

Experimental study of the impact of the chrome from high energetic efficient fertilizers on the soil

Brazilian environmental legislation on the effects of some chemical elements discarded on the soil is still very recent, especially regarding the various transformations of different types of chromium that can be used together with fertilizer made of leather scraps. This fact is mainly due to lack of experimental data that show clearly the various modifications undergone by the various types of chromium released into the earth's crust, associated with fertilizers. This very fact does not occur in many developed countries, such as Italy for example, where there are already several studies on the effects of various types of chromium, which are used in conjunction with leather fertilizer. This work presents an experimental study on the behavior of chromium (III) in arable soil, using hydrated leather fertilizer as energy-efficient fertilizer.

Palavras-chave: Hydrated Leather Fertilizer; Effects on The Soil; Fertilizer Efficiency.

Estudo experimental do impacto do cromo a partir de fertilizantes altamente energeticamente eficientes no solo

A legislação ambiental brasileira sobre os efeitos de alguns elementos químicos descartados no solo ainda é muito recente, especialmente no que diz respeito às várias transformações de diferentes tipos de cromo que podem ser usados em conjunto com fertilizantes feitos de restos de couro. Este fato é principalmente devido à falta de dados experimentais que mostram claramente as várias modificações sofridas pelos vários tipos de cromo liberados na crosta terrestre, associados a fertilizantes. Este fato não ocorre em muitos países desenvolvidos, como a Itália, por exemplo, onde já existem vários estudos sobre os efeitos de vários tipos de cromo, que são usados em conjunto com fertilizantes de couro. Este trabalho apresenta um estudo experimental sobre o comportamento do cromo (III) em solo arável, utilizando fertilizante de couro hidratado como fertilizante eficiente em energia.

Keywords: Fertilizante em Couro Hidratado; Efeitos Sobre o Solo; Fertilizantes Eficientes.

Topic: **Química Agrícola e Ambiental**

Received: **02/02/2016**

Approved: **05/04/2016**

Reviewed anonymously in the process of blind peer.

Elizete Maria Possamai Ribeiro

Universidade Federal do Rio Grande do Sul, Brasil
<http://lattes.cnpq.br/5228899163052587>
elizete@ifc-sombrio.edu.br

Luciano Cavani

Università di Bologna, Itália
<https://www.unibo.it/sitoweb/luciano.cavani/cv>
luciano.cavani@unibo.it

Claudio Ciavatta

Università di Bologna, Itália
<https://www.unibo.it/sitoweb/claudio.ciavatta/cv>
claudio.ciavatta@unibo.it

Pedro Barbosa Mello

Universität Stuttgart, Alemanha
<http://lattes.cnpq.br/2188183903167580>
mello@mecanica.ufrgs.br

Rafael dos Reis Paulo

Universidade Federal de Pelotas, Brasil
<http://lattes.cnpq.br/1449294392943584>
rafael.drp@hotmail.com

Renata Possamai Ribeiro

Fundação Universidade Regional de Blumenau, Brasil
<http://lattes.cnpq.br/1724859629535246>
renatapossamai@yahoo.com.br



DOI: 10.6008/SPC2179-6858.2016.002.0002

Referencing this:

RIBEIRO, E. M. P.; CAVANI, L.; CIAVATTA, C.; MELLO, P. B.; PAULO, R. R.; RIBEIRO, R. P.. Experimental study of the impact of the chrome from high energetic efficient fertilizers on the soil. **Revista Ibero-Americana de Ciências Ambientais**, v.7, n.2, p.16-28, 2016. DOI: <http://doi.org/10.6008/SPC2179-6858.2016.002.0002>

INTRODUÇÃO

In Brazil, environmental legislation is fairly recent, the concerns and studies on the environment move in small steps, what makes us think that we live in a country that lacks research and investments, especially those that refer to the behavior of chromium (III) present in fertilizers.

Chromium is the tenth most abundant metal in the earth's crust. The main mineral is chromite (FeCr_2O_4) which is chromium in oxidation state III (BARTLETT, 1997).

The compounds of Cr (III) present in or added to the soil are inert. The Cr (III) can be oxidized to Cr (VI) because it is quite soluble and reactive, according Gallon and Giacomolli (2006). It is also a goal of this study, from an economic and environmental point of view, to present an alternative for the management of solid waste from tanneries.

Cr (VI) requires temperatures above 423K and a very acidic environment, ie pH <1. These conditions in agricultural soils are practically nonexistent.

Adding Cr (III) to a soil containing oxygen, hydrogen and manganese, some ions are oxidized. On the other hand, if Cr (VI) is added to the same soil, many ions, or maybe all the ions, will be immediately reduced (CIAVATTA; SEQUI, 1989).

In soils, the Cr (III) is relatively immobile due to its strong adsorption capacity. In contrast, Cr (VI) is highly unstable and mobile, since it is not easily adsorbed by the soil under natural conditions. The redox reaction (oxidation of Cr (III) to Cr (VI) and reduction of Cr (VI) to Cr (III) is an important process which affects the specificity and consequently, bioavailability and toxicity of chromium in the soil. The oxidation can occur in the presence of manganese and iron oxides in cool, moist soils (anaerobic conditions) and under mildly acidic conditions. The reduction can occur in the presence of sulfide and iron (II) (anaerobic conditions) but is also accelerated by the presence of soil organic matter (MUKHERJI; ROY, 1977).

