DOI: 10.2428/ecea.2013.20(12)128 ECOL CHEM ENG A. 2013;20(12):1423-1430

Tomasz CZECH[1*], Marcin CZORA[1],
Florian GAMBUŚ[1] and Jerzy WIECZOREK[1]

CHROMIUM CONTENT IN SOILS AND PLANTS IN THE AREA UNDER INFLUENCE OF MMP "BOLESLAW" ENTERPRISE IN BUKOWNO NEAR OLKUSZ

ZAWARTOŚĆ CHROMU W GLEBACH I ROŚLINACH W REJONIE ODDZIAŁYWANIA ZAKŁADÓW „BOLESŁAW" W BUKOWNIE KOŁO OLKUSZA

Abstract: Chromium belongs to the group of trace elements. Plants take it up from the substratum passively, therefore Cr content in plants is usually correlated with its concentrations in the soil solution. Toxic effect of chromium on plants depends both on its degree of oxidation and on the kind of compound in which it occurs. Due to the hazard of excessive chromium accumulation in plants in the areas with its elevated contents, particularly post-industrial and transformed areas, an on-going monitoring of this metal content in soils and fodder plants is recommended. The investigations were conducted to define and describe chromium transfer in the soil-plant system in the areas with various degrees of heavy metal pollution, using Surfer 8.0 programme for the presentation of spatial distribution of the metal in plants and soil in the area under investigations. The investigated area covered 100 km^2 in the vicinity of MMP (Mine and Metallurgical Plants) "Boleslaw" SA in Bukowno near Olkusz. Samples of soil and plant material were collected in 139 localities, during the period from June to August 2008. In each investigated point soil was sampled from two layers: 0–10 cm and 40–50 cm, together with the aboveground parts of mono- and dicotyledonous plants. In dissolved samples of plant and soil material chromium content was assessed using atomic absorption spectrometer with inductively coupled argon plasma (ICP-AES).

Soils from the investigated area revealed diversified contents of chromium, however no diversification was observed between the analysed soil layers. Slightly higher values occurred in the soils from 0–10 cm layer, particularly in the immediate vicinity of "Boleslaw" enterprise. Chromium accumulation in the mono- and dicotyledonous plants growing around MMP "Boleslaw" enterprise revealed weak diversification. No significant differences were observed either in the chromium accumulation in both analysed plant groups.

Keywords: chromium, mono- and dicotyledonous plants, MMP "Boleslaw" SA

[1] Department of Agricultural and Environmental Chemistry, University of Agriculture in Krakow, al. A. Mickiewicza 21, 30–120 Kraków, Poland, phone: +48 12 662 43 49, fax: +48 12 662 43 41, email: Tomasz.Czech@ur.krakow.pl, marcin.czora@wp.pl, rrgambus@cyf-kr.edu.pl, rrwieczo@cyf-kr.edu.pl

* Corresponding author: Tomasz.Czech@ur.krakow.pl

Introduction

Chromium belongs to trace element group. It is passively absorbed by plants from the substratum, so Cr content in the individual plant parts is the resultant of its concentration in the soil solution. Plants tolerate chromium in the amounts between 1 and 24 mg · kg^{-1} d.m. Chromium toxicity for plants depends on both the degree of its oxidation and the kind of compounds in which it occurs [1].

The soil reaction [2], organic matter content and soil redox potential [3, 4] are the main factors affecting this element availability to plants and the form in which it occurs in the soil environment [1]. In the soil environment chromium occurs on two levels of oxidation C^{3+} – the form hardly absorbed by plants and Cr^{+6} – the easily absorbed form [5], but in excessive amounts both forms become toxic for plants and animals [2, 6, 7].

Excessive quantities of chromium in soil may occur in places of chromate containing waste storage, on wood calcination sites, in places of textile manufacturing, electric and thermal energy generating, as well as in the areas where sewage sludge are used for fertilization [8]. Besides, soils formed from metamorphic rocks may have naturally high concentrations of chromium of geochemical origin [1].

Due to the hazard of excessive chromium accumulation in plants and its considerable toxicity, an on-going monitoring this metal concentrations in soils and plant material meant for animal feed is recommended. It applies to areas with elevated heavy metal content in soils, particularly in post-industrial and anthropogenically transformed areas, such as among others the region in the vicinity of MMP (Mine and Metallurgical Plants) “Boleslaw” SA in Bukowno.

