Towards Better Management of Soils Contaminated with Tannery Waste

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Preface

Leather production is a major industry in India and makes a significant contribution to the country's export earnings. Numerous tanneries process animal hides to semi-finished products within the country. A major concern to the industry, regulatory bodies and the general public is the safe and long-term management of chromium-rich and saline waste effluents from tanneries. In some areas of India contamination resulting from tannery waste disposal has limited cropping and the use of groundwater because of elevated concentrations of salts and hexavalent chromium. Such problems are not unique to India, and the productive use of contaminated land for plants that tolerate salt and do not accumulate chromium has substantial economic and environmental potential in both developing and developed countries. Australia has a legacy of tannery contamination of soil and water from discharges of long-closed plants. The Australian Centre for International Agricultural Research funded a project in Tamil Nadu, India, and South Australia to assess the extent and severity of chromium and salt dispersal from tanneries, and to devise safe means of utilising the wastes whilst maintaining some production.

This workshop brought together delegates from India, Bangladesh, Sri Lanka, Nepal, Indonesia and Australia to share experiences and demonstrate that certain commercial tree and flowering plants can be grown on land contaminated with tannery waste under a variety of conditions that are not suitable for conventional agricultural crops. The workshop considered the extent of land contamination following tannery waste disposal, the potential for migration of chromium and salt into groundwater, alternative land uses and secondary effluent re-use for commercial tree plantations.

We hope that the papers presented in these Proceedings will assist scientists, regulatory organisations and tannery industries in their endeavours to rehabilitate land contaminated by tanneries.

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Acknowledgments

Summary: the Tannery Waste-contamination Problem and Some Possible Solutions

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OF all the agricultural industries in India the leather industry appears to be the major source of pollution, and Tamil Nadu appears to be the state most affected. From data supplied by Indian scientists, and from direct observation of crop growth in affected agricultural areas, it is evident that borehole water beneath large areas is becoming salinised. Furthermore, soils surrounding tanneries are being polluted through the disposal of chromium-rich effluents to agricultural land.

Soils sampled in the vicinity of tanneries in the Vellore area have chromium (Cr) concentrations of up to 7% ($70\ 000$ mg kg^{-1}), and tannery sludges used in agriculture also have high Cr concentrations (up to 4% on a dry solids basis). Where effluent is treated before disposal, Cr-rich sludges are produced which are often used as soil additives for agricultural food crops without information on the phyto-availability and mobility of Cr in the soils.

A number of highly contaminated tannery waste disposal sites exist in Australia also, but the extent of pollution of land through tannery waste disposals is not as great as that reported in India. In particular, the old tannery waste disposal site near Adelaide is within the peri-urban region, and people have expressed concern for their children's and animals' health and for the quality of the crops that they grow.

The limited information on the potential impacts of Cr present in tannery wastes on soil and crop quality stimulated ACIAR-sponsored project 9322 in 1995 to devise strategies for rehabilitating contaminated sites. The major objectives of the project were:

• to characterise the tannery wastes and evaluate the extent of contamination of productive land;

• to quantify and predict the extent of pollution in relation to land use, soil type and other landscape features; and

• to provide a scientific basis for setting guidelines for the disposal of tannery effluent and solid wastes rich in Cr.

Detailed assessment of the tannery waste contaminated sites in Tamil Nadu, India, and Mount Barker near Adelaide, Australia, revealed extensive contamination of soil and of surface water and groundwater. Generally the contaminated soils were alkaline in reaction and contained high concentrations of Cr. Although no definite pattern was observed in the distribution of Cr at different depths, Cr accumulation ranged from <100 mg kg^{-1} to $\sim70\ 000$ mg kg^{-1} in subsurface (>50 cm) and surface soils (0–15 cm) soils, respectively. This is supported by the data on the concentrations of Cr and salt in effluent and sludge that have been discharged onto contaminated land. Analyses of effluent from a number of tanneries in India revealed that Na contents ranged from 2042 to 9000 mg L^{-1} and Cr contents from 620 to 26 200 µg L^{-1}. However, there were large variations between industries in the Cr concentrations in effluent. Samples collected from industries practising Cr recycling showed Cr concentrations below 10 µg L^{-1}. There was a marked difference in sludge Cr concentrations between Australian and Indian tannery industries. While the concentration of Cr in the Indian tannery industry sludges generally ranged from 1179 to 16 158 mg kg^{-1}, the sludges sampled in Australia showed concentrations ranging from 10 000 to 150 000 mg Cr kg^{-1}.

