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THESES of PhD

LOADING and TESTING of CHROMIUM CONTAMINATION in a SOIL-PLANT SYSTEM

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The sources of anthropogenic chromium to be found in the atmosphere is fly ash entering the air, created by the use of coal and oil burning techniques as well as through the incineration of sewage sludges. This increases the chromium pollution of soils when precipitating from the atmosphere.

The goals of our research work are the following:

1. Within the framework of the Soil Information Monitoring (SIM) system we have analysed the chromium content of certain local (Hungarian) soil types and were looking for connections between the chromium content and the physical and chemical properties of soils.
2. The concentration of rare earth metals of Hungarian soils were measured and the correlations between chromium content and rare earth meal concentrations were analysed. The normalization methods were applied and studied for the determination of both anthropogenic and geogenic chromium content of soils.
3. The isothermes of adsorption of some of the more important Cr(III)-complexes were determined in different soils and the values of the obtained adsorption capacities were compared.
4. The effect of the Cr(III)-picolinate complex were studied upon plants and the toxicity of the compound were examined in pot experiments.

10. Prokisch J., Szegvári I., Kovács B., Palencsár J. A, Győri Z. (1999) Ittrium normalizációs eljárás: új lehetőség a fémek antropogén és geológiai eredetének megkülönböztetésére talajban. Tiszántúli Mezőgazdasági Tudományos Napok, Agrokémiai és Talajtani Szekció. Lícium-Art Kft. Debrecen, 119-123.

Lectured conference proceeding in English

11. Simon, L., I. Szegvári, J. Prokisch (2000). Study of the phytoextraction of chromium from contaminated soils. In: Pais, I. (ed.), Proceedings of the 9th International Trace Element Symposium, September 2000, Budapest, Hungary, 239-255.

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12. Simon L., I. Szegvári, B. Kovács, J. Prokisch, Z. Győri (2001) Picolinic acid promotes chromium accumulation in fodder radish and komatsuna. 6th International Conference on the Biogeochemistry of Trace Elements, July 29-August 2, 2001, Guelph, Ontario, Canada. ICOBTE 2001 Proceedings, University of Guelph, Ontario, Canada, 130.

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13. Szegvári I., Simon L., Kovács B., Prokisch J., Győri Z. (2001) Növények krómtartalmának növelése króm-pikolináttal. VIII. Szemcseméret-analitikai, Környezetvédelmi és Portechnológiai Szimpózium, Eger, 2001. szeptember 13-14. (poster).

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15. Prokisch J., Szegvári I., Simon L., Kovács B. (2000) Króm(III)-vegyületek toxicitása és felvehetősége a talajban. XIV. Országos Környezetvédelmi Konferencia, Siófok, 2000. szeptember 19-21., Tanulmánykötet 157. (oral)

16. Prokisch J., Szegvári I. (1999) Új eredmények a króm környezeti hatásának vizsgálatához. XIII. Országos Környezetvédelmi Konferencia, Siófok, 1999. szeptember 24-26. (poster)

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17. Prokisch J., B. Kovács, Z. Győri, L Simon, I. Szegvári (2000) Chromium contamination of soil-plant system. 18th European Conference of the Society for Environmental Geochemistry and Health, Conference on Environmental Chromium Contamination and Remediation, 11-12 September 2000, Glasgow, Scotland, Book of Abstracts. (poster)

18. Simon, L. , I. Szegvári, J. Prokisch (2000) Enhancement of chromium phytoextraction capacity in fodder radish with picolinic acid. 18th European Conference of the Society for Environmental Geochemistry and Health, Conference on Environmental Chromium Contamination and Remediation, Glasgow, Scotland, 11-12 September 2000, Book of Abstracts. (oral)

19. Prokisch J., B. Kovács, Z. Győri, L Simon, I. Szegvári (2000) Chromium (III) complexes in soil: toxicity and bioavailability. 5th International Symposium on Enviromental Geochemistry, April 24-29, 2000, Abstracts, University of Cape Town, South Africa 83. (oral)

1. INTRODUCTION

One of the important environmental health problems of our days is the contamination of our environment by heavy metals. According to the data of the Agency of Toxic Substances and Disease Registry (ATSDR) the health of modern man is predominantly threatened by heavy metals (As, Pb, Cd, Hg, Cr). Of these elements chromium possesses extraordinary properties, as it appears in nature in two different oxidative states and with two different forms of toxicity. While the anions with a valency of six are potentially poisons, the cations with the valency of three are essential trace elements for mammals.

The modern day industrial use of chromium is very wide and this results that a huge amount of products containing chromium appear in the environment. The frequent use of this metal is based on the one hand on its stability, as it is able to protect materials coated by it from the oxidising effect of the environment. On the other hand it depends on its favourable physical properties. The most common application of chromium is found in the different types of steel (e.g. stainless steel, heat and corrosion resistant steel) made of various chromium alloys. Through this and its wide application chromium is present in large amounts in industry, agriculture and trade.

