

## Study of Cr<sup>+6</sup> behavior in three agricultural soils

A. E. Pradas<sup>1</sup>, M. C. Lobo<sup>2</sup>, M. Gil-Díaz, A. Pérez-Sanz<sup>3</sup>

<sup>1</sup> Department of Agroenvironmental Research, IMIDRA, 28800, Alcalá de Henares, Spain, ana.elena.pradas@madrid.org

<sup>2</sup> Department of Agroenvironmental Research, IMIDRA, 28800, Alcalá de Henares, Spain, carmen.lobo@madrid.org

<sup>3</sup> Department of Agroenvironmental Research, IMIDRA, 28800, Alcalá de Henares, Spain, araceli.perez@madrid.org

**Abstract.** Chromium is a heavy metal widely used in industry. Its two most stable oxidation states are Cr<sup>+3</sup> and Cr<sup>+6</sup>. Cr<sup>+3</sup> is less soluble and remains adsorbed or precipitated in soils, meanwhile Cr<sup>+6</sup> is soluble and also a high toxic specie for living organisms. In natural environments, Cr<sup>+3</sup> is the most common specie, but industrial sources of Cr(VI) could cause environmental problems in soils, especially in agricultural systems. To some extent Cr<sup>+6</sup> could be reduced to Cr<sup>+3</sup> by the action of low pH and organic matter. In order to evaluate the influence of soil characteristics on bioavailability and stability of Cr<sup>+6</sup>, three different agricultural soils from Madrid region (Spain) were spiked with K<sub>2</sub>O<sub>2</sub>O<sub>7</sub> to reach a Cr<sup>+6</sup> concentration of 250 mg·L<sup>-1</sup> and incubated at 25°C in dark. After 14, 28 and 42 days of incubation, Cr<sup>+6</sup> was measured in the following fractions: 1) water soluble fraction, 2) exchangeable fraction and 3) total in soil. Most of Cr<sup>+6</sup> remaining in soil was found in the water soluble or exchangeable fraction, especially in the batch of basic soil. Results from this study confirm the environmental hazard caused by chromium spills in soils as it is available to plants and could be leached to the ground water for long time.

**Keywords:** Cr<sup>+6</sup>, pH, organic matter, redox reaction, agricultural soils.

### Introduction

Chromium is a metallic element that exists primarily in the mineral chromite with is presents in soils, waters, rocks, fauna and gases. It can exit in several chemical forms between 0 and 6, but Cr<sup>+3</sup> and Cr<sup>+6</sup> are the most stable forms. In soils, Cr<sup>+3</sup> occurs as a cation which could be adsorbed to the negatively charged particles of soils, especially in the smallest fraction. It could also precipitate as insoluble oxide and hydroxide compounds. Cr<sup>+6</sup> is an oxyanion commonly occurring as chromate CrO<sub>4</sub><sup>-2</sup> or dichromate CrO<sub>7</sub><sup>-2</sup> that it is repelled by the negative charge of soil to be more soluble and bioavailable than Cr<sup>+3</sup>. Because of its solubility, Cr<sup>+6</sup> enters in the living cells easily where it generates reactive oxygen species (ROS) and causes severe oxidative injuries to cell constituents and DNA. In aqueous media, the presence of each chemical form is mainly affected by pH and redox potential. In acidic media, the high redox potential of Cr<sup>+6</sup>/Cr<sup>+3</sup> couple favours Cr<sup>+3</sup> stabilization. In contrast under alkaline conditions (pH 7-10) the redox potential decreases rendering in Cr<sup>+6</sup> stabilization.

In soils, thanks to the process of “dechromification”, organic matter acts as an electron donor in Cr<sup>+6</sup> reduction

and makes Cr<sup>+3</sup> the predominant form in natural environments (Bartlett. 1991). However the widely use of chromium compounds in industry has lead to the disposal of great amounts of Cr<sup>+6</sup> into soils that could be taken up by plants or leachate into the ground water causing a serious environmental hazard.

Once in soils, the soluble concentration of Cr<sup>+6</sup> could be reduced with the time by adsorption/desorption cycles and redox reactions. The objective of this word was to study the stabilizatization of Cr<sup>+6</sup> in three different agricultural soils in order to discuss the soil natural recuperation after Cr<sup>+6</sup> spilling.

### Materials and Methods

Three different agricultural soils from Madrid region (Spain) were selected: Talamanca (pH, 5.3; OM, 0.61), Encín (pH, 8.5; OM, 0.63) and Escorial (pH, 6.62; OM, 2.67). Soils were air dried, ground and screened through a 2-mm sieve. Each soil (100 g) were placed in Erlenmeyer flasks and spiked with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in water solution to reach a concentration of 250 mg·Kg<sup>-1</sup>. Three different Erlenmeyer flasks were used as independent replicates. Soil samples were kept at field capacity with MQ water