Presented investigations aimed at defining and describing chromium transport in the soil-plant system in the area under the influence of MMP “Boleslaw” SA in Bukowno near Olkusz, using Surfer 8.0 programme for spatial distribution of the analysed metal in the soil and plants.

Material and methods

The investigated area is situated in the southern part of Poland, on the border of the Malopolska and Silesia regions (Fig. 1). It covers the area of 100 km^2 surrounding MMP (Mine and Metallurgical Plants) “Boleslaw” SA in Bukowno near Olkusz.

The area of samples collection was divided into two zones: the first in the immediate vicinity of the enterprise, in which two sampling points were chosen at random for collecting 2 samples per 1 km^2 and the second situated at a longer distance from the enterprise, where 1 sample was collected per 1 km^2. The sampling method was so-called square net. Soil samples were collected in 139 points determined as above from the 0–10 cm and 40–50 cm soil layers. Moreover, the above-ground parts of mono- and dicotyledonous plants were sampled.

The following basic properties were determined in soils from both analysed layers:

– pH by potentiometric method in a suspension of 1 mol · dm^{-3} KCl solution,

– granulometric composition by Bouyoucose-Casagrande’s method in Proszynski’s modification,

– organic carbon content by Tiurin’s method,

– soil sorption capacity (hydrolytic acidity and base exchange capacity by Kappen’s method [10].

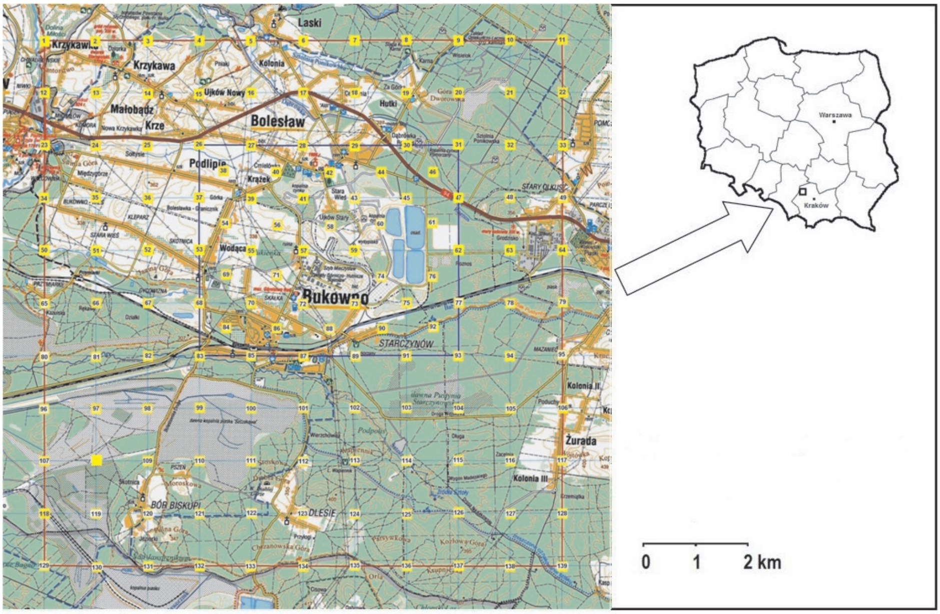


Fig. 1. Sampling sites in the region close to MMP “Boleslaw” SA [9]

Also total chromium concentrations were assessed in all collected soil samples. The samples were dissolved in a mixture of nitric and perchloric acids (2:1, *v*/*v*), after previous organic matter mineralization in a muffle furnace at 450 ^{o}C [10].

The next stage of research involved determining the content of analysed element in collected plant material samples. Dried and ground plant material was dry mineralized in a muffle furnace at 450 ^{o}C for 12 hours. Incinerated samples were dissolved in nitric acid (1:2) [4].