The use of organic waste in agriculture such as animal manure, sewage sludge, urban waste and industrial waste have as their main idea the usage of land as means for transforming and detoxifying the supply of nutrients to plants. However, these wastes contain different quantities of heavy metals which can reach the ground and accumulate to toxic levels for the food chain. In soil, adsorption reactions, complexation, precipitation and oxidation-reduction control the availability and the solubility of the metals. The limestone and manure applications decrease the solubility and availability of metals. Thus, the study of the agricultural use of urban waste containing high levels of heavy metals is of great importance, in that it seeks to reduce pollution, without, however, polluting another ecosystem (ANDREOLI et al., 1999).

The levels of soluble heavy metals in the soil are generally low. However, the usage of fungicides, mineral fertilizers and animal waste in agriculture, in addition to the disposal of urban waste, such as domestic waste, industrial waste and sewage sludge, may increase the concentrations of heavy metals in the soil at levels capable of causing damage the biota. Potential sources of soil contamination, urban and industrial wastes are those with greater variation in levels of heavy metals, which are closely related to regional economic activity (ANDREOLI et al., 1999).

According Andreoli et al (1999), the main sources of contamination of agricultural land by heavy metal in Paraná are: compost, animal manure, fertilizers, phosphate, limestone and fungicides. Other sources of contamination such as dust, smoke and sewage sludge are limited to the vicinity of industries, to mining areas and urban centers.

In pig manure analysis, widely used in western Paraná, Oliveira and Parizotto (1994) found 463 mg / kg of copper and 1,130 mg / kg of Zn. Kamogawa and Miyazawa (1996) observed the following levels of heavy metals in chicken manure: Cd <1.0 mg / kg; Co 4.67 mg / kg; Cr 111 mg / kg; Cu 321 mg / kg; Ni 40,3 mg / kg Pb 61 mg / kg and 1,064 mg Zn / kg. However, in Brazil, there are few studies on contamination of agricultural soils by heavy metals and also about their levels in used inputs.

Chromium (III) can enter the ground in various ways common to all heavy metals, including waste from mines, smelters, atmospheric deposition and tannery sludge. In many areas, chromium (III) is not the greatest soil pollution problem. In Italy, tanned leather leftovers with chromium (III) are converted into leather flour, which are accepted as rich in organic fertilizers and nitrogen regulated by Italian directive number 748 (CIAVATTA; SEQUI, 1989). This fertilizer contains organic matter with a high concentration of mineralized nitrogen, around 10-13% and further containing 1 to 3% of chromium (III) (CIAVATTA; SEQUI, 1989). Chromium (III) is considered one of the least toxic heavy metals in the soil, but the high concentrations found in the fertilizer residue derived from leather and the residence time in soil require careful monitoring. It is therefore necessary that all aspects of risks posed to the environment by chromium (III) added to the soil to be carefully explored. For example, while forms of chromium (III) present in the residues are considered immobile, the chromium (VI) is soluble and extremely toxic to plants (TURNER; RUST 1971). And mesofauna soil (UEDA et al, 1988). In the European Union there is no concentration limit for Cr (III) on the ground. As for heavy metals such as Cu (copper), Cd (cadmium) and Zn (zinc), limits restrict the amount accumulated in agricultural soil (BROOKES; TIWARI; GRACE, 1997). These limits are based on the effects of metals in plant and animal health. Effects and processes of soil microorganisms, that is, on organic materials or soil dynamic are not taken into account.

As described by Souza et al. (1996), heavy metals in the soil may be in free form (M^{n+}), such as oxides, hydroxides, phosphates, sulfates, carbonates, sulfides or inorganic complexes. These compounds are responsible for the availability and toxicity of metals to plants. However, the total contents of these elements in the environment are not sufficient to explain the availability and consequent absorption and toxicity to plants. Some typical examples of this fact are: the occurrence of iron deficiency in rice crops planted on soil that presents high levels of this element; reducing the phytotoxicity of Al (aluminum) with the addition of organic binders and the variation of the critical level of toxicity of a specific element, depending on the soil type.

Chromium (VI) is non-essential and toxic. Compounds are corrosive, and allergic skin reactions occur soon after contact, regardless of dose. Brief exposure to high levels of chromium (VI) can result in ulceration on the skin, perforations in the respiratory tract and gastrointestinal irritation (USPHS 1997 cited in Barros et al., 2001). Chromium tends to settle in the hair, kidneys, liver, bones, spleen and lungs, in contrast, the

accumulation in the muscles seems to be very limited or even non-existent (WALLACH, 1985). Moreover, the International Agency for Research on Cancer (IARC) classifies chromium (VI) compounds as carcinogens (IARC, 1998). Prolonged occupational exposure to levels of aerial chromium higher than those of the natural environment have been associated with lung cancer.

Individuals more at risk include those working in chromate production industries and those involved in the manufacture and use of chrome pigments. Similar risks may exist in workers dealing with chrome alloys, stainless steel and chrome welders (kimbrough et al 1999;. USPHS 1997 cited in BARROS et al., 2001).

The aquatic toxicology of chromium also depends on the chemical species, because chromium (III) is biologically available and less toxic than chromium (VI). This fact comes from the observation of crustaceans (barnacles *Balanus* sp.) And polychaete (arenaceodentata *Neanthes*) (BRYAN;. LANGSTON 1992 cited BARROS et al, 2001).