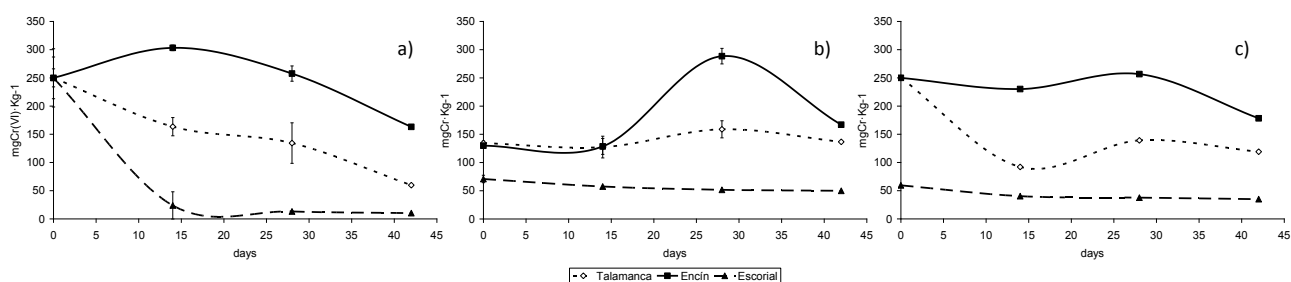


Fig.1 Cr<sup>+6</sup> concentrations in three soils after 14, 28 and 42 days of incubation in a) water soluble fraction, b) exchangeable fraction and c) total in soil

and incubated at 25°C in the dark. Samples were collected after 14, 28 and 42 days. Then, they were air dried. Leachate and plant available Cr<sup>+6</sup> were determined as water soluble and exchangeable fraction following the methods of Mandiwana (2008) and Scanar (2007) respectively. Total Cr<sup>+6</sup> were determined following the method stated also by Mandiwana (2008).

## Results and Discussion

Concentration of Cr<sup>+6</sup> in the three considered fractions are shown in figure 1. The total Cr<sup>+6</sup> concentration shows similar values to the exchangeable and water-soluble fraction indicating that Cr<sup>+6</sup> is not strongly adsorbed or bounded to soil particles but in solution or in easy to desorb form. The differences between the applied dose and Cr<sup>+6</sup> concentrations mean that Cr<sup>+6</sup> reduction to Cr<sup>+3</sup> would extended in the course of time. As expected, the soil which shown the highest pH (Encín), presented the highest Cr<sup>+6</sup> concentrations in the three fractions. This fact indicates that the reduction to Cr<sup>+3</sup> process is lesser than in soils from Escorial and Talamanca, both with pH<7 in which thermodynamics lead to the formation of Cr<sup>+3</sup> (Unceta et al. 2010).

This pH effect is clear when Encín and Talamanca soils are compared. Both soils have similar organic matter concentration, however, in the acid soil from Talamanca, the Cr<sup>+6</sup> concentration decreased by half the concentration regards to Encín. Due to high pH, the soil from Encín shows the lowest differences in the Cr<sup>+6</sup> concentration among the three fractions, indicating that Cr<sup>+6</sup> is completely in solution. However, not only the pH should be taking into account to predict the Cr<sup>+6</sup> concentration but also organic matter. Because Escorial soil has four times more organic matter than Talamanca, and also because the soil from Talamanca is more acid than the one from Escorial. This latter presents the lowest levels of Cr<sup>+6</sup>.

This soil is also the fastest to stabilize Cr<sup>+6</sup> as it shows the same Cr<sup>+6</sup> after two weeks and six weeks of incubation. This fact could be explained by the quick saturation of electron donor sites of organic matter. In Talamanca soil, the exchangeable and total

concentrations seem to be stabilised after 6 weeks. However in the soil from Encín (PH>7), the stabilization seems to be slower. In both soils, water soluble Cr<sup>+6</sup> seems to be still decreasing after 6 weeks of incubation indicating that remaining Cr<sup>+6</sup> in soil tends to be slightly adsorbed to soil.

## Conclusions

From the study of Cr<sup>+6</sup> evolution in three different agricultural soil after 6 weeks, it can be concluded i) Cr<sup>+6</sup> is presented in soil mostly in water solution or softly adsorbed to soils; the concentration decreases in the water soluble fraction with time; ii) in soils at pH<7, Cr<sup>+6</sup> is reduced to Cr<sup>+3</sup>; the process is accelerated by the organic matter presence, iii) in soil with pH<7, the stabilization of Cr<sup>+6</sup> is slow.

This work highlights the environmental hazard of Cr<sup>+6</sup> spills, especially in soils at pH>7. Soils show limited capability to reduce Cr<sup>+6</sup> and this specie remains long time available to plants and susceptible to leached to ground water.

## Acknowledgements

This work has been supported by EIADES PROGRAM S2009/AMB-1478 Consejería de Educación, Comunidad de Madrid, RTA000150-00-INIA; “Ayuda para la contratación de doctores INIA-CCAA” and IMIDRA for the financial support of the predoctoral granted of Ana Elena Pradas del Real.

## References

- Bartlett RJ. Chromium Cycling in Soils and Water - Links, Gaps, and Methods. *Environ Health Perspect* 1991;92:17-24.
- Mandiwana KL. Rapid leaching of Cr(VI) in soil with Na<sub>3</sub>PO<sub>4</sub> in the determination of hexavalent chromium by electrothermal atomic absorption spectrometry. *Talanta* 2008;74:736-40.
- Scanar J, Zupancic M, Milacic R. Development of analytical procedure for the determination of

exchangeable Cr(VI) in soils by anion-exchange fast protein liquid chromatography with electrothermal atomic absorption spectrometry detection. *Water Air and Soil Pollution* 2007;185:121-9.

Unceta N, Seby F, Malherbe J, Donard OFX. Chromium speciation in solid matrices and regulation: a review. *Analytical and Bioanalytical Chemistry* 2010;397:1097-111.