Chromium can be found in its oxidation state of six in heat- and corrosion resisting coatings and wood conserving agents (chromated copper arsenate-CCA) serving the protection of various metal and wood products, as well as in paints and catalysators. Chromium in its oxidation state of three is part of leather tanning substances, in paints and in protective coatings creating the water repellent state of leather-, textile- and other surfaces. Further it is found in coatings which serve the protection or decoration of metal surfaces. Among the organic Cr(III)-compounds Cr(III)-picolinate is common in human and animal nutrition as a dietary supplement. It moderates the symptoms created by both a high or low blood sugar level and, it helps in losing weight by regulating the amount of fatty tissues.

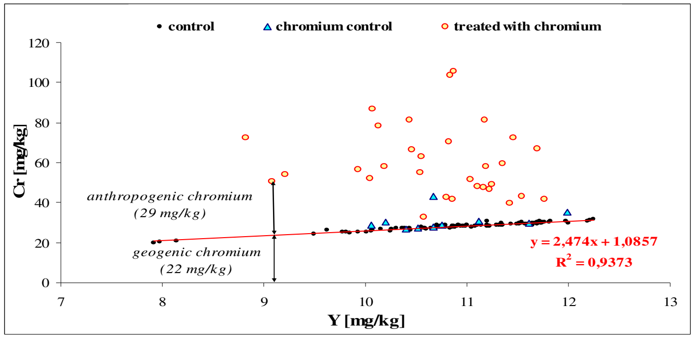
As a result of the wide use of chromium the chromium entering our environment originates in the first place from steel manufacturing and the processing of iron and also from the production as well as the usage of different chromates. The appearance of compounds in our environment containing Cr(VI) is a result of the chromite manufacturing as well as galvanisation processes in both small and large factories. Contributing to the chromium load of soils are inappropriate handling of industrial and communal wastes (waste waters, sewage sludges) and their above ground deposition.

Within the scope of the SIM measuring programme of 1998 soil samples were taken from areas of the north-eastern region of Hungary (4 counties, 314 soil profiles, 1202 samples). We compared total (cc.HNO_3+H_2O_2 soluble) chromium contents with pH-value, clay- and humus content of the soils based on the measuring results of this SIM programme. We compared Lakanen-Erviö soluble (LE) chromium contents with the pH-value, lime-, humus content and some physical properties of the soils (soli plasticity according to Arany, soil particle size).

2.2. The rare earth elements content of soils and the yttrium normalization method

We prepared soil samples for determination of contents of both total elements and of rare earth metals according to the procedures of Hungarian Standard 21470-50:1998, which could be dissolved by concentrated HNO_3 and H_2O_2 and measured it using a Perkin Elmer Optima DV 3300 model of an inductive coupled plasma optical emission spectrometer (ICP-OES). We applied the yttrium normalization method after PROKISCH et al. (2001)[1] both to the layer samples from the north-eastern region (4 counties, 1202 samples) of Hungary, which are in the SIM data base, and the samples of the topsoils originating from the entire area of the country (1236 samples).

The essence of this procedure is that we regard the deviation measured from the valid correlation curve, which had been established for yttrium and chromium of that given soil, as anthropogenic chromium quantity. With this we could show an anthropogenic effect in the chromium content of soils which was smaller by a factor of one or two, as compared to traditional methods (Figure 2).



2. ábra: Figure 2: Proof of chromium contamination by using the yttrium normalization after PROKISCH et al. (2001)

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[1] Prokisch, J., Kovács, B., Szegvári, I., Győri Z. (2001) Yttrium normalisation: a new tool for detection chromium contamination in soil samples. Environmental Geochemistry and Health **22,** 317-323

VI. The effects of organic and inorganic Cr(III)-compounds have different effects on the chromium uptake of plants and also on the transport within the plant. The picolinic acid and ethylene-diamine-tetraacetic acid which was used besides high dosega of $CrCl_3$ raised the chromium uptake of plants and translocation thereof within plants. After multiple application of picolinic acid chromium was mobilized, especially when $CrCl_3$ was added artificially to the soil. This mobilizing effect was slight when soils were contaminated withchromium by using leather factory sewage sediment and it was negligible in soils contaminated with galvanic mud. The singular or multiple application of Cr(III)-picolinate enhances both the chromium accumulation in plants and its translocation within plants.

VII. Cr(III)-picolinate above a concenrtation of 20 mg·kg^{-1} already exerted phytotoxic effects on the test plants.

PUBLICATION LIST

Lectured publications in English

1. Simon L., I. Szegvári, J. Csillag (2003) Impact of picolinic acid on the chromium accumulation in fodder radish and komatsuna. Plant and Soil **254**, 337-348.

2. Simon, L., I. Szegvári, J. Prokisch (2001) Enhancement of chromium phytoextraction capacity in fodder radish with picolinic acid. Environmental Geochemistry and Health **23**, 313-316.