The chromium content in all the refined products such as sugar, cereals, bread, is always lower than those found in raw materials, since the refining process removes 80% of the natural chromium (BURTON, 1995).

Several investigations show that chromium interacts with glucose and/ or lipid metabolism in cats, monkeys, rabbits, squirrels, turkeys, pigs, poultry, calves and humans (ANDERSON, 1988). The GTF, where chromium is an essential component, are essential for the metabolism of sugar, protein and lipids. Moreover, chromium favors the interaction between insulin and its specific receptors located on target organs such as muscles and fat tissues (MOORANDIAN; MORLEY, 1987).

Based on this assumption, it is possible to offer an explanation for the marked effect of insulin by the GTF. When the hormones bind to specific receptor and, in doing so, allowing the cellular uptake of circulating glucose and amino acids. The sugar is subsequently used as energy source under hormonal effects, promotes protein synthesis and therefore muscle development (MORDENTI; PIVA, 1997).

The required chromium (daily dose) in human adults, according to the American parameters is between 50 and 200 mg. Considering the fact that in modern nutrition often we resort to refined products, it is estimated that an American adult has a diet deficient in chromium (it covers only 40-60% of the required amount), in 90% of cases. Taking into account, of course, the fact that the daily average is around 30 mg (ANDERSON, 1987).

The need for chromium, on the other hand, appears to increase in humans and animals as a result of factors described generally as "stressing", such as fatigue, trauma, pregnancy, various nutritional forms (high glucose diet), metabolic, physical, and also as a result of environmental and emotional stress (BURTON, 1995). During stress there is increased cortisol secretion, which acts as an antagonist to insulin and thus increases the concentration of glucose in plasma. The increase in blood glucose stimulates the mobilization of chrome reserves that are irreversibly expelled in the urine. All factors that can lead to stressful situations increase the levels of chromium in the urine. This explains the fact that all factors that favor the preservation of high glucose levels and high insulin levels in the blood create predisposition for deficiency in chromium (ANDERSON et al., 1990).

The form of chromium used as a supplement is very important. Anderson (1993) added nine different forms of chromium in the diet of rats and concluded that, for some forms, including chromium chloride, there was little understanding of their action on the tissue. These variants change greatly, depending on the chemical speciation of chromium ingested the same variants do not provide information on how to estimate the amount of chromium in the diet.

The reports in the scientific literature justify many positive effects that can be obtained in animal production with the use of chromium in creating conditions in practice, very often environmental, nutritional, metabolic, and social stress. Thus, this study aims to verify and analyze the behavior of chromium (III) in the soil after application of organic fertilizer hydrolyzate bovine leather so you can use this fertilizer in the development of vegetables.

TOOLS AND METHODS

For the experiment two types of soil were used and the collection was made horizontally, 5 cm surface in the same horizon. One soil sample was collected from banana production site, located in highway Jacinto Machado-SC. The location of soil is: 04'24,73 29 'S and 49 48'05,38' 'W and its classification is clayey red soil made of basaltic source material.

The other soil sample used in the experiment was taken from the town of Praia Grande-SC typically used for manioc production. The location of soil is: 29 03'41.11 " S and 49o47'31.79 " W and its classification is sandy - quartzarenic neosoil.

After collection, soils were crumbled, air-dried, sieved (2 mm) and divided into 12 portions for each soil type. These portions divided in fractions of 200 g (dry basis) that were placed in polypropylene flasks of approximately 178 cc in volume. These fractions had water added twice a week for a year. The incubation period was conducted in the laboratory of Bologna University (UNIBO) with ambient air temperature and humidity.

The design of the experiment was completely randomized in a factor of 3x2x4, which corresponds to three soil portions, two leather fertilizer (powder and pellet) and four repetitions of the measurements. The fractions of each soil composed 24 samples.

The treatments consisted in the use of one control sample and a type of leather fertilizer with particle size less than or equal to 2 mm in 4 soil portions, with 14% base nitrogen (dose 0 = 0 control, Dose 1 = 143 mg of fertilizer per 100 mg of soil, Dose 2 = 714 mg of fertilizer per 500 mg of soil and 3 = 1430 mg dose of fertilizer per 1000 mg of soil). The fertilizer particle size larger than 2 mm had 13.3% of base nitrogen (Dose 0 = 0 control, 1 dose = 150 mg of fertilizer per 100 g of soil, Dose 2 = 750mg of fertilizer for 500mg of soil and Dose 3 = 1500 mg of fertilizer per 1000 mg of soil), noting that all samples were done in triplicate.

To make a comparison of the experimental results of Brazilian soil three types of soil were used, in two soil-depths and three control samples from three different properties in the city of Pistol in the province of Tuscany, Italy. The criteria of the sampling was that one was soil taken from farms that use leather fertilizer for over thirty years, and another was taken from soil from the same property but that has never had contact

with the leather fertilizer. In Nanni farm at 0-30 and > 30 cm of deep, Lord Franco Alessandro's seedplot, in San Pierino Casa al Vesgovo - Pistoia; On the farm Nicolai farm at a depth of 0-50 and > 50 cm from Mr. Nicolai Giorgia's seedplot in Quarrata - Pistoia; On the Buong farm 0-30 and > 30 cm deep in the Lord Buongiovanni's seedplot in Badia a Pacciana - Pistoia. The control samples are from Nanni farm at 20 cm of depth, Bongiovanni's farm at 15 cm of depth and Nicolai's farm at 50 cm of depth.