In India the amount of Cr in the soils is particularly high around the closed (old) tanneries relative to the existing tanneries. This may be attributed to the more stringent guidelines imposed by the Tamil Nadu Pollution Control Board

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recently (in the last 15 years). In general, at the time of these studies, the concentration of Cr in soil samples taken around tanneries in India and at the historically contaminated sites in Australia exceeded the WHO, USEPA and Australian National Health and Medical Research Council guidelines for contaminated soils. This indicates the extensive and severe contamination of soils due to tannery waste disposal on land in India and Australia. The presence of high concentrations of soil Cr poses significant risks to animals and humans living in the close vicinity of the contaminated sites, especially from contaminated dust particles during the dry summer season in Adelaide and the winter months in India.

Chromium below surface

The presence of Cr in soils more than 100 cm below surface was surprising because Cr is considered to be an element of low mobility. However, at all sites where Cr concentrations exceeded 1000 mg kg^{-1}, an appreciable concentration of Cr was detected in surface and subsurface water samples in lysimeters, piezometers and tubewells, suggesting high mobility of Cr at the contaminated sites. Groundwater collected from borewells around the tanneries at Ambur, Walajapet, Vaduganthangal, Pernampet, Vaniyambadi and Vinnamuthi villages in Vellore district, Tamil Nadu, showed total Cr ranging from 50 to 990 µg L^{-1}. The water sampled from borewells located 2 km away from a closed tannery at Walajapet had exceptionally high Cr content (>950 µg L^{-1}); the normal average background value is 4–7 µg L^{-1} in different parts of India. At the Mount Barker site near Adelaide, the concentrations of Cr were not as high; values ranged from <20 µg L^{-1} to >500 µg L^{-1} in water samples taken from lysimeters and shallow and deep tubewells. In most water samples the Cr concentration exceeded the maximum permissible limit (50 µg L^{-1}). The results demonstrate that Cr is highly mobile in contaminated soils around tanneries.

This evidence of the high mobility of Cr is supported by Cr speciation studies which indicate that 80–96% of Cr in the tubewell, lysimeter and piezometer samples is present as Cr(VI). This form of Cr is mobile and highly toxic. Solid phase speciation of Cr, by a sequential fractionation procedure, indicated that 80–99% of Cr was extractable by HNO$_3$ acid, showing that there is Cr present in the residual fraction. This form of Cr is not mobile. The Cr extractable by NaOH (organic) and EDTA (remaining organic components plus iron oxide) constituted only 0.5–15%. A concentration ranging from 5.5 µg kg^{-1} to 128 µg kg^{-1}, obtained in KNO$_3$ extracts of Indian soils, is of concern because this fraction represents the exchangeable and sorbed-Cr which comprises the labile Cr pool. The concentration of Cr in water extracts ranged from undetectable levels (in Indian soils) to >10 mg L^{-1} in the tannery-waste-contaminated soils near Adelaide.

Detailed studies on the seasonal variation in solutes at the contaminated sites found an appreciable increase in the concentration of Cr in the piezometer water samples following wet winter months. A similar and much more marked increase was also recorded in salt levels in subsurface- and groundwater samples during the wet winter months, confirming our hypotheses that Cr and salt are highly mobile in the high pH soils at the contaminated sites.

Factors in Cr mobility

The factors controlling Cr mobility at the contaminated sites at Mount Barker were investigated using intact cores (300 mm internal diameter and 1 m height). Since Cr can occur in a number of different oxidation states—Cr(III) and Cr(VI)—mini-electrodes (platinum electrodes constructed in the laboratory) were installed to monitor in situ changes in redox potential. Moisture probes were installed to trace changes in the moisture potential, with Time Domain Reflectometry. The pH of the soils was measured at the same time. These parameters were measured automatically and recorded in a data logger. At regular intervals, soil solution was sampled using fibreglass wick samplers that were installed at several depths in the core to provide a profile of changes in soil solution chemistry. The leachate samples obtained from the wick samplers showed that the pH in the soil cores (columns) decreased from >8 in the surface soils to <4 at depths exceeding 40 cm. A similar trend was recorded for soluble Cr, with values exceeding 1 mg L^{-1} in the surface 10 cm and <0.1 mg L^{-1} at depths exceeding 40 cm. However, chromium was not detected in the leachate from the wick samplers installed in

the acidic soil layer and the solution eluting out of the soil column. This indicates that mobile Cr is transformed into an immobile form in the acidic soils. While the mechanism of the immobilisation process in this profile is not clear, similar studies in the field sites indicate elevated levels of Fe^{2+} in the subsurface acidic soils. Presence of Fe^{2+} may contribute towards the redox transition of mobile Cr(VI) to Cr(III). Lower pH and lower redox potential at deeper levels in the cores favoured reduction of Cr(VI) to Cr(III).