3. Prokisch J., B. Kovács, A. Palencsár, I. Szegvári, Z. Győri (2000) Yttrium normalisation: a new tool for detection of chromium contamination in soil samples. Environmental Geochemistry and Health **22**, 317-323

4. Prokisch J., P. Marth, G. Podmaniczky, I. Szegvári (2000) Soil Information and Monitoring System in Hungary. Newsletter of the Society for Environmental Geochemistry and Health, 8-10.

Lectured publications in Hungarian

5. Szegvári I., Simon L., Prokisch, J. (2005) Króm(III)-pikolinát vizsgálata a talaj-növény rendszerben. Agrokémia és Talajtan (under publication)

6. Szegvári I., Prokisch J., Simon L., Várallyai L. (2003) Króm(III)-pikolinát adszorpciójának vizsgálata néhány talajtípuson. Acta Agraria Debreceniensis különszám, 190-193.

7. Várallyai L., Szegvári I., Kovács B., Prokisch J. (2003) TIM talajminták statisztikai értékelése. Acta Agraria Debreceniensis különszám, 194-197.

Books in Hungarian

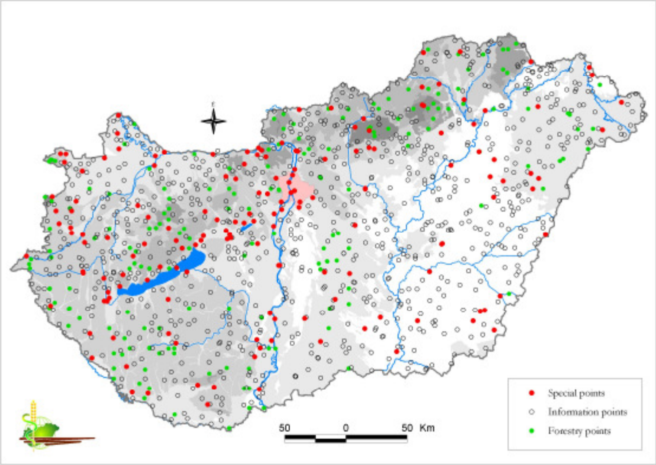
8. Szegvári I., Simon L., Prokisch J., (2003) Pikolinsav és króm(III)-pikolinát hatása a takarmányretek és a komatsuna krómfelvételére In: Simon L. és Szilágyi M. (szerk.), 2003. Mikroelemek a táplálékláncban. Bessenyei György Könyvkiadó, Nyíregyháza, 238-251. ISBN:963 9385 81 6

9. Prokisch J., Kovács B., Szegvári I., Győri Z., (2002) A krómkutatás tíz évének eredményei a Debreceni Egyetem Agrártudományi Centrum Műszerközpontjában. Az agrokémia időszerű kérdései, Lícium-Art, Debrecen, 211-221.

2. MATERIALS AND METHODS

2.1. The chromium content of soils in Hungary

The aim of the Soil Information Monitoring (SIM) system is to register changes taking place in the quality of the soil stock of Hungary, and the follow-up in time of the changes of soil condition, in the interest of the corresponding regulations. Certain parts of the studied parameters were determined only once at the inventory of the actual state (parent material, soil type, morphological description of the soil profile, Global Position System coordinates). Depending on the temporal changeability of each given soil property the laboratory analyses need to be repeated at an interval of one-, three- respectively six years. Figure 1 shows the distribution of the SIM points on the territory of Hungary.



1. ábra: SIM measuring points as provided by the Geographical Information System Laboratory of the Central Services of the Plant and Soil Protection (2003)

The soil sample used as control received only deionised water. In the 1st treatment we applied to the soil 1 mg·kg^{-1}, 10 mg·kg^{-1} and 100 mg·kg^{-1} chromium in the form of $CrCl_3·6H_2O$. In the 2nd treatment we extended the previous chromium treatment with 7 mg·kg^{-1}, 70 mg·kg^{-1} és 700 mg·kg^{-1} of picolinic acid. In the 3rd treatment we used only 7 mg·kg^{-1}, 70 mg·kg^{-1} és 700 mg·kg^{-1} of picolinic acid. In the 4th treatment we applied freshly prepared picolinic acid to the soil in the concentration series of 0,5-1-2-5-10-20-50-100-200 mg·kg^{-1}.

In the second experiment we studied the uptake and translocation of chromium using fodder radish as well as a Japanese lettuce plant, the komatsuna (*Brassica campestris* L. subsp. *napus* f. et Thoms. var. komatsuna Makino, cv. Kuromaru) as indicator plants. We used soils either contaminated artificially by Cr(III)-salt, mixed with leather factory sewage sediment containing considerable quantities of chromium (total chromium 760 mg·kg^{-1}), respectively polluted by galvanic mud (total chromium 121 mg·kg^{-1}). In the 1st treatment we applied the different chromium forms to the soils and added the Cr(III)-picolinate in the 2nd treatment to it once or several times, respectively we added at the middle of the vegetation period either picolinic acid or EDTA to it.