Each sample of both soil and plant material was analysed in two replications and to each analysed series a blind sample was attached. If the analysis results from two parallel replications differed from each other by more than 5 %, subsequent two analyses of the same sample were conducted. In the dissolved plant and soil samples chromium content was assessed using atomic emission spectrometer with inductively coupled argon plasma ICP-AES JY 238 ULTRACE (Jobin-Yvon).

Statistical analysis and presentation of the obtained results were conducted with the use of Microsoft Excel 2007 calculation sheet, Statistica 9.0 programme and SURFER 8.0 programme for data visualisation. It was used to create the maps of spatial distribution of chromium content in the analysed samples of soil and plant material.

Results and discussion

The soil samples presented in this paper, collected from the area of 100 km^2 around MMP “Boleslaw” SA in Bukowno near Olkusz, are characterized by a diversified cadmium, lead and zinc accumulations (from the concentrations close to assumed as natural to very high ones [11].

Chromium contents in the vicinity of MMP “Boleslaw” SA assessed in both analysed soil layers: 0–10 cm and 40–50 cm were within a similar range 1.46–18.12 mg and 0.97–16.18 mgCr $\cdot$ kg^{-1} d.m., respectively. However, diversification of the analysed element content in the lower soil layer was clearly higher and in both layers it was described by coefficients of variance 51.3 and 70.90 %, respectively (Table 1).

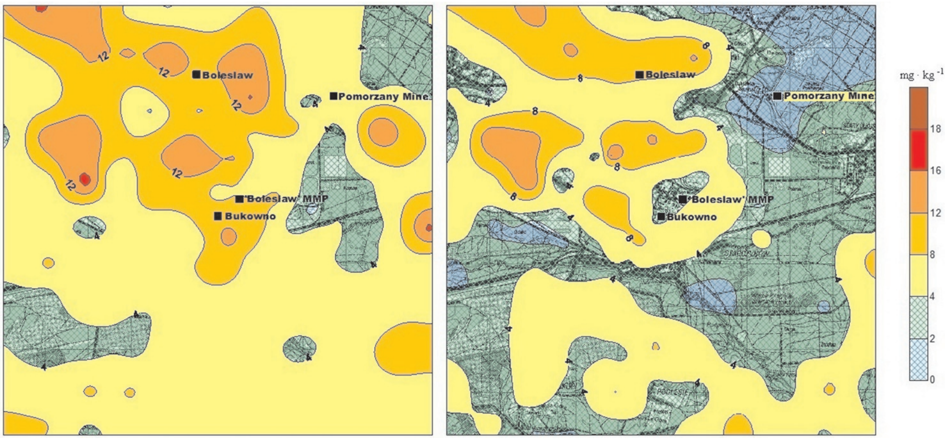
Table 1

Statistical parameters of total Cr content in soils and plants from the vicinity of MMP “Boleslaw” SA

Parameter	Cr content [mg $\cdot$ kg^{-1} d.m.]			
	Soil		Plants	
	0–10 cm	40–50 cm	Monocotyledonous	Ddicotyledonous
Minimum value	1.46	0.97	0.49	0.01
Maximum value	18.12	16.18	5.36	3.96
Arithmetic mean	7.18	4.83	1.57	1.32
Geometric mean	6.30	3.81	1.42	1.07
Median	6.23	3.52	1.35	1.07
Variation coefficient [%]	51.3	70.9	50.1	59.4

Numerical data sets describing polluted environment are usually characterised by skewed left data distribution [12, 13], therefore the characterization of chromium contents in the samples gathered in the vicinity of MMP “Boleslaw” SA used geometric mean, which is more approximate to median of a data set than arithmetic mean (Table 1). At a similar range of chromium occurrence in both investigated soil layers, geometric mean and median of its content in the top layer (6.30 and 6.23 mg $\cdot$ kg^{-1} d.m., respectively) are much higher than in the samples collected from the 40–50 cm layer. If one assumes the above-mentioned statistical characteristics for the top soil layer as 100, then with the reference to the lower analysed soil layer they would be: 60 and 57, respectively (Table 1). It suggests that some quantity of chromium contained in the top soil layer might have originated from the atmosphere, from fallout of dust abundant in this metal. The hypothesis seems additionally supported by the spatial distribution of this element content in the soils of the investigated area (Fig. 2).