It is Cr(III) that is predominantly used during the tanning process, so the presence of Cr(VI) in subsurface water samples (as determined by the colorimetric diphenyl carbazide indicator method) is surprising. What are the potential mechanisms that enhance the oxidation of the Cr(III) added to soils in the tannery? Microbial activity found in the water sampled in such locations is a positive indication that the microbial oxidation–reduction system might have favoured the transformation. For this reason, bacteria were isolated from a dried sludge (SL21-3) and their capacity to oxidise Cr(III) was evaluated. The results from this study show that one of the bacterial isolates was capable of oxidising Cr(III) to Cr(VI) in liquid culture; however, the kinetics of the oxidation process were low. The role of microbes in Cr transformations in soils is being studied by a postgraduate student as part of her PhD studies.

Management and reuse of sludge and effluent

The rehabilitation of Cr contaminated sites is one of the major problems confronting the affected farmers and the pollution control board and agricultural scientists. The production of large volumes of secondary effluent and solid waste material by operational tannery industries poses a considerable challenge to both the industries and the pollution control board. For this reason, potential methods for rehabilitating contaminated land and making alternative use of secondary effluent and solid waste material were investigated.

The effect of secondary effluent on the growth of multipurpose tree species was investigated in Vellore, India. Three tree species, namely *Acacia leucophloea*, *Casuarina equisetifolia* and *Eucalyptus tereticornis*, and three effluent concentrations (100% effluent, 50% effluent + 50% water, and 100% water) were tested. The trials measured the effects of secondary effluent on tree production and soil chemical properties, and they monitored the quality of surface- and groundwater at the study site. The treated effluent has a high content of total dissolved solids (13 245 mg L^{-1}), sodium (5640 mg L^{-1}), chlorides (4517 mg L^{-1}) and sulfates (426 mg L^{-1}). There was a marked effect of the effluent on the soil properties, on the ionic composition of surface- and groundwater, and on plant growth. In general the electrical conductivity (EC) of surface soils increased from 3 dS m^{-1} in the water treatment plots to ~3.5 dS m^{-1} at the highest effluent application rate. The exchangeable sodium percentage (ESP) of top-soil increased from 34 in the control soils to 39 in soils irrigated with 100% effluent. Comparison of the EC and the sodium adsorption ratio (SAR) of surface and subsurface soils indicates that irrigation with water leaches salt from the surface soils thus enhancing subsurface sodicity. The impact of salt is also evident from the groundwater data that showed a marked increase in the concentrations of Na (4400–5280 mg L^{-1}) with effluent irrigation. Effluent irrigation also had a significant impact on plant growth. The results show that there is potential for using diluted effluent (50:50 effluent:water) for tree production.

The effect of tannery chrome sludge in India on the growth of three vegetable crops (Bhendi, *Abelmosches esculentus*; Brinjal, *Solanum melongena*; and chillies, *Capsicum annum*) was studied. In general, there was an appreciable increase in both shoot and produce yield up to a total Cr concentration of 750 mg kg^{-1}; above this there was a sharp decline in yield with all the crops except chillies, but the decrease was not statistically significant relative to the control. However, there was significant Cr uptake by all the test crop plants. Of the total plant Cr uptake, 30–40% was accumulated in shoots and 10–15% in fruits. The critical plant concentration was 30–40 mg Cr kg^{-1} of dry matter; above it, toxicity symptoms were noted that persisted throughout the growth period.