During the 1st treatment we applied deionised water (for the control), as well as 10 mg·kg^{-1} and 100 mg·kg^{-1} chromium in the form of $CrCl_3$-solution onto the sandy soil with humous (from Debrecen-Pallag). We mixed the uncontaminated soil with leather factory sewage sediment in the amount of 2,5 w/w%. During the 1st treatment we only moisturised the brown forest soil, polluted with the galvanic mud, with deionised water (control).

We repeated each treatment three times. The total chromium content of the soils and the plant parts was determined with an ICP-OES apparatus from extractions gained through the use of concentrated mixtures of HNO_3 and H_2O_2. The pH-value of the soils was determined in suspensions using deionised water and 1 mol·l^{-1} KCl-solution in the ration of 1:2,5 w/V. The exchangeable chromium content was measured using 0,01 mol·l^{-1} $CaCl_2$-solution, and the amount of chromium which can be taken up by the plants was determined from the Lakanen-Erviö extractions.

2.6. Statistical methods

We used the Microsoft Excel 7.0 programme to treat the measured data, the experimental results and to fit the resulting curves. The statistical analysis of the results of the pot experiments were carried out with the SPSS 12.0.1 programme, employing analyis of variance according to the Tukey b-test.

Figure 8. shows the dry matter accumulation of fodder radish after different treatments, in relation to the control.

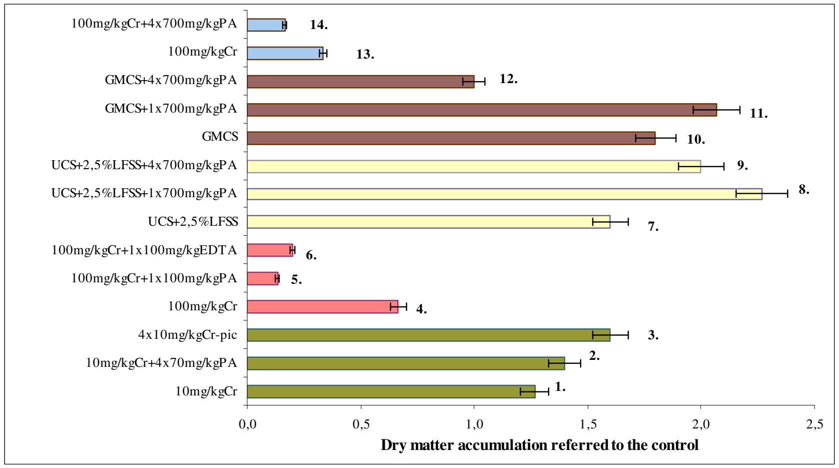


Figure 8: The biomass production of the test plants after different treatments, in relation to the control (pot experiment, at Nyíregyháza, 2000)

Abbreviations: *Cr–$CrCl_3$, PA–picolinic acid, GMCS–galvanic mud contaminated soil, UCS–uncontaminated soil, LFSS–leather factory sewage sediment, Cr-pic–Cr(III)-picolinate*

The application of chromium at small dosages (columns 1-3) slightly increased biomass production of fodder radish compared to that of the control. The application of chromium at high dosages (columns 4-6) decreased the dry matter accumulation of fodder radish, singular application of picolinic acid (column 5) and EDTA (column 6) halted the plants' growth and they withered. The dry mass of fodder radish (columns 7-9) grown on soils contaminated with leather factory sewage sediment containing relatively high amounts of chromium was similar to that of the control. In the case of plants developing on soils contaminated by galvanic mud (columns 10-12) the higher metal concentration of the soil did not disturb the plants' dry mass accumulation as compared to the control treatment. The multiple application of picolinic acid proved to be phytotoxic to plants grown on contaminated soils. The treatment with high dosages supplemented by picolonic acid has halved the dry mass production of komatsuna (columns 13-14) as compared to the treatment control.

4. NEW SCIENTIFIC RESULTS

I. Based on the measuring results of the soils from the SIM study points the characteristic chromium content of agricultural soils dissolvable by concentrated $HNO_3+H_2O_2$ is 20-25 mg·kg^{-1}. By the coefficients the tightest correlation is the chromium content and the clay content (r=0,764). In soils belonging to the different main soil types a higher chromium concentration appears together with a higher clay content.

II. Based on the measuring results of the soils from the SIM study points the Lakanen-Erviö soluble chromium is 0,10-0,13 mg·kg^{-1}. By the coefficients there is no correlation between the plant-absorbable and the total chromium content (r=0,102) and that the solvable chromium after Lakanen-Erviö is mainly dependent on the lime content (r=0,738) and to a smaller degree on pH-value (0,424).

III. We measured the concentration of both the scandium- and the lanthanides group in the SIM soils. By the coefficients there are tight correlations among the concentrations of these elements (yttrium-itterbium r=0,967) and other elements (yttrium-chromium r=0,705). We drew up a method for the determination of the soils' anthropogenic chromium content, with this we could determine those sample sites from the SIM soils which were critical from the point of view of their chromium contents. The applicability of these methods was demonstrated for the entire area of Hungary. The smallest still detectable anthropogenic influence with the aid of the normalization methods is between 5-20 mg·kg^{-1}, depending on the soils' chromium contents.