The design of the experiment was casual, but the depths of the soil were chosen to match the type of produce. In the province of Pistoia -Toscana, leather fertilizer is widely used for seedplots and ornamentals. This fertilizer is applied to the soil's surface. The amount used by property is the average of 1000 to 1600 kg per hectare per year.

The farms were chosen specifically because of their intense use of leather fertilizer: up to twice a year, in spring and autumn. The producers claim that to increase the quality of the produce and to increase the fertility and growth of the plants an analysis of soil should be done at least once every 5-8 years.

To obtain the extractable chromium in the Brazilian soil, 1 g of each prepared moist soil (i.e. containing the leather fertilizer in proportions previously mentioned) was weighed and put in plastic mini-vials with 50 ml of 10 mM citric acid ($C_6H_8O_7$) and 20 mM sodium hydroxide (NaOH), then stirred intermittently for 18 hours to measure the extractable chromium. Once the 18 hour period was over the samples were left at rest for decantation. The solid material was filtered on Whatman 42 filter paper and afterwards transferred to plastic vials and stocked at 4 °C. Chrome levels were read in the equipment atomic absorption spectrometry (ICP

The phosphate method was used to detect and measure the Cr (VI) and is described step-by-step below:

1. The extraction of Cr (VI) from soil-samples was performed using a saline buffer solution of Potassium dihydrogen phosphate (K_2HPO_4 / KH_2PO_4) in a volume of ten-thousandth part of the mole (10 mM) at pH 7. Fifteen milliliters (15 ml) of K_2HPO_4 / KH_2PO_4 were added to 5 g of dry soil (a proportion of 3 to 1).
2. The sample spent an hour in an automatic stirrer.
3. The process of separating the solid and liquid parts of the sample was done in a Beckman Coulter centrifuge. The solid particles of samples sunk to the bottom of the container, leaving the liquid portion on top. The sample was centrifuged at 10,000 rpm for 10 minutes at a temperature of 19 °C;
4. The sample was filtered on Whatman 42V filter.
5. Reaction: to prepare the solution of diphenylcarbazide (DFC), 0.4 g of this reactant was dissolved in 100 ml of ethanol, containing 120ml H_3PO_4 at 85%, and 280ml of distilled water. The solution was transferred and maintained in amber vial to avoid photochemical degradation of the reagent.
6. To 5 ml of the extract it was added 1 ml of CFD reagent and allowed to react for 20 minutes. The spectrophotometer was used to measure the intrinsic capacity of the soil to absorb radiation at a specific frequency in very small magnitude unit (nm) to 540 nm.

To measure the total amount chromium through the soil mineralization the steps were the following:

1. Pick fine-grained samples of the soils to be mineralized.
2. Weigh 0.25 g triplicates of each sample with a precision scale, masking the positions in the pump. The pumps are cylindrical containers on white teflon, which have an wide or narrow top edge (Picture 2).

3. Put 6ml of hydrochloric acid (HCl) and 2 ml of nitric acid (HNO₃) with special pipettes.
4. Put the pumps inside "the linear" (a heat sink) secured with a teflon cap and add a ventilation ring to release gases from strong acids and two safety valves to withstand the increase in pressure (P > 100atm) due to formation of CO₂.
5. Put the container in a microwave oven with the same settings as shown in Picture 3.
6. Wait 20 minutes from the beginning of the system and to allow room for ventilation.
7. Take the container from the microwave oven and wait until the pumps are at room temperature, then remove the covers and caps. Rings and valves should be washed with distilled water.
8. Carefully pour the contents of the pumps in 20ml flasks with the help of a funnel and add MilliQ water to fill the rest of the volume. It's important not to use regular distilled water as not to cause misreadings with the ICP.
9. Cap the flasks and stir, then filter the contents, name them and do the reading with the ICP.

With the documented extraction procedures of Cr from Brazilian and Italian soil, it is necessary to determine the fractionation of total Cr and Cr (VI) that are soluble in water. Samples underwent a series of extractions procedures, with six different reactants: potassium dihydrogen phosphate - KH₂PO₄ (0,015 mol dm⁻³) to measure the amount of soluble chromium -, ammonium Chloride - NH₄Cl (1mol dm⁻³) to measure the exchangeable chromium -, sodium pyrophosphate - Na₄P₂O₇ (0,1mol dm⁻³) to measure the chromium attached to the organic matter -, sodium acetate - NaCH₃COO (1 mol dm⁻³) in a pH of 5 to measure chromium connected to carbonates -, hydroxylamine hydrochloride - NH₂OH·HCl (0,04 mol dm⁻³) with 25% v/v of acetic acid at pH 2 to measure chromium connected to oxides and hydroxides - and Nitric acid - HNO₃ (1 mol dm⁻³) to measure chromium connected to sulfates.

A total of 9 soil samples in duplicate from Toscana were analysed, weighed and put in plastic flasks of 50ml to be centrifuged. The different reactants were packed in a freezer until all were used. All extracts were done in duplicate. The concentration of these extracts were measured in the atomic absorption spectrometer (ICP). To extract the Cr the steps are the following.

First extraction - water soluble Cr, with potassium dihydrogen phosphate:

1. Weigh 2,00g of soil, add 20ml of KH₂PO₄ (0,015 mol dm⁻³), stir for 2 hours and centrifuge for 20 minutes at 10000 rpm.
2. Filter the liquid with Whatman No. 42 paper into another set of plastic flasks and store them in a freezer.
3. Weigh the solid left on the filter, put it back into its original vial, add 20ml of deionized water, stir it with a vortex mixer and centrifuge it for 20 minutes, let it rest then discard the water.