Also, the effect of tannery waste sludge on the growth of clover (*Trifolium fragiferum*) was studied in three acidic soils from South Australia in a replicated glasshouse study. The composition of the sludge material varied considerably, with Cr concentration ranging from 1 to 3%. When the pots were sown with clover, germination was

recorded in all treatments. However, seedling emergence and plant shoots in 'high' Cr treatment pots showed symptoms similar to those induced by metals such as Al. These symptoms persisted throughout the growth period. Marked declines in yield were recorded at sludge levels exceeding 3 g kg^{-1} in two sludge treatments (M1 and M3 in which Cr concentrations were 1.7% and 1.2%, respectively), and 2 g kg^{-1} in the other sludge treatment, (M2, with Cr concentration 3.3%). Examination of the plant composition data together with soil solution Cr showed severe toxic effects of Cr on plant growth in soil solutions exceeding 40 mg Cr L^{-1}. These results confirm the toxic effect of Cr on plant growth. In a pattern similar to that of the yield data, the Cr concentration of plant tissues increased initially with sludge application and then decreased at high sludge additions. The decrease was mainly related to the Cr toxicity to plant roots. These data from glasshouse studies suggest that tannery sludge may not be appropriate for growing food crops.

An alternative strategy, managing tannery wastes using earthworms, was investigated in field studies. The roles of earthworms and microbes in sludge decomposition were examined under field conditions. Treatments were established that tested the efficiency of both organisms, separately and in combination, for decomposing sludge. Composting led to a marked increase in the concentration of all major plant nutrients: viz., nitrogen (N), phosphorus (P) and potassium (K). A sludge bed with added earthworms and microbes produced a greater increase in N and P, while the maximum increase in K (two-fold) was recorded in the sludge bed that included sawdust and microbes. Appreciable reduction in pH, EC, and C:N ratio was also observed in all the treatments. The C:N ratio was reduced below the preferred level of 20 during the 120 days period, except in control beds. The Cr content in the sludge was also reduced by 40%. Examination of the microbial

activity during the composting process revealed marked changes in the populations of bacteria and fungi and, to a certain extent, actinomycetes. Further investigation of large-scale vermiculture is being continued in India.

Based on the above findings, guidelines for disposing of tannery wastes and for remediation strategies were devised for tannery-waste-contaminated sites. The remediation of soils contaminated with Cr is an important task that not only will help sustain agriculture but also will minimise adverse environmental impacts. Strategies include revegetation of Cr-contaminated soils using commercial tree plantations and flower crops tolerant to both salt and Cr. Other remediation strategies include:

- phytroremediation using plant species which are Cr tolerant or hypoaccumulators;
- bioremediation using microbial strains (both native and introduced) to reduce the bioavailability of Cr through biotrans-formation of toxic Cr(VI) to Cr(III), and using compost to complex Cr compounds; and
- chemical remediation using certain chemical amendments to immobilise Cr through complexing and thereby reduce the solution phase concentration of Cr.

Guidelines for the disposal of tannery wastes identify critical factors that existing industries need to consider before disposing of their wastes. The guidelines emphasise that environmental impact assessment must be conducted before new industries are established. Critical factors considered in the guidelines include the water table depth, and the odour, total Cr content, COD, BOD, nitrate, phosphate, sodium, chloride and other heavy metals such as Cd and As in the wastes. The guidelines are currently being finalised by the Tamil Nadu Agricultural University in consultation with the Tamil Nadu Pollution Control Board and tanning industries.

Tanning Industries in the SE Asia Region: Overview and Environmental Concerns

Status of Tanning Industries in India

K. Ramasamy[1] and R. Naidu[2]

Abstract

The tanning industry in India is among the country's largest external income earners. Consequently during the past 50 years the industry has had significant government support and has multiplied throughout India. Tanneries range from tiny cottage industries to large-scale operations with over 500 employees. Primarily because of the industrial contribution to the local and international economy the industry has enjoyed significant support from the local and federal governments. However, during the past 10 years, the adverse environmental impact of the industry's waste disposals on productive agricultural land and groundwater bodies has resulted in a public outcry. It is estimated that over 55 000 ha of land has been contaminated by waste disposals in the State of Tamil Nadu. Similar contamination may also occur in other states although no data could be found in the literature. The skin and hides of the animals are processed for leather through vegetable and chemical tanning. Chrome tanning is preferred, but the use of Cr(VI) during processing poses the problem of its release in waste water. This paper presents an overview of the tanning industry in India, and describes the current management and waste treatment strategies and the challenges posed both to the industry and to the public.

THE tanning industry has been the subject of much public discussion for the past few years, both because of its foreign exchange earning potential and because of its pollution. While both the international and the local communities appreciate the financial potential of the industry, there has been an outcry across the world about the adverse impacts of tannery wastes on agroecosystems. As a result, many developed countries have stopped leather processing, and now rely solely on developing countries such as those in the Indian subcontinent. It is estimated that tanning industry wastes have already contaminated over 50 000 ha of productive agricultural land.