IV. The formation of Cr(III)-picolinate complex takes place in the solution phase during 10-15 days. The compound is forming with measurable speed already at 5°C. This reaction, while in soils of different ion strength and pH-value this will need several weeks.

V. The adsorption capacities of Cr(III)-picolinate are different in applied soils. The adsorption capacities of different organic and inorganic Cr(III)-compounds are different in leached chernozem soil. The chromium content of soil solutions can be enhanced thirty times by Cr(III)-picolinate and Cr(III)-oxalate in comparison with the use of Cr(III)-chloride.

2.3. Establishing the speed of Cr(III)-picolinate formation

Because of the inert state Cr(III)-complexes, Cr(III)-picolinate does not develop immediately at room temperature. Therefore we aimed at finding out the [illegible] f its formation both in aqueous solution and in soil at two different temperatures (at 20°C and at 5°C). The reaction of complex formation in aqueous environment is accompanied by a change of colour. We followed up this reaction using a spectrophotometer recording the entire spectrum of the solution in the range of 350-700 nm. We determined the concentration of Cr(III)-picolinate by the calibration curve we took within the concentration range of 10-1000 mg·l^{-1}. The formation of Cr(III)-picolinate within soil was studied in sandy soil with humous, meadow soil and leached chernozem soil.

2.4. The adsorption isotherms of Cr(III)-complexes

The majority of ions available to plants are those which are bound to the soil by adsorption. We can characterise the adsorption capability of soils and the adsorption affinity of different materials by adsorption isotherms. We determined the adsorption isotherme of Cr(III)-picolinate in four different soil types (sandy soil with humous, meadow soil, leached chernozem soil and meadow solonetz soil). We studied the adsorption isotherms of Cr(III)-complexes formed by seven different ligands (ascorbic acid, citric acid, ethylene-diamine-tetraacetic acid-EDTA, histidine, malonic acid, nicotinic acid, oxalate) on the same soil type (leached chernozem soil). To record the adsorption isotherms we took ten points from each soil type, fitting to it the Langmuir isotherme equation. Based on the slope of the linear equation and knowing the point of intersection of the axes, we calculated for the soils used in the experiments both the maximum adsorption capacity for the given complex and the value of the Langmuir constant.

2.5. The study of Cr(III)-picolinate in soil-plant systems

The biologically absorbable complex of the Cr^{3+}-ion is the Cr(III)-picolinate. Its role played in the nutrition of men and animals is well known together with that of picolinic acid however, our knowledge on its effects upon the soil-plant system is deficienty. We studied the effects Cr(III)-picolinate effects on plants using pot experiments. In the first experiment we studied which effects has the application of both inorganic ($CrCl_3$) and of organic forms (Cr(III)-picolinate) of chromium as well as of applying purely picolinic acid, on the accumulation and translocation of chromium in fodder radish (*Raphanus sativus* L. convar. *oleiformis* Pers., cv. Leveles olajretek).

Among soils belonging to the main soil types a raised clay- and humus content as well as a neutral pH-value are characteristics of a higher chromium concentration, while with a decrease in the clay- and humus fractions lower chromium values can be expected.

The physical and physico-chemical properties as well as the chromium content of soils is greatly influenced by the amount and proportion of those particles of various solid dimensions which are forming the solid state of soils. Together with the increase of the clay content and the upper limit of plasticity according to Arany also the total amount of chromium increases, as the clay fraction consists mainly of clay minerals. Chromium in soils is present in various quantities within the fractions of different particle sizes. In clay fractions with smaller sized particles it is found in higher amounts (Fig. 4).

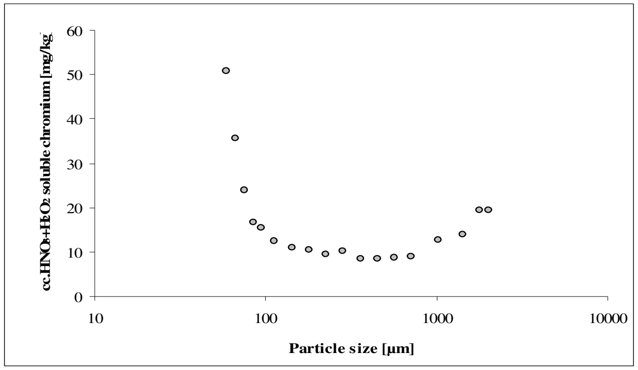


Figure 4: Total chromium concentrations measured in the various sized fractions of a sandy soil with humous

3.2. General characterization of the plant-absorbable chromium content

The plant available chromium content of soils under agricultural use can inform us about the chromium load of food plants cultivated on them. Compared to the total chromium content the plant available chromium content of soils is smaller by a factor of two; it is generally 0,10-0,13 $mg\cdot kg^{-1}$. In some cases higher concentrations appeared at deeper soil layers, which are characterised by high pH values (pH>8) and lime contents ($CaCO_3$>10%). There is no detectable correlation between the soluble chromium content after Lakanen-Erviö (LE), the upper limit of plasticity according to Arany or the clay-, silt- and sandy fractions.