Second extraction - exchangeable Cr, with ammonium chloride:

1. Add 20ml of NH₄Cl (1mol dm⁻³) to the washed soil sample, stir for 4 hours and centrifuge for 20 minutes at 10000 rpm.
2. Filter the liquid with Whatman No. 42 paper into another set of plastic flasks and store them in a freezer.
3. Weigh the solid left on the filter, put it back into its original vial, add 20ml of deionized water, stir it with a vortex mixer and centrifuge it for 20 minutes, let it rest then discard the water.

Third extraction - Cr attached to the organic matter, with sodium pyrophosphate:

1. Add 20ml of $\text{Na}_4\text{P}_2\text{O}_7$ ($0,1\text{mol dm}^{-3}$) to the washed soil sample, stir for 4 hours and centrifuge for 20 minutes at 10000 rpm.
2. Filter the liquid with Whatman No. 42 paper into another set of plastic flasks and store them in a freezer.
3. Weigh the solid left on the filter, put it back into it's original vial.

The fourth extraction used the same methodology and reactant of the the third extraction, but the stirring time is 18 hours. There was no need to wash the soil with water after the third extraction but it was washed after the fourth extraction with 20ml of deionized water just like it was done in the 3rd step the first and second extractions. The extracts obtained from the 3rd and 4th extractions were analysed separately but the concentrations results were summed.

Fifth extraction - Cr connected to carbonates, with sodium acetate:

1. Add 20ml of NaCH_3COO (1 mol dm^{-3}) to the washed soil sample, stir for 4 hours and centrifuge for 20 minutes at 10000 rpm.
2. Filter the liquid with Whatman No. 42 paper into another set of plastic flasks and store them in a freezer.
3. Weigh the solid left on the filter, put it back into it's original vial.

The sixth extraction used the same methodology and reactant of the the fifth extraction, but the stirring time is 18 hours. There was no need to wash the soil with water after the fifth extraction but it was washed after the sixth extraction with 20ml of deionized water just like it was done in the 3rd step the first and second extractions. The extracts obtained from the 5th and 6th extractions were analysed separately but the concentrations results were summed.

Seventh extraction - Cr connected to oxides and hydroxides, with hydroxylamine hydrochloride:

1. Add 20ml of $\text{NH}_2\text{OH}\cdot\text{HCl}$ ($0,04\text{ mol dm}^{-3}$) with 25% v/v of acetic acid to the washed soil sample, stir for 5 hours and centrifuge for 20 minutes at 10000 rpm.
2. Filter the liquid with Whatman No. 42 paper into another set of plastic flasks and store them in a freezer.
3. Weigh the solid left on the filter, put it back into it's original vial.

The eighth extraction is a repeat of the seventh extraction but afterwards the sample was washed 20ml of deionized water just like it was done in the 3rd step the first and second extractions.

Ninth extraction - Cr connected to sulfates, with nitric acid:

1. Add 20ml of HNO_3 (1 mol) to the washed soil sample, stir for 4 hours and centrifuge for 20 minutes at 10000 rpm.
2. Filter the liquid with Whatman No. 42 paper into another set of plastic flasks and store them in a freezer.
3. Weigh the solid left on the filter, put it back into it's original vial.

The tenth extraction used the same methodology and reactant of the the ninth extraction, but the stirring time is 18 hours. There was no need to wash the soil with water after the ninth extraction.

RESULTS

For the experiment of chromium extraction with Brazillian soils, the samples were made using a mixture of the two types of soils with the leather fertilizer according to the particle size (powder and pellet).

Considered P fertilizer with a particle size <2 mm the following proportions: P1 = 143mg of leather fertilizer to 100 g of soil, P2 = 714 mg of leather fertilizer to 500 mg of soil and P3 = 1430 mg of leather fertilizer to 1000 mg of soil. However, the fertilizer particle size larger than 2 mm were based G1 = 150 mgof leather fertilizer to 100 g of soil, G2 = 750 mg of leather fertilizer to 500 mg of soil and G3 = 1500 mgof leather fertilizer to 1000 mg of soil). The analyzes were performed at four times: in time T0 on 09/08/2011, T1 on 12/09/2011, T2 on 12/10/2011 and T3 on 12/11/2011.

According to the extraction method of extractable chromium, one can observe that the values become smaller with the passing months (Table 1 and 2). And in the third month it was not detected any extractable chromium concentration in some leather fertilizer quantities. It is noted that the extractable chromium does not influence in nitrogen mineralization, since the organic material in leather fertilizer is relatively easy to decompose, which confirms that the organic material contained in the fertilizer plays a role in the high fraction of nitrogen mineralization and also adds a significant amount of total N.

Table 1: Amount of extractable Cr on sandy soil.

Time (Days)	Amount of powdered fertilizer				Amount of pelleted fertilizer		
	Branco (mg kg ⁻¹)	P ₁ (mg kg ⁻¹)	P ₂ (mg kg ⁻¹)	P ₃ (mg g ⁻¹)	G ₁ (mg kg ⁻¹)	G ₂ (mg kg ⁻¹)	G ₃ (mg kg ⁻¹)
T ₀ = 0	1,77	2,13	3,23	5,07	2,12	3,58	4,52
T ₁ =30	1,47	1,59	2,31	4,57	1,65	2,37	4,33
T ₂ = 60	0,1	0,9	0	0	0	2,47	0,1
T ₃ = 90	0,36	0,1	0,49	2	0,5	0,93	1,83

Table 2: Amount of extractable Cr on clay soil.