Tanning involves the conversion of animal hides into leather. The process includes dehairing and

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removal of flesh and fat, and treatment with chemicals to form stable, durable material. These processes daily use thousands of litres of water. In fact, phase one of the conversion of raw hides into finished leather uses approximately 30 kL water/t raw hide or skin. At the tannery, the cleaning operation starts with the removal of the sodium chloride used for temporary preservation. To facilitate hair removal the skin or hide is treated with a mixture of sodium sulfide and lime. The sulfides used in this operation can produce the toxic and foul smelling gas hydrogen sulfide. The common salt used in curing is removed in soaking and the soak liquor is disposed of. The effluents from these operations are commonly discharged onto land and into water bodies.

In chrome tanning, 276 chemicals and 14 heavy metals are used. It is estimated that approximately 32 000 t of basic chromium (Cr) sulfate salts are used annually in Indian tanneries. This amounts to an annual loss of nearly 2000–3200 t of Cr (on an elemental basis). The concentration of Cr in the

Table 1. India's exports of major commodities and their ranking

Description	Value in crores*	(%)	Ranking
Textiles & textile articles	22570.98	(27.4)	I
Pearls, precious or semi-precious stones / metals & articles thereof, etc.	14172.97	(17.2)	II
Chemicals & allied products	6478.36	(7.8)	III
Leather & leather products	5113.04	(6.7)	IV
Mineral products	4147.71	(5.0)	VI
Machinery & parts; electrical equipment & parts	3841.51	(4.7)	VII
Base metals & articles thereof	4549.68	(5.5)	V
Coffee, teas	2340.94	(2.8)	X
Fish & crustaceans, molluscs & others	3582.20	(4.2)	VIII
Transport equipment	2419.31	(2.6)	IX

Source: Monthly Statistics of the Foreign Trade of India, Volume I: Exports & Re-Exports, March issue of 1994–95.
*1 crore = Rs 10 000 000 = A$400 000.   Figures given in parentheses indicate the % share to grade total.

effluents from the chrome tanning yard is in the range 2000–5000 mg L^{-1}. International regulations stipulate that the Cr concentration in industrial waste shall not exceed 2 mg L^{-1}.

Importance of the Leather Industry to the Indian Economy

The leather industry is one of the major exporting industries in India. Table 1 compares it to others, such as the textiles, pearls and precious stones, chemicals, mineral products, machinery parts, base metals, coffee and transport equipment industries. A survey of the growth of the Indian leather industry over the past four decades reveals that there are 1008 units in the small-scale industries sector and 75 units in the large-scale sector. The industry employs about one million workers apart from those who work in the cottage-based sector.

Worldwide, leather processing is one of the oldest industries, having existed for over 200 years. Although old, it is unique in the fact that it is still growing. A number of factors contribute to this characteristic of the leather and leather products industry. The various markets for leather and leather products develop in different countries depending upon the state of eco-development and the standard of living of the people.

Once India was a net exporter of raw hides and skins. After the Second World War, the demand for leather products internationally and locally compelled the government to start a tannery to meet its requirements. This was the beginning of the growth of the leather industry in India. The accessibility of the techniques and the need for labour rather than machinery paved the way for the setting up of many tanneries. In the beginning, the tanneries started processing vegetable tanned or East India (E.I.) tanned leathers. These leathers attracted a good demand and price at that time. It became evident that E.I. leathers were favoured as a basic raw material from which the importers could reprocess any type of finished leathers of interest to them. Table 2 shows the foreign exchange earnings from export of tanned leather.

Location of Processing Centres

After the initial establishment of the leather industry, new processing units were set up in places where labour and capital were available. In Southern India especially, the Tamil Nadu State (then the Madras State) had a lead over the other states, with labour and capital readily available. In contrast, in North India, Uttar Pradesh and Rajasthan only cottage units were established. Tanning also became popular in West Bengal in the east, and Maharastra in the west. Skin-based processing units (goat, sheep and calf skins) were established in Tamil Nadu while cattle-based hides centres were set up in West Bengal and heavy buffalo hides were processed in Northern India (Kanpur).