The highest values for maximally bound chromium in leached chernozem soil were measured in the case of inorganic Cr(III)-chloride, a value of similar magnitude appeared with Cr(III)-ascorbate. In the case of the organic complexes of Cr(III)-oxalate, Cr(III)-citrate, Cr(III)-ethylenediamineteraacetate, Cr(III)-malonate, Cr(III)-histidinate, with a lessening of the acidic character also the amount of Cr(III)-ions in the solution decreases and therefore more and more of it gets adsorbed to the soil's adsorption-complex.

3.7. The effect of Cr(III)-picolinate upon the chromium absorption of plants

The low chromium content of plants is based on the one hand on the low solubility of Cr(III)-ions in soils and, on the other hand on the poor translocation of chromium within the plants. Organic acids or complex-building compounds added to the soil enhance the change of chromium to a dissolvable form and, thereby a larger quantity of chromium becomes available to plants. In pot experiments twice as much chromium can be shown in the roots and four times more in the shoots of fodder radish as a result of a combined, large dose (100 $mg\cdot kg^{-1}$) treatment (combined use of $CrCl_3$ and picolinic acid) as compared to a treatment with $CrCl_3$ of eaqual concentration alone. The combined treatment stimulated translocation of chromium from roots into the shoots. A higher chromium content appearing in plant tissues points to a formation of organic Cr(III)-picolinate (in soils), a compound which will be easier taken up by plants due to its better solubility. The sole application of picolinic acid did not change the chromium content of certain plant parts, which means that presumably no considerable amount of Cr(III)-picolinate is formed with those Cr(III)-ions being present already in the soil.

A treatment of Cr(III)-picolinate (Cr-pik) at small concentrations (0,1-5 $mg\cdot kg^{-1}$) leads to a slow increase in the chromium content of plant organs (Fig. 7). A rapid increase can be shown at dosages of 5 $mg\cdot kg^{-1}$ in the roots and of 20 $mg\cdot kg^{-1}$ in the shoots and this continues up to a value of 100 $mg\cdot kg^{-1}$. After the application of freshly prepared (100 $mg\cdot kg^{-1}$) Cr(III)-picolinate to the soil twice as much chromium appeared in the roots and one and a half times as much in the shoots as in the case of a combined treatment (combined use of $CrCl_3$ and picolinic acid) at equal concentration.

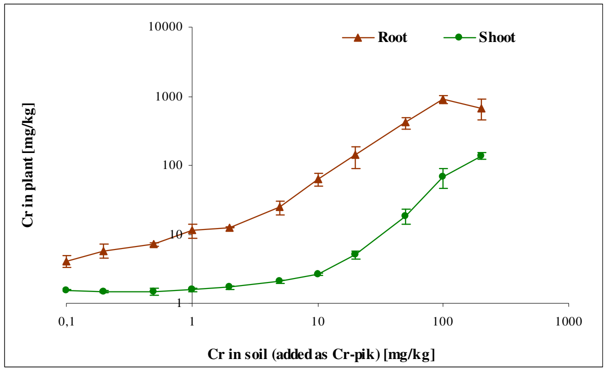


Figure 7: The effect of Cr(III)-picolinate applied at different concentrations upon the chromium accumulation of fodder radish (pot experiment, at Nyíregyháza, 1999)

When applying Cr(III)-picolinate by watering several times in small quantities, the chromium concentration in the roots of the fodder radish reached levels seventy times higher than in the comparable untreated culture, while in the shoots it became fourty five times higher. The high dosage (100 mg·kg^{-1}) treatment with $CrCl_3$ combined with picolinic acid increased equally both in fodder radish and in komatsuna the translocation of chromium. As a result of this the appearing chromium amount in the shoots of the fodder radish was two and a half times higer and in the shoots of komatsuna it was twice higher than in a treatment with only $CrCl_3$. EDTA brought out together with highly concentrated (100 mg·kg^{-1}) $CrCl_3$ achieved similar effects than picolinic acid. Treatment with highly concentrated (100 mg·kg^{-1}) $CrCl_3$ in combination with picolinic acid enhanced beside the uptake of chromium also that of copper, iron, manganese and molybdenum in the roots of fodder radish and, in the shoots of komatsuna it enhanced the absorption of copper, iron and nickel. Applying EDTA together with highly concentrated (100 mg·kg^{-1}) $CrCl_3$ had similar results than with picolinic acid, it increased the accumulation of chromium, copper, iron and maganese in the roots of fodder radish and in the shoots it increased that of chromium and copper.

No effects were shown on the chromium uptake of fodder radish after the multiple application of picolinic acid onto soils contaminated with leather factory sewage sediment. Also the single or multiple application of picolinic acid on soils contaminated by galvanic mud did not help much in the absorption of chromium into roots and shoots of fodder radish, respectively with the translocation of chromium within these organs.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. General characterization of the total chromium content

In the soil samples representing the north-eastern region of Hungary the measured total chromium content is between 5-50 mg·kg^{-1}, with more than 80% of the results being in the range of 20-25 mg·kg^{-1}. In light of the measured results and the known land use we can state that the chromium content of soils in the studied counties is well below the acting value (of 150 mg·kg^{-1}). Both the land areas used for agriculture and those being outside of it do not contain chromium quantities which are toxic or could become toxic.

