

THE RISK TO GROUNDWATER FROM WASTEWATER IRRIGATION USING HIGH CHROMIUM TANNERY EFFLUENT

M E STUART AND C J MILNE

1. INTRODUCTION

The city of León, Mexico, is a major centre for the Latin American leather processing and shoe manufacturing industries, with more than 500 leather curing and tanning establishments. The city produces wastewater containing significant quantities of chromium that has been used untreated over a period of 40 years to irrigate agricultural land overlying an important aquifer. The city is highly dependent on these groundwater resources for public water supply. Wastewater is discharged from the sewerage system into a complex system of open distribution canals with some water being used directly for irrigation and the remaining passing through the El Mastranzo storage lagoon. The irrigated area has progressively increased in size to the present 3,000 ha.

There was concern that wastewater irrigation was the cause of high concentrations of chromium detected in an area of the aquifer. The work described here on the behaviour of chromium formed part of a larger project looking at the impact of wastewater reuse on groundwater quality in León (BGS et al., 1995).

2. METHODS

Soil samples were collected from a range of sites: former settlement lagoon beds, fields irrigated with water from different wastewater sources, fields irrigated with wastewater over different timescales and control fields that had never been irrigated with wastewater. Samples were air-dried, disaggregated and sieved to a maximum 5 mm particle size. Metal contents were determined by ICP-OES analysis of 0.43 M nitric acid extracts removing exchangeable, sorbed or organically bound metals but not those occluded in clays or oxide minerals.

Wastewater samples were collected from the main collectors, lagoon exits, the Río Turbio and irrigation channels. Groundwater samples were taken from both inside and outside of the wastewater irrigation area for both shallow dug wells used to provide irrigation water and deep boreholes used for public supply. Samples were analysed for a wide range of elements, including total Cr by ICP-MS and for Cr(VI) colorimetrically as the 1,5-diphenyl carbazide complex.

3. RESULTS AND DISCUSSION

3.1 Soils

There is clear evidence that chromium is accumulating in soils affected by wastewater irrigation. Soil chromium concentrations correlate well with age of wastewater irrigation at each site and there are negligible concentrations at control sites irrigated with groundwater (Figure 1). The sites of former wastewater storage lagoons have particularly high concentrations of chromium suggesting they were important locations of deposition. At all sites the major fraction of the chromium was contained in the top 0.3 m of the profile, which agrees well with other reported studies (McGrath, 1995).

The mechanism for Cr sorption in the soils is not clear since Cr(VI) is not strongly sorbed by organic matter. However, Cr(VI) can be reduced to Cr(III) by aqueous organic species such as fulvic acids, as well as Fe(II) and sulphide (Wittbrodt and Palmer, 1995), and Cr(III) is both readily precipitated as

hydroxide complexes and can also be chelated by organic matter attached to mineral surfaces (James and Bartlett, 1983).

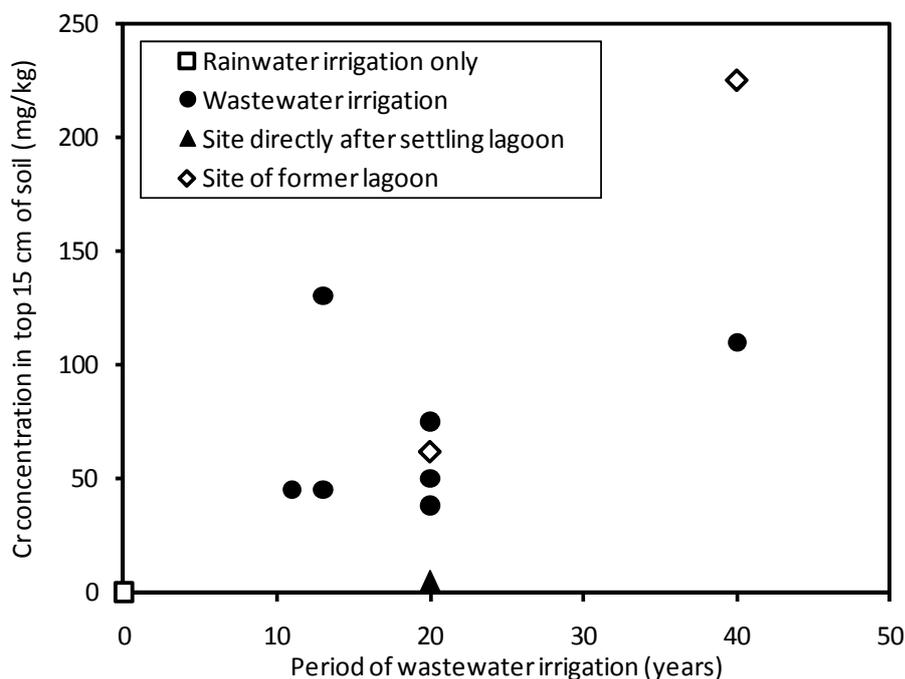


Figure 1. Variation of Cr concentrations in the soil with the number of years of wastewater application.