The Environment and the Leather Industry

After 1973, the growth of the leather industry was spectacular and on a par with other industrialised

Table 2. The value (in million Rs) of India's exports of tanned leathers

Description	1988–89	1989–90	1990–91	1991–92	1992–93
Hides					
E.I. tanned hides	25.65	26.33	57.84	65.87	32.31
Chrome tanned hides	176.71	72.52	37.65	23.68	27.65
Other tanned hides	11.19	12.19	1.05	3.72	0.02
Skins					
E.I. tanned skins	46.94	21.51	20.17	0.33	Nil
Chrome tanned skins	31.40	11.08	6.82	17.78	15.60
Other tanned skins	–	11.49	4.02	1.16	2.01
Finished products					
Finished leathers	6494.06	7285.69	7985.36	7164.28	7997.11
Tanned fur skins	11.51	0.25	Nil	0.31	Nil

countries. Transformation from the production of E.I. leather to chrome tanned leathers increased the volume and pollution load of effluent produced by the tanneries. Land-based disposal of this waste resulted in severe environmental degradation in and around the tanneries. The adverse impacts on productive agricultural land and surface water and groundwater created alarm among the public and the government.

Seeing the loss in agricultural productivity and realising the adverse environmental threat of tannery wastes, the government of Tamil Nadu called for stringent measures; the waste was to be treated effectively before discharge onto land and into water bodies. Increasing pressure is now being applied by the regulatory bodies for effective containment of pollution, both to address the requirements of the law and as a social obligation to the public. It is therefore pleasing to note that the government and the industry are now jointly working towards establishing procedures that minimise pollution and have minimal impact on the growth of the industry.

Indian leather sector: attitudes

The tanning sector ranges from small-scale cottage units to large-scale tanneries, so the environmental awareness of the tanning industry in the country varies substantially. The mental preparedness of the Indian tanning sector for waste water treatment is very low. It is now established that groundwater is seriously affected in some areas where tanneries are concentrated (Mahimairajah et al. these Proceedings). The public view of the tanneries with

respect to environmental issues is negative. Litigation against the tanneries has started in law courts to get a clear direction for redressing the environmental degradation. The courts have issued various decrees for the closure of tanneries and the levy of compensation fees for polluting agencies. These steps were initiated by the courts to make sure that the tanners accept regulatory guidelines aimed at ensuring that appropriate procedures are followed for discharge of tannery effluents. They paved the way for the permanent and commercial solutions now evolving, for the survival of the leather sector.

Severity of the environmental problems

Market forces and economic considerations have prompted the export of chrome-based processed leather and leather products. These processes have led to many changes in the traditional E.I. tanning industry and have overloaded the effluent treatment system. It is estimated that in India 17 000 t of hides and skins are daily converted into leather. Latest estimates indicate that 35–40 litres of water are used per kilogram of leather processed. This implies that 680×10^6 L of tannery waste water are generated in this country each day. Table 3 shows the average composition of tannery waste water in the current production system. Typical parameters observed for the treated waste water from tanneries are also listed in the table.

It was the desire to meet international demand, together with the need to maintain a competitive edge internationally, that led to the establishment of many chrome tanning industries, discharging the

Table 3. Characteristics of tannery effluent

Characteristic	Before treatment	After treatment
pH	7.0–9.0	6.5–8.5
Total suspended solids (mg L^{-1})	2000–4000	10–10
Total dissolved solids (mg L^{-1})	11 000–16 000	5000–10 000
Chlorides as Cl^- (mg L^{-1})	6000–9500	1600–5000
Sulfates as SO_4^{2-} (mg L^{-1})	2400–4000	800–2000
BOD (mg L^{-1})	1000–3000	30–150
COD (mg L^{-1})	2500–8000	150–400

spent Cr-containing waste water onto land. At present the tanning industries are working closely with the United Nations Industrial Development Organization (UNIDO) to develop technologies that efficiently recycle Cr and reduce the sulfide by $MnSO_4$. However, one of the major constraints to using $MnSO_4$ is the potential for Mn to oxidise trivalent chromium, Cr(III), to toxic hexavalent chromium, Cr(VI):

$$Mn(II) + Mn\text{-oxidising bacteria} \Rightarrow Mn(IV) \quad (1)$$

$$Cr(III) + Mn(IV) \Rightarrow Cr(VI) + Mn(II) . \quad (2)$$
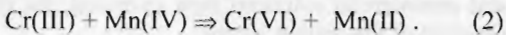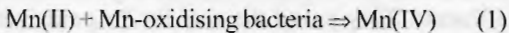
This is particularly feasible in those environments where there are Mn oxidising microbes. As shown above, Mn(II) could provide catalytic reaction following biotic conversion to Mn(IV). Indeed Cr(VI) has been reported at the long-term contaminated sites in both Australia and India.