Time (Days)	Amount of powdered fertilizer				Amount of pelleted fertilizer		
	Branco (mg kg ⁻¹)	P ₁ (mg kg ⁻¹)	P ₂ (mg kg ⁻¹)	P ₃ (mg kg ⁻¹)	G ₁ (mg kg ⁻¹)	G ₂ (mg kg ⁻¹)	G ₃ (mg kg ⁻¹)
T ₀ = 0	1,85	2,23	4,12	6,67	2,17	3,68	4,73
T ₁ =30	1,55	1,72	2,90	4,71	1,80	2,88	4,46
T ₂ = 60	0,15	1,3	0	0	0,083	1,03	0,15
T ₃ = 90	0,41	0,57	1,03	1,62	0,53	0,83	1,33

Results of Cr (VI) extraction by the phosphate solution were based on the cyclic process of NRIAGU e NIEBOER in relation to the oxidation and reduction of chromium. That said, chromium's complete cycle is thermodynamically stable in relation to water and air, but is less stable on soil. The HCrO₄⁻ (Cr₆⁺) anion is removed temporarily from the cycle, being absorbed, precipitate or washed into the ground-water system, or extracted by living organisms. It eventually returns to the cycle, probably reduced (NRIAGU; NIEBOER, 1988). This ion is reduced in a process known as decromification, analogous to denitrification which is the most important part of the nitrogen cycle. Such reduction of Cr₆⁺ is carried out by carbon through photosynthesis. After the reduction of Cr (VI), the resulting Cr (III) reacts with several ligands which may make it unreactive. Mobile binders, such as citrate, complexed with Cr (III) and bind with the manganese oxide on the soil surface, which is where the chromium and citrate are oxidized. It is also oxidizable it by the oxygen in the air under UV radiation but that is beyond the scope of this wo.

When the organic binders are present in excess relative to Cr (III), these organic compounds tend to induce reverse reaction of MnO₂ connecting the Mn₃⁺ ion. That ion can prevent the formation of Cr (IV) or lower so this is formed by accelerating the rotation cycle (BARTLETT, 1986, NRIAGU: NIEBOER, 1988).

With this principle has led to study the chrome behavior in soil, it was observed that with all the amount of manganese oxide (MnO₂), the amount of organic matter in the bovine leather fertilizer were no detectable amounts of Cr (VI) in Results of samples.

According to the method of extraction of total chrome, it can be observed that the soil Nanni property of the total amount of chromium found in the studied depth is 244.8 mg / kg. In Nicolai property of soil at a depth of 0-50 cm and greater than 50 cm presented 244.8 mg / kg, once the Buongiovanni property 0-30 cm and greater than 30 cm is 282.4 mg / kg. The clay soil Brazil the total chromium was 63.4 mg / kg and sandy was 3.6 mg / kg, The results are shown in Table 3.

Table 3: Extraction of the total Cr of soils from Brazil and Toscana.

Locations	Extraction	Total amount of Cr (mg/kg)	Mean (mg/kg)
1-Nanni 0-30	1,88	150,4	
2- Nanni 0-30	1,91	152,8	151,6
3- Nanni>30	2,07	165,6	
4- Nanni>30	1,41	112,8	139,2
5- Nanni testemunha	1,8	104	
6 Nanni testemunha	1,07	85,6	94,8
7- Nicolai 0-50	1,67	133,6	
8- Nicolai 0-50	1,57	125,6	129,6
9- Nicolai >50	1,62	129,6	
10- Nicolai >50	1,26	100,8	115,2
11- Nicolai testemunha	0,97	77,6	
12- Nicolai testemunha	1,14	91,2	84,4
13- Buong 0-30	1,74	139,2	
14- Buong 0-30	1,94	155,2	147,2
15- Buong >30	1,87	149,6	
16- Buong >30	1,51	120,8	135,2
17- Buong testemunha	1,01	80,8	
18- Buong testemunha	1,2	96	88,4
19- Clay Brazil	0,783	62,64	
20- Clay Brazil	0,803	64,24	63,44
21- Sandy Brazil	0,048	3,84	
22- Sandy Brazil	0,043	3,44	3,64

The values of total chromium from Nanni property of 0-30cm if divided by 30 cm the result is equal to 1.34, just as the values ??of the total chromium from Nicolai property 0-50 cm if divided by 50 the result is 1.13. The values ??of total chromium from Property Buongiovanni 0-30 is divided by 30 cm the result is 1.09. This data can be used as an indicator of where the total chromium originates. The results show that the chromium from the leather fertilizer was located on the surficial layer of ther soil (0-50 cm). This surface enrichment with total chromium is due to anthropogenic processes, i.e. are derived from human activities processes. The results of the division between the two depths does not exceed 2, it can said that the values ??found are the process in which it was determined the impact of man's activities due to the use of fertilizers used in agriculture in ornamental plant seed plots.

