR fractionation of the Cr in the anthropogenically contaminated soil, 4 replicates, mean, standard deviation (SD)

Sample	A	SD	B	SD	C	SD	Σ BCR	AQ	SD	XRF	SD
BCR fractionation of Cr (mg/kg) anthropogenically contaminated soil											
Original K 1/1	15.3	3.63	13.2	1.63	472	7.94	500	846	68.4	2767	204
Original K 1/2	27.7	1.00	40.8	1.13	727	39.4	796	1351	52.7	3967	258
SRE K 1/1	15.5	1.26	12.2	0.49	447	8.09	475	894	14.6	2526	94.5
SRE K 1/2	30.1	1.60	38.7	3.88	693	14.5	762	1497	131	3562	87.6
AW K 1/1	13.7	0.16	11.2	0.31	421	7.13	446	1043	53.9	2331	37.3
AW K 1/2	25.6	0.49	38.4	0.66	731	16.6	795	1553	50.0	3409	78.6
Sample	A	B	C	AQ tot	A	B	C	XRF tot			
BCR fractionation of Cr (%)											
Original K 1/1	1.81	1.56	55.8	100	0.55	0.48	17.1	100			
Original K 1/2	2.05	3.02	53.8	100	0.70	1.03	18.3	100			
SRE K 1/1	1.73	1.36	50.0	100	0.61	0.48	17.7	100			
SRE K 1/2	2.01	2.58	46.3	100	0.85	1.09	19.5	100			
AW K 1/1	1.32	1.07	40.4	100	0.59	0.48	18.1	100			
AW K 1/2	1.65	2.47	47.1	100	0.75	1.13	21.4	100			

BCR – Community Bureau of Reference; A – BCR exchangeable fraction; B – BCR reducible fraction; C – BCR oxidisable fraction; SRE – simulated root exudates; AW – acidified water; K 1/1 – an. contaminated soil upper layer 0 – 15 cm; K 1/2 – an. contaminated soil lower layer 15 – 30 cm; Σ BCR – sum of the BCR fractions; AQ tot – share of the BCR fractions calculated from the pseudo-total content (*Aqua regia*); XRF tot – share of the BCR fractions calculated from the total content (XRF)

3.02% to 2.58% and 2.47%) and oxidisable fraction (from 53.8% to 46.3% and 47.2%) after the SRE and AW leaching experiments, respectively (Table 6).

This corresponds to the results of Li et al. (2012). Their study showed that citric acid/sodium citrate soil washing decreased the content of the reducible and oxidisable fractions of Cr in the studied samples. The amount of the exchangeable fraction in their study significantly increased. Li et al. (2012) proved that the exchangeable fraction of Cr was released from all of the other fractions (reducible, oxidisable and residual) during washing, which was explained as the Cr being redistributed from difficult to assess by BCR extractants into easier for extraction after soil washing with the solutions (Li et al. 2012).

Moreover, the organic matter, which is part of the oxidisable fraction, plays a significant role in the Cr mobility in the soil due to its reducing and immobilising behaviour. It can be assumed that the leaching of Cr with the decreased content of organic matter could be even higher (Banks et al. 2006; Chopala et al. 2015).

In comparison with the total content of the Cr bound in this anthropogenically contaminated soil, the share of Cr bound on the exchangeable fraction is not higher than 0.85% and the reducible fraction does not ex-

ceed 1.09%. Part of the Cr bound on the oxidisable fraction ranges from 17.1% (original K 1/1 sample) to 21.4% (K 1/2 AW). The major part of Cr is bound on the residual fraction. The difference between the pseudo-total (AQ tot) content and the sum of the BCR fractions (Σ BCR) is used as a residual Cr fraction in the samples (Table 6).

Different findings were observed in the study of Al-lué et al. (2014), where sludge-derived Cr was mainly distributed in the moderately reducible fraction (which is the extended fraction of the five-step BCR extraction, including treatment with acid oxalate), and lesser than in the residual fraction.

Also, the data of Milacic and Stupar (1995) show a different trend after a tannery waste application on sandy and clayey soils. After the experiment, the water-soluble and exchangeable Cr were partially eluted from the topsoil with rainwater and part of the Cr was converted into the less-soluble fractions. Sewage sludge amended soils lead to a slight increase in the Cr in the water-soluble and exchangeable fractions. The distribution of these two fractions decreased in the continuation of the experiment to its natural content in the soils (Milacic & Stupar 1995).

Another research described the efficiency of two different chelating agents, ethylenediaminetetraacetic

acid (EDTA) and citric acid. Citric acid leached out more Cr, which should have been affected by a substitution reaction with Cr(VI). The Cr and Ni also continued leaching after following washing with water, which was possibly caused by the increased mobility due to the residual chelants and to the dissolution or mobilisation of the mineral and organic soil fractions (Jean-Soro et al. 2012).

CONCLUSION

It was found that an anthropogenically contaminated soil leached out many times more Cr after treatments with both AW and SRE than a serpentine soil.

The weakly bound fraction of Cr in the serpentine soil doubled after the SRE leaching experiment. A significant increase occurred in the fraction bound to the Fe-/Mn- oxides in horizon B. The Cr bound on the oxidisable fraction in the serpentine B horizon significantly decreased after both leaching experiments. In the case of the anthropogenically contaminated soil, the share of the Cr in the upper layer moderately bound on the exchangeable, reducible and oxidizable fraction decreased after the leaching experiments. Also, the lower layer decreased the share of Cr bound on the Fe-/Mn- oxides and on the oxidisable fraction after both the SRE and AW leaching experiments.

Generally, all the samples showed enhanced leaching from the bottom layer, respectively the horizon, after both treatments. The sample's behaviour was quite similar, only the anthropogenic soil showed some differences in the bottom layer (K 1/2). It was more susceptible to the AW treatment than to the SRE one. The sample (K 1/2) has the lowest pH and highest Cr content. As the pH did not significantly change during leaching experiments, only the pH increased rapidly in the case of the bottom layer (K 1/2) during the treatment. On the contrary, while the Cr concentration in the extracts of all the other samples during the leaching experiments continuously decreased, the levels of the Cr in the leachates from bottom layer (K 1/2) continuously increased after both treatments. This opposite behaviour of the bottom layer (K 1/2) is presumed to be due to the calcite dissolution.

These findings show the high dependence of the leachability of the Cr in the studied soil materials on the contamination origin. It has been proven that naturally enriched sites where elevated levels of Cr originate from the bedrock are more resistant to Cr leaching than anthropogenically contaminated soils.

Acknowledgement: For conducting of chemical microanalyses of the specimens, we would like to acknowledge N. Mészárosová from the Institute of Geology of the Czech Academy of Science.

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Received: September 16, 2021

Accepted: January 17, 2022

Publish online: February 11, 2022