We have studied the total chromium content of the soils of Hungary according to the main types as determined by the genetical and soil-geographical classification system (Fig. 3). The chromium content of the different soil types is fundamentally influenced by the amount of the clay fraction and the humus content, which can be modified through the influence of pH-value.

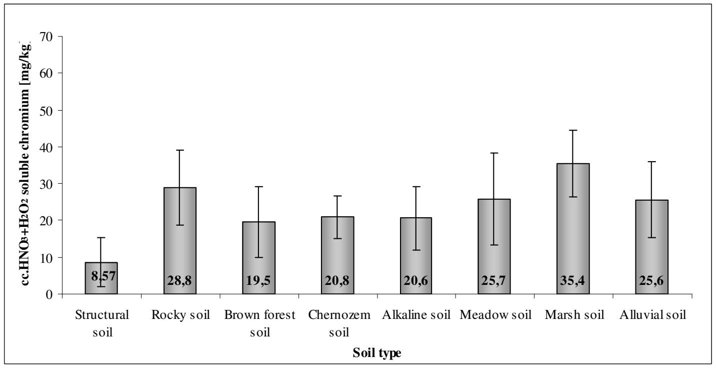


Figure 3: The general chromium content of the main soil types (SIM, 1998)

While applying the methods we assumed that the majority of the studied samples is not contaminated with chromium and that the element content of the samples is of geogenic origin. Figure 5 shows the connection between the concentrations of yttrium-chromium and aluminium-chromium from the soils of the studied regions.

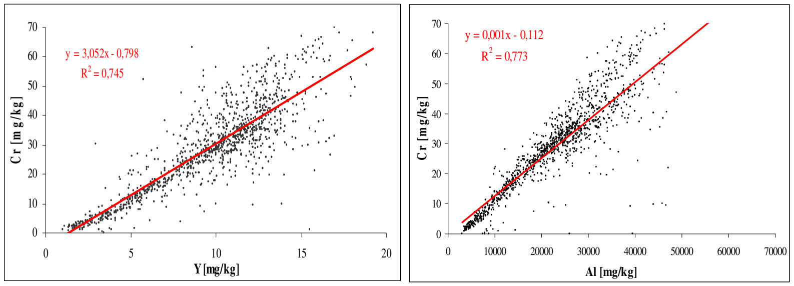


Figure 5: Correlations between the yttrium-chromium and the aluminium-chromium from soils of the north-eastern region of Hungary (SIM, 1998)

The geogenic chromium concentration of the studied soils can be calculated with close approximation if knowing the yttrium or aluminium concentrations, which were established by measuring the equations of the fitted curves. The slightest contamination which can still be detected by methods of normalization is 15-20 mg·kg^{-1}, which is however, not independent of the concentration. It will decrease in soils with smaller yttrium or aluminium contents (e.g. sandy soil) to 5-10 mg·kg^{-1}.

We extended both kinds of the normalization methods, which we have applied to the north-eastern regions of our home country, also to the whole of Hungary, thereby examining the correlations between chromium-yttrium and chromium-aluminium from the upper layers of SIM soil samples from the country's whole area. We can call those SIM sample taking places „hot spots“ where the arithmetical mean of the amount of chromium of non-natural origin, – which had been determined using the two different methods of normalization –, shows a value larger than 20 mg·kg-1. We have found in six soil profiles of the entire country chromium concentrations which can be regarded as „hot spots“. On those locations the contaminating sources could be identified each time and besides this it was characteristic that the examined soils were situated on the flood plains of rivers or brooks. The chromium contamination was carried by the sediments of the flooded river and due to these floodings the chromium content of the adjoining soils increased.

3.5. The speed of formation and the adsorption isotherms of Cr(III)-complexes

At room temperature the formation of Cr(III)-complexes is a slow process, while little is known about the reaction mechanism and its speed taking place in soils. The study of both the geogenesis of Cr(III)-picolinate in soils and of the speed of this reaction is essential to the Cr^{3+} content of the soil-solution and, thereby also from the point of view of the amount of plant-absorbable Cr(III) ion forms. Cr(III)-picolinate complex develops in aqueous solution at temperatures of 5-20°C with measurable speed; the reaction proceeds within 10-15 days. Complex formation in soils takes place generally according to a kinetical model of second order and at measurable speed. In soils with different ion strength and different pH-value the speed will vary accordingly. The established data for the reaction kinetics have only information character, they refer to the magnitude of the reaction's speed which are proof of the formation of Cr(III)-picolinate in soils.