The soils of Toscana's seed plots were used to verify the amount of chromium due to usage of the leather fertilizer, since it's been in use there for over 30 years. To determine fractionation of the total of Cr and Cr (VI) soluble in water, the samples were followed by several sequential extractions with six different reactants:

(I) Potassium dihydrogen phosphate - KH_2PO_4 ($0,015 \text{ mol dm}^{-3}$) for soluble chromium.

(II) Ammonium Chloride - NH_4Cl (1 mol dm^{-3}) to determine the exchangeable chromium.

(III) Sodium pyrophosphate - $\text{Na}_4\text{P}_2\text{O}_7$ ($0,1 \text{ mol dm}^{-3}$) to check the chromium bound to organic substance.

(IV) Sodium acetate - NaCH_3COO (1 mol dm^{-3}) in a pH 5 to verify chromium connected to carbonates.

(V) Hydroxylamine hydrochloride - NH_2OHHCl ($0,04 \text{ mol dm}^{-3}$) with 25% v/v acetic acid to pH 2 to determine chromium connected to oxides and hydroxides.

(VI) Nitric Acid - HNO_3 (1 mol dm^{-3}) to determine chromium connected to sulfates.

The seventh (VII) extraction was not in the same sequence, the total chrome was extracted with hydrochloric acid (HCl) and nitric acid (HNO_3). The amount of Cr (VI) was not detected in analyzes.

Table 4: Sequential Extraction of total Cr from Toscana's soil.

Locations	KH_2PO_4 (Mg/kg)	NH_4Cl (Mg/kg)	$\text{Na}_4\text{P}_2\text{O}_7(1)+(2)$ (mg/kg)	$\text{NaCH}_2\text{COO}(1)+(2)$ (Mg/kg)	NH_2OHHCL (1)+(2)(Mg /kg)	$\text{HNO}_3(1)+(2)$ (mg/kg)	Total (mg: kg)
Nanni 0-30	0,08	0,04	7,39	0	39,88	6,65	54,04
Nanni >30	0	0	3,60	0	13,13	5,15	21,88
Nanni testemunha	0	0	3,76	0	9,81	4,79	18,36
Nicolai 0-50	0	0	5,62	0	30,33	5,3	41,25
Nicolai>50	0	0	4,32	0	17,93	4,75	27
Nicola testemunha	0	0	2,81	0	11,87	4,05	18,73
Buong 0-30	0,24	0,15	17,91	0	31,07	4,86	54,23
Buong >30	0	0	4,38	0	12,14	5,02	21,54
Buong testemunha	0,06	0,05	9,42	0	22,39	6,06	37,98

The results of the six columns of the table 4 were summed to calculate the percentual fraction of total chromium (Table 5) due to the soluble chromium, the exchangeable chromium, and the chromium bound organic substances, carbonates to oxides and hydroxides and sulphates. The total chromium fractions linked to oxides and hydroxides showed higher concentrations in all soils. However, the total Cr linked to organic substances and sulfates showed a lower concentration compared to chromium connected to oxides and hydroxides. Results of this study are shown in Table 5.

Table 5: Percentual fraction of total Cr from Toscana's soil.

Soils	KH_2PO_4 (%) (I)	NH_4Cl (%) (II)	$\text{Na}_4\text{P}_2\text{O}_7$ (%) (1)+(2) (III)	NaCH_2CO (%) (1)+(2) (IV)	NH_2OHHCL (%) (1)+(2) (V)	HNO_3 (%) (1)+(2) (VI)
Nanni 0-30	0,15	0,08	13,68	0	73,79	12,31
Nanni>30	0	0	16,45	0	60,00	23,54
Nanni testemunha	0	0	20,48	0	53,43	26,10
Nicolai 0-50	0	0	13,63	0	73,53	12,85
Nicolai>50	0	0	16,0	0	66,41	17,59

Nicolai						
testemunha	0	0	15,01	0	63,38	21,62
Buong 0-30	0,45	0,28	33,03	0	57,29	8,97
Buong >30	0	0	20,00	0	56,37	23,30
Buong						
testemunha	0,15	0,14	24,80	0	58,96	15,96

(I) Potassium dihydrogen phosphate - KH_2PO_4 ($0,015 \text{ mol dm}^{-3}$) for soluble chromium; (II) Ammonium Chloride - NH_4Cl (1 mol dm^{-3}) to determine the exchangeable chromium; (III) Sodium pyrophosphate - $\text{Na}_4\text{P}_2\text{O}_7$ ($0,1 \text{ mol dm}^{-3}$) to check the chromium bound to organic substance; (IV) Sodium acetate - NaCH_3COO (1 mol dm^{-3}) in a pH 5 to verify chromium connected to carbonates; (V) Hydroxylamine hydrochloride - $\text{NH}_2\text{OH}\cdot\text{HCl}$ ($0,04 \text{ mol dm}^{-3}$) with 25% v/v acetic acid to pH 2 to determine chromium connected to oxides and hydroxides; (VI) Nitric Acid - HNO_3 (1 mol dm^{-3}) to determine chromium connected to sulfates.

CONCLUSIONS

Through analysis it was shown that the total amount of chromium found in the surface layer of Toscana's soil is the result natural Pedogenic processes. These soils have been subjected to the use leather fertilizer for over thirty years. In the first 5-8 years of implementation it was applied a quantity 1600 kg of fertilizer per hectare per year, in later years it was 1000 kg of fertilizer per hectare per year.