The highest Cr contents were assessed in the samples collected in the immediate vicinity of MMP “Boleslaw” SA and in the north-western part of the investigated area, *ie* in the direction of a nearby “Katowice” ironworks and other energy plants and industries of the Upper Silesia. On the other hand, analysing values of simple correlation coefficients between chromium accumulation in both layers of the studied



0–10 cm soil layer

40–50 cm soil layer

Fig. 2. Spatial distribution of chromium in soils from the vicinity of MMP "Boleslaw" SA

soils and their various physical and chemical properties, one should notice the strongest relationship between the content of analysed metal and occurrence of the finest soil fractions, described by correlation coefficients 0.72 and 0.78 in the upper and lower soil layer, respectively (Table 2). These values are substantial at the significance level $\alpha \le 0.001$. On the other hand this relationship indicates that a big part of chromium in the studied soils may have its source in natural processes of bedrock transformations.

Table 2

Effect of soil properties on total Cr content in both analysed soil layers and in top parts of mono- and dicotyledonous plants – expressed as simple correlation coefficients (r)

Soil property	Soil layer [cm]	Cr_{tot} content		Cr_{tot} content	
		Soil layer [cm]			
		0–10	40–50	monocotyledonous	dicotyledonous
pH_{KCl}	0–10	0.22**	—	–0.003	–0.09
	40–50	—	0.25**	–0.03	0.03
Content of < 0.02 mm fractions	0–10	0.72***	—	–0.14	–0.33***
	40–50	—	0.78***	–0.09	–0.20**
Content of organic matter	0–10	0.52***	—	–0.12	–0.17*
	40–50	—	0.22**	–0.10	–0.08
Sorption capacity [T]	0–10	0.43***	—	–0.06	–0.18*
	40–50	—	0.39***	–0.11	–0.01
Cr_{tot} content	0–10	—	0.58***	–0.21**	–0.15
	40–50	0.58***	—	–0.04	–0.11

Simple correlation coefficient r significant at: * $\alpha \le 0.05$, ** $\alpha \le 0.01$ and *** $\alpha \le 0.001$.

If the value of 20 mgCr · kg^{-1} d.m. of soil suggested by Kabata-Pendias et al [14] is assumed as the highest permissible content of this metal in agricultural soils, all analysed soil samples meet this criterion. However, it should be noted, that many areas in the investigated terrain, a particularly in the immediate vicinity of MMP "Boleslaw" SA, should be excluded from cultivation because of excessive accumulation of heavy metals.

In order to determine bioavailability of chromium present in the studied soils, its concentrations were also assessed in mono- and dicotyledonous plants, which were growing in places where the soil was sampled.

Mean Cr contents in the analysed top parts of mono- and dicotyledonous plants were 1.42 and 1.07 mg · kg^{-1} d.m., respectively (Table 1). The greatest content of the studied element, 5.36 mg · kg^{-1} d.m. was assessed in a sample of monocotyledonous plants; it was about 1/3 bigger than the maximum content of this element determined in the dicotyledonous plant top parts. Assuming 20–30 mg · kg^{-1} d.m. [13, 14] as the permissible chromium content in fodder, it should be stated this value has not been exceeded in any of the studied plant samples, so the analysed material may be used for fodder.

Spatial distribution of the analysed element in both plant groups was approximate, the highest Cr contents were registered in plants of both plant classes growing in points in various places of the investigated area (Fig. 3).

