Bull. Environ. Contam. Toxicol. (2001) 66:189–195

DOI: 10.1007/s001280000224

Bulletin of Environmental Contamination and Toxicology

Chromium in a Tannery Wastewater Irrigated Area, León Valley, Mexico

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Received: 31 May 2000/Accepted: 11 October 2000

León city is México's most important shoe-manufacturing area, with about 600 tanneries. More than 80% of them use chromium as a tanning agent. Their wastewaters go directly to the municipal drainage system, which flows to the León river and to the Mastranzo dam at the south edge of the city. Finally, these waters are used for irrigation. Besides, 13 km southwest of León city a factory (QC) produces chromium compounds.

Groundwater pollution in different parts of the valley has resulted from several anthropogenic and one natural source. The highest concentrations, up to 50 mg/L of Cr(VI), were produced by the improper solid waste disposal of the chromate factory (QC). Lower contents, up to 0.04 mg/L of Cr(VI) resulted from the practice of using rubble ashes from brick factories as fertilizer. Weathering of the Sierra the Guanajuato ultramafic units and their alteration products contaminated (up to 0.015 mg/L of total chromium) the superficial and groundwater at the East of the valley (Armienta et al., 1993).

The environmental chemistry of chromium has been widely studied (Richard and Bourg, 1991; Kotás and Stasicka, 2000). The knowledge of the oxidation state, total Cr concentration and the reacions occurring in different environmental compartments (water, soils, plants) determines the evaluation of the actual risk of chromium contamination. The toxicity, mobility and bioavailability of Cr depend fundamentally on its chemical form. Chromium in the environment might be present mainly as Cr(III) and Cr(VI). Cr(VI) is highly soluble and about 300 times more toxic than Cr(III). On the other hand, Cr(III) precipitates at the average pH of natural waters. Tannery wastewaters contain mainly Cr(III) (Rutland, 1991).

This study was performed with the aim of determining the concentrations, the speciation, and the mobility of chromium in different environmental compartments of an area irrigated with tannery wastewaters, within the León Valley, México.

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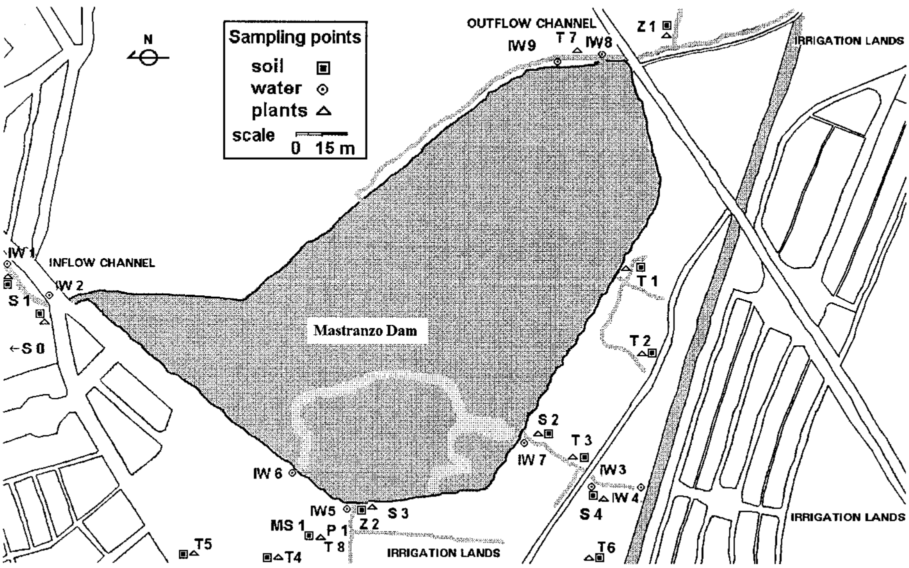

Figure 1. Sampling points location.

MATERIALS AND METHODS

Soil and plant samples were collected around the wastewater dam (El Mastranzo). Water samples from the El Mastranzo and from the inflows and outflows of the dam were also collected (Fig. 1). Temperature, pH and Eh were measured in the field. Cr(VI) was determined by colorimetry through its reaction with diphenylcarbazide. Total chromium was determined by flame atomic absorption spectrometry. Detection limits of 0.004 mg/L for Cr(VI) and 0.05 mg/L for total chromium were obtained. The accuracy of the methods was verified with fortified samples, a recovery between 95% and 100% was determined. Chemical Oxygen Demand was measured by oxidation and titration of the oxidated sample (APHA, 1989).