The results of the oxidation of chromium (III) to chromium (VI) were not found in the amount of Mn in the soil studied here and in the organic matter in the leather fertilizer. The extractable chromium was observed in the first 30 days after the application of the leather fertilizer, followed by the decrease in the second period of the experiment. Chrome oxidation capacity was found insignificant on Toscana's soils. The leather fertilizer can be safely applied in soils studied here. Care must be taken with other soil types because poor in organic matter and manganese-rich soils are capable of oxidizing chromium.

It was observed through the total chromium fractionation analysis in Toscana's soils that much of the total chromium is linked to oxides and hydroxides, as well as to organic matter and sulfates, but there is a lower concentration of the chromium linked to oxides and hydroxides.

REFERENCES

ANDERSON, R. A.. Chromium. In: **Trace Elements in Human and Animal Nutrition**. 5 ed. San Diogo: Mertz, 1987. p.225-244

ANDERSON, R. A.. Chromium. In: Dekker, M.. **Trace Minerals in Foods**. New York: K Smithp, 1988. p.231-247

ANDERSON, R. A.. Recent Advances in The Clinical and Biochemical Effects of Chromium Deficiency. In *Essential and toxic trace elements in human health and disease*. **Wiley Liss**, New York, p.221-227, 1993.

ANDERSON, R. A.; BRYDEN, N. A.; POLANSKY M. M.; REISER, S.. Urinary Chromium Excretion and Insulinogenic Properties of Carbohydrates. **American Journal of Clinical Nutrition**, v.51, p.864-868, 1990.

ANDREOLI, C. V.; LARA, A. I.; FERNANDES, F.. **Reciclagem de Biosólidos: Transformando Problemas em Soluções**. Finep, 1999.

BARROS, M. A. S. D.; ARROYO, P. A.; AGULAR, E. F. S.; GARCIA, P. A.. **Problemas Ambientales com Soluções Catalíticas**. Madrid: Cytel, 2001.

BARTLETT, R. J.. **Characterizing Soil Redox Behavior in Soil Physical Chemistry**. Boca Raton: CRC Press, 1997.

BROOKES, P. C.; TIWARI, B. K.; GRACE, C. A.. The Role of Microbial Parameters in Monitoring Soil Pollution By Chromium. Endorsed by SISS (Società Italiana di Scienza Del Suolo) In: CANALI, S.; TITTARELLI, F.; SEQUI, P.. **Chromium Environmental Issues**. Milano: Franco Angeli, 1997. p.41-59

BRYAN, G. W.; LANGSTON, W. J. B.. Accumulation and Effects of Heavy Metals In Sediments With Special Reference to United Kingdom Estuaries: A Review. **Environmental Pollution**, v.76, p.89-131, 1992.

BURTON, J. L.. Supplemental Chromium: Its Benefits to the Bovine Immuno System. **Animal Feed Science Technology**, v.53, p.117-133, 1995.

CIAVATTA, C.; SEQUI, P.. Evaluation of Chromium Release During Decomposition of Leather Mealfertilizers to the Soil. **Fertilizer Research**, v.19, p.7-11, 1989.

GALLON, M. E.; GIACOMOLLI, G.. **Soluções Tecnológicas para sua Empresa**. Porto Alegre: SENAI, 2006.

KAMOGAWA, M. Y.; MIYAZAWA, M.. **Avaliação da Absorção e Toxidez de Metais Pesados em Feijoeiros**. Relatório Técnico do IAPAR, 1996.

KIMBROUGH, D. E.; COHEN, Y.; WINER, A. M.; CREELMAN, L.; MABUNI, C.. A Critical Assessment of Chromium in the Environment. **Critical Reviews in Environmental Science and Technology**, v.29, n.1, p.1-46, 1999.

MORDENTI, A.; PIVA, G.. Chromium in Animal Nutrition and Possible Effects on Human Health. In: Chromium Environmental Issues. In: CANALI, S.; TITTARELLI, F.; SEQUI, P.. **Chromium Environmental Issues**. Milano: FrancoAngeli, 1997. p.131-151.

MUKHERJI, S.; ROY, B. K.. Toxic Effects of Chromium on Germinating Seedlings and Potato Tuber Slices. **Biochem. Physiol. Pflanzen**, v.171, p.235-238, 1977.

OLIVEIRA, E. L. E.; PARIZOTTO, M. L. V.. Características e Uso de Fertilizante do Esterco de Suíno. **Circular IAPAR**, n.83, 1994.

SOUZA, M. L. P., ANDREOLI, C. V., AMARAL, M. B. e DOMASZAK, S. C.. Levantamento Preliminar dos Teores de Metais Pesados em Alguns Solos do Paraná. **Sanare**, Curitiba, v.5, n.5, p.68-75, 1996.

TURNER, M. A.; RUST, R. H.. Effect of Chromium on Growth and Mineral Nutrition ou Soybeans. **Soil Science Society American Proceeding**, v.35, p.755-758, 1971.

UEDA K.; KOBAYASHI, M.; TAKAHASHI, E.. Effect of Chromate and Organic Amendments on the Composition and Activity of the Microorganism Flora. **Soil Science and Plant Nutrition**, v.34, p.233-240, 1988.

USPHS. United States Public Health Service. **Toxicological Profile for Chromium**. Agency for Toxic Substances and Disease Registry. U.S. Public Health Service USPHS, 1998.

WALLACH, S.. Clinical and Biochemical Aspects of Chromium Deficiency. **Journal of the American College of Nutrition**, v.4, p.107-120, 1985.