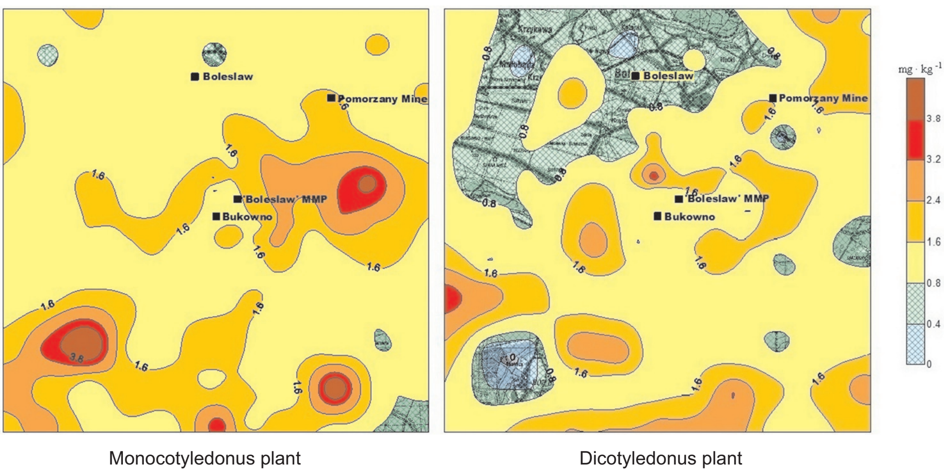


Fig. 3. Spatial distribution of chromium content in top parts of mono- and dicotyledonous plants in the vicinity of MMP "Boleslaw" SA

The places do not overlap the zones where the highest total chromium content in the studied soils was registered. It means that the assessment of total chromium content in soil cannot be an indicator for estimating its concentrations in plants growing in this soil. Considering the monocotyledonous plants, even a significant negative correlation ($r = -0.21$, $\alpha \le 0.01$) was registered between this element concentrations in plants and soil (Table 2).

No apparent effect of the analysed properties of the studied soils on chromium accumulation in plants was registered (Table 2). A slightly lower uptake of this metal by plants growing in more compact soil, more abundant in organic matter was observed for the dicotyledonous class. If, following Kabata-Pendias et al [14], one assumes that chromium is passively absorbed from the soil solution by plants, its solubility in soil must be affected other soil properties not investigated in the presented research or it is a simultaneous resultant effect of several soil properties.

Conclusions

1. The analysed soils in the area of influence of MMP “Boleslaw” SA engaged in extraction and processing of lead-zinc ores, are characterized by a diversified chromium content which does not exclude agronomic use of these soils. Increased chromium concentrations were assessed in the soil around MMP “Boleslaw” SA and north-west of the enterprise.
2. Solubility and bioavailability of chromium in soil to a greater extent depends on various soil properties than on its total content in the substratum.
3. Chromium accumulation in monocotyledonous plants growing in the areas to various extent polluted with cadmium, lead or zinc was slightly higher than in dicotyledonous plants and in all cases did not lower the fodder value of these plants.

References

[1] Kamaludeen SPB, Megharaj M, Juhasz AL, Sethunathan N, Naidu R. Chromium-Microorganism Interactions in Soils: Remediation Implications. Rev Environ Contam Toxicol. 2003;178:93-164.
[2] McGrath SP. Chromium and nickel. In: Heavy Metals in Soil. London: Blackie; 1995:152-178.
[3] Liao Y, Wang Z, Yang Z, Chai L, Chen J, Yuan P. Migration and transfer of chromium in soil-vegetable system and associated health risks in vicinity of ferro-alloy manufactory. Trans Nonferrous Met Soc China. 2011;21:2520-2527. DOI: 10.1016/S1003-6326(11)61045-5.
[4] Skowronski G, Seide M, Abdel-Rahman M. Oral bioaccessibility of trivalent and hexavalent chromium in soil by simulated gastric fluid. J Toxicol Environ Health A. 2001;63:351-362. http://scholarworks.umass.edu/soilsproceedings/vol11/iss1/5.
[5] Fendorf SE. Surface reactions of chromium in soils and waters. Geoderma. 1995;67:55-71. DOI: 10.1016/0016-7061(94)00062-f.
[6] Becquer T, Quantin C, Sicot M, Boudot JP. Chromium availability in ultramafic soils from New Caledonia. Sci Total Environ. 2003;301(1-3):251-261. DOI: S0048-9697(02)00298-X.
[7] Broadway A, Cave MR, Wragg J, Fordyce FM, Bewley RJF, Graham MC, Ngwenya BT, Farmer JG. Determination of the bioaccessibility of chromium in Glasgow soil and the implications for human health risk assessment. Sci Total Environ. 2010;409:267-277. DOI: 10.1016/j.scitotenv.2010.09.007.
[8] Dhal B, Thatoi HN, Das NN, Pandey BD. Chemical and microbial remediation of hexavalent chromium from contaminated soil and mining/metallurgical solid waste: A review. J Hazard Mater. 2013;250-251:272-291. DOI: org/10.1016/j.jhazmat.2013.01.048.
[9] Mapa powiatu olkuskiego. Kraków: Wydawnictwo Compass; 2009.
[10] Ostrowska A, Gawliński S, Szczubiałka Z. Metody analizy i oceny właściwości gleb i roślin. Katalog. Warszawa: Instytut Ochrony Środowiska; 1991:333 pp.
[11] Stewart M, Jardine P, Barnett M, Mehlhorn T, Hyder L, McKay L. Influence of soil geochemical and physical properties on the sorption and bioaccessibility of chromium (III). J Environ Dual. 2003;32:129-137. http://www.esd.ornl.gov/earth_aquatic/projects/estcp/stewart_etal_2003a.pdf.