Soil samples were air-dried and ground to pass a 2mm sieve and quartered. Cr(VI) was extracted by treating 2.5 g of the soil with 25 ml deionized water, shaken for 2.5 h and filtering. For total chromium analysis, 1 g of the sample was digested with a volume ratio 1:3 concentrated HCl/HNO_3 and filtered. Cr(VI) and total Cr were analyzed by the same method used for water analysis. Accuracy of the method was verified with the soil reference sample IAEA-SOIL-7. Selected soil samples were treated by sequential extraction following the method described by Tessier et al. (1979). Plants were washed with deionized water; roots, spikes, leaves and stems were separated and dried at 70°C, and cut into 0.5 cm pieces. One gram of the sample was digested with 8 ml HNO_3 concentrated and 2 ml

Table 1. Chromium concentration in irrigation waters. bdl = below detection level, ND = non determined.

Sample	Total Cr (mg/L)	Cr(VI) (mg/L)	Eh (mV)	pH	COD (mg/L)
IW1	0.020	bdl	506	7.22	140
IW2	0.08	bdl	55	7.78	80
IW3	bdl	bdl	425	8.18	80
IW4	bdl	bdl	428	8.74	ND
IW5	0.20	bdl	-25	7.68	215
IW6	0.10	bdl	-10	7.41	80
IW7	0.045	bdl	-47	7.58	55
IW8	0.05	bdl	20	7.66	110
IW9	0.52	bdl	31	7.55	55

$HClO_4$ concentrated, filtered and made to a volume of 25 ml with deionized water. Chromium was analysed by atomic absorption spectrometry. A 80% percent recovery was obtained with this methodology.

RESULTS AND DISCUSSION

Total chromium and Cr(VI) concentrations in the water samples are shown in Table 1. IW1 and IW2 correspond to samples taken from a cannal with municipal wastewaters flowing from León city to the El Mastranzo dam. IW7, IW8 and IW9 were obtained from the outflows of the dam. IW3 and IW4 were collected from small lagoons within the irrigated lands, and IW5 and IW6 were obtained in different points of the dam, showing a red and green appareance respectively. Cr(VI) was not detected in any of the samples, indicating that Cr is mainly present as Cr(III). Chromium concentrations were below the stablished limits for irrigation waters (1 mg/L dialy average) in México (DOF, 1997). On the other hand, samples IW5 and IW9 were above the recommended value (0.1 mg/L) stablished in other countries (Prokisch et al., 1997). The nature and behavior of Cr in watewater depends on the physicochemical conditions of the effluents originating from various industrial sources (Kotás & Stasicka, 2000). As expected, Eh and pH values control the chemistry of chromium in the studied area. Chromium precipitates in the samples with the higher pH resulting in non-detectable amounts of dissolved chromium in samples IW3 and IW4. The presence of various inorganic and organic ligands can promote redox reactions and increase the concentration of the hexavalent form. Neverthless, at León, the reducing Eh values keep chromium as Cr(III). The more oxidizing Eh of sample IW1 is not enough to oxidize de Cr(III) coming from tannery wastes. Cr is in the trivalent state in all samples at this area of León valley. Chemical Oxygen Demand (COD) values indicate a high content of organic matter. Presence of chromium in the samples in spite of the low solubility of $Cr(OH)_3$, might result from complex formation with the organic matter present in the wastewaters.

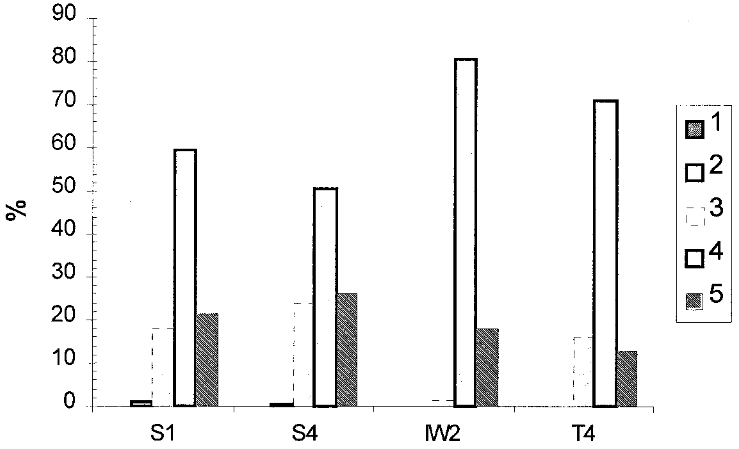

Figure 2. Chromium distribution in different soil fractions in four selected sites. 1)Exchangeable, 2) Carbonatic, 3) Reducible (hydrous Fe/Mn oxides), 4) Oxidizable (sulfides and organic phases), 5) Residual.