3.2 Water

The soluble fraction of Cr in the wastewater appears to be present as Cr(VI), although the remainder must be present as insoluble Cr(III) and therefore be associated with the particulate phase. Chromium concentrations in groundwater remain low and chromium must be effectively attenuated by the soil (Table 1). Elevated conductivities in shallow polluted water are mainly due to sodium chloride residues from skins preserved in salt prior to tanning. The restriction of elevated chromium concentrations in groundwater to the edge of the irrigated area close to a chromium ore processing plant has been confirmed by subsequent work (Armienta et al., 1997).

Table 1. Typical water quality in the different stages of the water distribution system.

Water type	Total Cr (mg l^{-1})	Conductivity (μScm^{-1})
Tannery discharge	200	20,000
Industrial collector	40	9,000
Domestic collector	20	3,500
Río Turbio	4-29	1,800
Lagoon exits	0.1-0.4	2,000-2,300
Irrigation canal	0.06	1,200
Shallow polluted groundwater	0.002-0.005	2,700
Regional background quality	0.002-0.005	480

3.3 Chromium Fluxes

Soil and water analyses were used to produce an estimate of the distribution of Cr in the study area and to identify the major source and sinks. The components of a provisional budget are:

- Inputs: The collectors are well characterised, but input will be overestimated since measurements were only taken during the working day.
- Out: The outflow from the Presa San Germán is typically relatively low in chromium. The flow was estimated from calculated losses of incoming water to the area from irrigation, infiltration and evaporation.
- Soil and disused lagoon accumulation: this was calculated by extrapolating from the soil measurements. Over a 40-year period this only represents a small proportion of the total even allowing for the recent rapid expansion of the tanning industry.
- Plant uptake: This was assumed to be low.
- Lagoon accumulation: Inflows and outflows of the present day lagoons reveal significant accumulation, and deposition of chromium in the former and current lagoons and the canal distribution system must be the dominant removal process (Table 2).

Table 2. Chromium budget in the wastewater irrigation area

Element	Flux (t/year)
Total inputs from collectors	1033
Soil accumulation	25
Disused lagoon accumulation	5
Total outputs from Río Turbio	20
Calculated annual accumulation in lagoons and distribution system	983

4. CONCLUSIONS

Wastewater from León containing high concentrations of chromium from the tanning industry is used to irrigate agricultural land overlying an aquifer used to supply potable water. Chromium from irrigation water is accumulating in agricultural soils and in the lagoon and canal sediments but groundwater appears to be unaffected and chromium concentrations remain low. A limited area of very high chromium concentrations in groundwater was confirmed to be derived from a factory supplying the tanneries.

ACKNOWLEDGEMENTS

The project was carried out jointly by the British Geological Survey and the Comisión Nacional del Agua with support from Sistema de Agua Potable y Alcantarillado del Municipio de León and funding from the Department for International Development and the European Commission. This paper is published by permission of the Executive Director of the British Geological Survey (NERC).

REFERENCES

ARMIENTA M A, RODRIGUEZ R, CENICEROS C AND AGUAYO, A 1997. Identification of the main source of chromium pollution from various potential sources. In: P J Chilton et al. (ed) *Groundwater in the Urban Environment: Problems, Processes and Management*, Balkema, Rotterdam pp 365-370.

BGS, CAN, SAPAL AND UAH 1996. Effects of wastewater reuse on urban groundwater resources of León, Mexico. *British Geological Survey Technical Report WD/95/64*.

JAMES B R AND BARTLETT, R J 1983. Behaviour of chromium in soils, VI. Interactions between oxidation-reductions and organic complexation. *Journal of Environmental Qualitative*, **12**, 173-176.

MCGRATH S P 1995. Chromium and Nickel. In: B J Alloway (ed) *Heavy Metals in Soils*, Blackie, pp 152-178.

WITTBRODT P R AND PALMER C D 1995. Reduction of Cr(VI) in the presence of excess soil fulvic acid. *Environment of Science & Technology* **29**, 255-263.