[12] Cabała J. Metale ciężkie w środowisku glebowym olkuskiego rejonu eksploatacji rud Zn-Pb. Katowice: Wyd Uniwersytetu Śląskiego; 2009:130 pp.
[13] Dudka S. Ocena całkowitych zawartości pierwiastków głównych i śladowych w powierzchniowej warstwie gleb Polski. Praca habilitacyjna. Puławy: IUNG Puławy; 1992:293 pp.
[14] Kabata-Pendias A, Pendias H. Trace Elements in Soils and Plants. 3rd ed. Boca Raton, FL: CRC Press; 2001:315 pp.

ZAWARTOŚĆ CHROMU W GLEBACH I ROŚLINACH W REJONIE ODDZIAŁYWANIA ZAKŁADÓW „BOLESŁAW” W BUKOWNIE KOŁO OLKUSZA

Katedra Chemii Rolnej i Środowiskowej
Uniwersytet Rolniczy im Hugona Kołłątaja w Krakowie

Abstrakt: Chrom należy do grupy pierwiastków śladowych. Jest on pobierany z podłoża przez rośliny biernie, przez co jego zawartość w roślinach jest zwykle skorelowana z zawartością chromu w roztworze glebowym. Toksyczne działanie chromu na rośliny zależy zarówno od jego stopnia utlenienia, jak również od rodzaju związku w jakim występuje. Ze względu na zagrożenie nadmierną kumulacją chromu w roślinach w terenach z podwyższoną zawartością chromu, szczególnie poprzemysłowych i przekształconych, zaleca się stały monitoring zawartości tego metalu w glebach i roślinach przeznaczonym na paszę. Celem przeprowadzonych badań było zdefiniowanie i opisanie transferu chromu w układzie gleba-roślina w terenach w różnym stopniu zanieczyszczonych metalami ciężkimi, z wykorzystaniem programu Surfer 8.0 do prezentacji przestrzennego rozmieszczenia metalu w roślinach i glebie na terenie objętym badaniami. Obszar badań obejmował 100 km^2 w sąsiedztwie Zakładów Górniczo-Hutniczych „Bolesław” SA w Bukownie koło Olkusza. Próbki gleby i materiału roślinnego zebrano w 139 miejscach, w okresie od czerwca do sierpnia 2008 r. W każdym punkcie badań pobrano glebę z dwóch poziomów: 0–10 i 40–50 cm oraz części nadziemne roślin jedno- i dwuliściennych. W roztworzonych próbkach materiału roślinnego i glebowego oznaczono zawartość chromu przy użyciu spektrometru emisji atomowej z indukcyjnie wzbudzoną plazmą argonową (ICP-AES).

Gleby z badanego obszaru wykazywały zróżnicowane zawartości chromu, jednak nie stwierdzono znacznego zróżnicowania jego zawartości pomiędzy badanymi warstwami gleb. Nieco większe zawartości występowały w glebach z warstwy 0–10 cm, zwłaszcza w bezpośrednim sąsiedztwie ZGH „Bolesław” SA. Zawartość chromu w częściach nadziemnych roślin jedno- i dwuliściennych rosnących wokół ZGH „Bolesław” SA wykazywała słabe zróżnicowanie. Nie stwierdzono także znaczących różnic w nagromadzeniu chromu w obu badanych grupach roślin.

Słowa kluczowe: chrom, rośliny jedno- i dwuliścienne, ZGH „Bolesław” SA