

# The chromium issue in soils of the leather tannery district in Italy

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## Abstract

Among heavy metals, up to now chromium has received little attention. The reasons for this lack of interest are diverse. One is that Cr was considered a “local source” contaminant, thus constituting a non-widespread environmental problem. A second reason is that the dominant naturally occurring form of chromium, Cr<sub>2</sub>O<sub>3</sub>, is considered essentially immobile in the environment, in contrast with the highly mobile and toxic Cr(VI).

Based on these assumptions, we have started a research program aimed at assessing the actual chromium accumulation in soils and plants of a tannery industrial district in NE Italy.

Further objectives of our study were:

- to highlight possible contamination of soils, plants and waters;
- to ascertain the potential risk to human health.

Large differences in Cr concentration were observed in the area investigated, with a very scattered distribution. Mean Cr concentration in soils is 210 mg/kg (range 50–10,000). Most of the investigated sites present surface Cr concentrations higher than subsurface, suggesting local sources of Cr to be responsible for soil contamination.

Chromium concentrations in selected plants (*Taraxacum officinale*, *Plantago lanceolata*) present wide ranges in both the species examined, with little translocation from roots to leaves (barrier effect).

To determine the groundwater pollution hazard in the surveyed district, we have compared the soil Cr concentration with the soil vulnerability map. Surface soils having the highest Cr concentration correspond to sites with very high to high vulnerability. Therefore, considering the present soil Cr concentrations and the pollution hazard, precaution and control acts are needed, in order to avoid more damage to land and waters. Moreover, considering all the above items, hazard for human health by direct contact with soil, ingestion, and inhalation should be taken in consideration by decision makers.

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## 1. Introduction

### 1.1. The chromium issue

Chromium is a chemical utilized in many industrial activities (electroplating, fertilizers, varnish, metallurgy, wood preservation), and is considered the major

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contaminant in the tanning industry. Land application of tannery waste as organic fertilizer has led to extensive Cr contamination of agricultural areas (Adriano, 2001), and may constitute a major concern for the (bio) accumulation of this metal in soils and plants. Up to now, limited effort has been directed towards the assessment of tannery-waste contaminated land and the potential risk for waters, plants and the environment.

Current studies report a range of plant species taken into consideration for Cr accumulation not only in roots, but also in the aerial parts (Barcelo and Poschenrieder, 1997; Loeppert et al., 1997; Pichtel and Salt, 1998; Bini et al., 2000b, 2001). These studies evidenced that root shortening, seedling development deficiency, membrane damage and metabolic disorders are common toxic effects. Moreover, recent works point to chromium severe toxicity with respect to human health. The oxidized form Cr(VI), readily mobile at usual soil pH, is considered a skin irritant and a class A carcinogen by inhalation, and the reduced form Cr(III), though much less mobile, has low acute and chronic toxicity (James et al., 1997).

## 1.2. Chromium in the environment

### 1.2.1. Chromium in soils

Rocks contain variable Cr concentrations (Table 1). In normal conditions, chromium in soils derives from that contained in the parent material. Soils derived from ultramafic igneous rocks are expected to contain high levels of Cr (up to thousands) in comparison to normal soils (average 40 mg/kg, range 10–150 mg/kg; Adriano, 2001). Soil texture has a profound effect on the Cr content. Mc Grath (1995) reports a value of 59 mg/kg Cr for clayey soils, and 13 mg/kg for sandy soils of 5700 British surface samples. Sterckeman et al. (2006) found strong significant correlation ( $R=0.71$  at  $P<0.05$ ) between Cr and clay in French soils from loess. Given its little mobility, especially in the reduced form Cr(III), the pattern of Cr profile distribution is nearly inconsistent. Chromium concentrations in the B or C soil horizons tend to be higher than in the A horizon, where Cr may

accumulate naturally as a consequence of atmospheric deposition of volcanic ash and erosion of soil materials with high Cr content. Vertical fluxes, however, may occur due to changing redox conditions, or complexation by organic matter. A negative correlation ( $R=-0.37$ ) between Cr and organic carbon was recorded by Sterckeman et al. (2006) in French soils from loess, and this is consistent with the little affinity of Cr to organic matter.

Frequently, however, significant Cr enrichment in soils is of anthropogenic origin. Anthropogenic sources of chromium are industrial (electroplating, varnish, metallurgy, wood preservation, tannery: Adriano, 2001) and agricultural activities (chemical and organic fertilizers and compost: Mc Grath, 1995; Bini et al., 2000a). Moreover, sewage sludge disposal on agricultural soils contributes to increase Cr concentration in surface horizons. The residence time of chromium in soils is estimated to be  $10^3$ – $10^4$  years (Mc Grath, 1995).

### 1.2.2. Chromium in plants

Plants have generally little capacity to uptake chromium and to transfer it to aerial parts. In normal conditions, Cr concentrations in plants are less than 1  $\mu\text{g/g}$ . In plants grown on soils treated with tannery waste, concentrations may increase significantly (Barcelo and Poschenrieder, 1997). In serpentine soils the mean Cr concentration is 45 mg/kg, but plants growing on these soils may contain up to 100 mg/kg Cr (Brooks, 1987). Some hyperaccumulator plants contain high amounts of Cr: 1500  $\mu\text{g/g}$  were found in leaves of *Dicoma niccolifera*, and 2400  $\mu\text{g/g}$  in *Sutera fodina* from Zimbabwe (Baker and Brooks, 1989; Brooks, 1998). Cr translocation from roots to aerial parts is difficult because of the formation of insoluble Cr compounds. The soluble fraction is stored in vacuoles (Barcelo and Poschenrieder, 1997), and may be mobilized in the form of organic complex (e.g. Cr-EDTA).

Chromium has a direct toxic effect on roots, where it is concentrated; root hairs and epidermal cells are highly damaged (Maleci et al., 2001). Cr(VI) has a degenerative effect on cells, caused by the reaction with nucleic acids of unstable intermediate compounds, formed during Cr reduction, within the cells.

Cr(III) may form complexes with phosphoric groups of nucleotides, altering the reproduction capacity of cells. These effects, besides the microscopic evidence, appear at macroscopic level as stress symptoms (Barcelo and Poschenrieder, 1997):

- inhibition of the germination phase;
- inhibition of root elongation and lateral root development;

Table 1  
Cr Concentrations (mg/kg) in common rocks (McGrath, 1995)

Rocks	Range (mg/kg)	Mean (mg/kg)
Igneous-ultrabasic	1000–3400	1800
Igneous-basic	40–600	220
Igneous-acid	2–90	20
Shales	30–590	120
Clays	26–1000	100
Limestones		10
Sandstones		35
Litosphere		100

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