Plants and soil concentrations sampled around the dam are shown in Table 2. Cr(VI) was not detected in any of the soil samples. The average natural concentration in various kinds of soils ranges between 1.04 and 3016 mg/kg (Kotás & Stasicka 2000). A concentration of 200 mg/kg has been recommended as a maximum value in agricultural soils (Prokish et al., 1997). Cr is usually present as Cr(III) in soils. Neverthless, oxidation-reduction reactions can convert Cr(III) to Cr(VI) and viceversa (Kotás & Stasicka 2000). Cr(III) from irrigating waters has concentrated over time on the soils of the studied area producing the high contents measured in some of the samples (up to 3171 mg/kg). Concentrations from 14.2 to 2878 mg/kg have been found in fluvial sediments polluted with tannery wastes in Brazil (Jordão et al., 1997). Oxidation of Cr(III) to the more soluble and toxic Cr(VI) was not observed at León. This stability of Cr(III) was found also in another area of León valley (Armienta and Queré, 1995).

Chromium concentration in the sampled plants showed different values between species and among organs in the same plant. Plants usually contain 0.2 to 1 mg/kg on dry weight basis (Jordão et al., 1997), a mean of 0.52 has been measured in non-polluted areas (Sánka et al., 1995). Poaceae (grass) had the highest content of chromium of the sampled species in the studied area (19.75 mg/kg). Similar concentrations were measured in grass growing on sediments contaminated by tannery wastes in Brazil (mostly between 6.7 and 24.8 mg/kg) (Jordão et al., 1997). Sorghum spikes did not have chromium contents above the detection level in any of the samples. Some of the sorghum leaves have values above the detection limit (up to 1.75 mg/kg in leaves). Much higher concentrations were measured in Sorghum plants in Brazil (11.5 mg/kg) for plants growing in soil with 50.2 mg/kg of chromium (Jordão et al., 1997).

Table 2. Chromium concentrations in plants and soils at El Mastranzo area. Nd = non determined, bdl = below detection level

Plant	Sampling site	Cr (mg/kg)	Cr tot in soil (mg/kg)	Cr(VI) in soil (mg/kg)
Sorghum	S1	Leaves 1.75	295	bdl
Sorghum	S0	Leaves 1.00 Spikes bdl	70	bdl
Sorghum	S2	Leaves bdl Spikes bdl	155	bdl
Sorghum	S3	Leaves 1.71 Spikes bdl	89	bdl
Sorghum	S4	Leaves 1.00 Spikes bdl	675	bdl
Zea mays	Z1	Leaves 1.18	Nd	nd
Zea mays	Z2	Leaves bdl	675	bdl
Triticum a	T1	Root 2.50 Stem bdl Leaves bdl Spikes bdl	3171	bdl
Triticum a	T2	Root bdl Stem bdl Leaves bdl Spikes bdl	111	bdl
Triticum a	T3	Root bdl Stem bdl Leaves bdl Spikes bdl	33.2	bdl
Triticum a	T4	Root 5.5 Stem bdl Leaves 1.15 Spikes bdl	593	bdl
Triticum a	T5	Root 4.1 Stem bdl Leaves 1.75 Spikes bdl	156	bdl
Triticum a	T6	Stem bdl Leaves 7.5 Spikes bdl	146	bdl
Triticum a	T7	Stem bdl Leaves 1 Spikes bdl	35	bdl
Triticum a	T8	Stem bdl Leaves 6.75 Spikes bdl	410	bdl
Medicago sativa	MS1	Leaves 8.0 Stem 1.0 Root 10	410	bdl
Poaceae	P1	19.75	410	bdl

Some samples of Triticum a and Medicago sativa had high concentrations of chromium in roots and leaves. Chromium was mostly retained by the roots in all the sampled plants. Neverthless, traslocation to aerial parts was observed in Triticum a and Medicago sativa. No correlation seemed to exist between total chromium content in soils and plants. Factors like soil characteristics, concentration and speciation of the metal in soil solution, transport of the metal from the root surface into the root, and translocation from the root to the shoot affect the amount of metals absorbed by the plants (Alloway, 1995).

Chromium distribution in different fractions of the soil is shown in figure 2. The organic fraction contained most of the chromium, whereas exchangeable chromium was below 0.1% in all the samples. The high percentage of chromium in the organic fraction seems to be caused by its absorption by plants. Increasing the absorption of Cr(III) by plants has been found as a function of concentration of organic acids through complex formation (Srivastava et al., 1999). This finding contradicts the usefulness of reling on the exchangeable fraction for determining the bioavalability of some heavy metals (Novozamsky et al. 1993). The higher concentrations found in the forage plants Medicago sativa and Poaceae is a concern in the studied area, since this plants are used in cattle raising. On the other hand, the lack of chromium in the spikes of sorghum makes them suitable for their industrialization as cattle foodstuff.

Acknowledgments. We thank DGAPA (Dirección General de Suntos del Personal Académico, UNAM) for financial support, project IN102997. We thank E. Hernández for her participation in the chemical analyses.

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