3.6. The adsorption isotherms of Cr(III)-complexes

With the determination of the adsorption isotherms of Cr(III)-complexes we can characterise the behaviour of both Cr^{3+} ions which are added to the soil or which develop in the soil with organic bonds. By this method we can establish the amount of metal ions in the soil. The adsorption of Cr(III)-compounds is – besides the adsorption capacity of the soil –, also strongly influenced by the soil's pH-value. At slightly acidic chemical reactions (pH>5,5) the Cr(III) ions already precipitate from the solution. Therefore its concentration is determined by the solubility product and not by the adsorption equilibrium.

For the mapping of the adsorption isotherms we recorded the concentration of the equilibrium solution as a function of adsorbed chromium in the soil. Then, after linearizing the curves we got the adsorption lines (Fig. 6) and calculated the respective adsorption parameters of the examined soils.

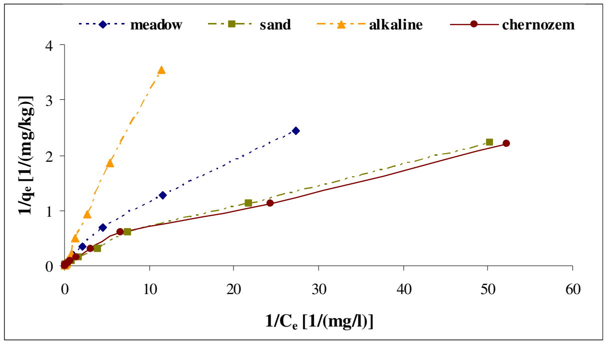


Figure 6: The adsorption lines of Cr(III)-picolinate at different soils and room temperature

From the slopes of the curves we can conclude that the adsorption places of the different type have a common presence. The adsorption curves of leached chernozem and humous sandy soils have similar slope. Among the studied soils the meadow solonetz had the largest slope. While examining the adsorption of Cr(III)-picolinate we found that the meadow solonetz soil can adsorb six times more and the meadow soil twice as much as either the humous sandy or the leached chernozem soils.

Of the inorganic form of Cr(III) twenty times more can be adsorbed in sandy soils and fifty times more on chernozem soils than in the case of the organic form of Cr(III). Cr(III)-picolinate adsorbs less to the examined soils than the inorganic Cr(III) ion. Therefore it is present in larger concentration in the soil solution and it becomes more available for plants. Based on this results we may conclude that the the chromium content of plants can be increased with Cr(III)-picolinate.

The measured equilibrium solution concentrations gained from studying the adsorption of various Cr(III)-complexes in leached chernozem soil support the statement by JAMES and BARTLETT (1983a)[2] that compounds containing several ligands (e.g. citric acid) keep Cr(III) ions in solution. The stability of Cr(III)-complexes increases with a rise in either the number of carboxyl groups, respectively in the case of acids with equal valence it increases with the rise in its acidic character.

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[2] James, B. R. és Bartlett, R. J. (1983a) Behavior of chromium in soils. V. Fate of organically complexed Cr(III) added to soil. Journal of Environmental Quality **12**, 169-172.

Should the total chromium amount measured in the soil remain below the limit value however, be above the limiting value after Lakanen-Erviö for dissolvable chromium (3 mg·kg^{-1}), then by all means the determination of Cr(VI) is recomended. Cr(VI) ions as well as by the reduction of Cr(VI) ions newly formed Cr(III)-complexes and Cr(III)-hydroxide dissolve better in the solution of Lakanen-Erviö than chromium found on clay minerals. Therefore a higher LE chromium concentration is generally indicative of Cr(VI) contamination.

3.3 The rare earth elements content of soils of Hungary

Of SIM soil samples from the north-eastern region of Hungary the elements of the scandium group and the lanthanides can well be measured. Some of them can not really be regarded as rare, e.g. the average concentrations of neodymium and chromium are in the same range (Figure 3, Table 1).

Table 1: Concentration of rare earth metals in soil of Hungary (SIM, 1998)

Symbol of element	Minimum [mg·kg^{-1}]	Maximum [mg·kg^{-1}]	Median [mg·kg^{-1}]	Mean [mg·kg^{-1}]	Deviation [mg·kg^{-1}]
Gd	0,05	19,9	10,4	9,64	3,68
Nd	0,10	87,6	21,7	21,6	12,0
Pr	0,10	29,2	5,03	5,23	2,90
Sc	0,01	20,7	4,78	4,74	2,33
Sm	0,10	16,7	6,76	6,19	2,34
Tb	0,10	1,47	0,62	0,56	0,36
Y	0,02	40,7	10,2	9,62	4,06
Yb	0,02	2,74	0,79	0,74	0,41

Comparing the results with data from international samples we can see that the values agree in their order of magnitude. We have conducted analysis of correlation with the data of the scandium group and of the lanthanides according to which the tightest correlation (r=0,967) can be found among the yttrium-ytterbium. Analysing the correlation between yttrium and (all) the studied elements, the closest correlation appeared with chromium (r=0,705) and with aluminium (r=0,680).

3.4. Applying the methods of normalization

When working out the normalization procedures we started out from the close correlation between chromium-yttrium and chromium-aluminium.