Chromium and salt are potential pollutants of soil, surface water, groundwater, sediment and air. Where the soils do not originate from serpentine minerals, high Cr content of the soils is often associated with human-induced contamination, mainly from industrial operations such as tanning and direct disposal of sludge and waste water for land application. The toxicity and mobility of chromium depend on its oxidation state. The trivalent forms are relatively immobile, more stable and much less toxic than the hexavalent forms. Chromium forms a large number of relatively kinetically inert complexes which can be isolated as solids. Well known complexes are amines. Chromium is not a significant contaminant of plant tissues except at sites with specific discharge points. Growth inhibition in aquatic plants generally occurs at 0.5–5 mg Cr(VI), but potassium dichromate may stimulate the growth of some species. However, little is known of the factors influencing the uptake of Cr in aquatic plants. Toxicity to plants depends on the pH of the media and hence the availability of the free and chelated ions. Other factors, such as the presence of organic chelators, cations, nutrients, and other heavy metals in solution, influence the toxicity to plants.

Chromium is not acutely toxic to humans. This is due to the high stability of natural Cr complexes in abiotic matrices. In addition, the acid nature of Cr imparts strong affinity for oxygen donors rather than sulfur donors present in biomolecules. However, Cr(VI) is more toxic because of its high rate of absorption through intestinal tracts. In contrast to the biomagnification of methyl- mercury and cadmium, Cr is not thought to accumulate and biomagnify, but biomagnification through the food chain is known. Accumulation of Cr above the average levels occurs in both the plant and animal kingdoms. In normal soils with total Cr concentrations between 20 and 100 mg kg^{-1}, plants have less than 1 μg Cr g^{-1} dry wt, and seldom exceed 5 μg g^{-1}. The only exceptions are the serpentine soils which contain 1000–50 000 mg Cr kg^{-1}: plants that are endemic to this soil may accumulate toxic concentrations of Cr. As with plants, the majority of invertebrate animals appear to die before accumulating Cr that might prove toxic to predators. Among the animals, gastropods are the known accumulators of Cr, to concentrations of 140–440 mg Cr kg^{-1} dry weight, including shells.

Our attempts to characterise the effluent and the rate of pollution have indicated that underground water, as well as surface water, contains toxic levels of Cr, mostly Cr(VI) (Table 4).

Known Solutions for Chromium Toxicity

Although Cr(III) is the major Cr salt that is used during the tanning operations, concentrations of Cr(VI) exceeding 1 mg L^{-1} have been reported in groundwater in close proximity to tanning industries by Handa (1978) and more recently by Mahimairajah et al. (these Proceedings). This is surprising given that, thermodynamically, Cr(III) is more stable than Cr(VI). Primarily because of

this, many investigators used to recommend that land-based disposal of tannery waste was a safe procedure (see references in Naidu and Kookana, these Proceedings). The presence of Cr(VI) in surface and groundwater samples has led to detailed studies on factors controlling Cr chemistry at tannery waste-contaminated sites. Several approaches have been attempted for the remediation of Cr(VI) in the environment:

• heap leaching and collection;
• phyto-remediation with Cr accumulators;
• gaseous bioreduction;
• organic matter stimulation of Cr(VI) reduction by soil microbes;
• inoculation of Cr-tolerant bacteria for reduction of Cr(VI) to Cr(III).

Reduction and immobilisation of Cr(VI)

Microbial reduction of Cr(VI) is attractive for several reasons. Microbes reduce Cr under either aerobic or anaerobic conditions. The reason that some microbes have developed a capacity for Cr(VI) reduction has not yet been adequately explained. It has been suggested that:

• the reduction may be a mechanism for chromate resistance;
• Cr(VI) reduction may be a fortuitous reaction carried out by enzymes that have other physiological substrates;
• Cr(VI) reduction may provide energy for microbes.

Chromium reductase is widespread in microbes, but it is primarily present in the soluble fractions of the microbial cell. It reduces the Cr(VI) to Cr(III) with the oxidation of three moles of NADH per mol of Cr reduced. It has been reported that NADH could non-enzymatically reduce Cr(VI) to Cr(V) in the absence of enzyme. A membrane protein also appears to be important for Cr(VI) reduction by bacteria. Direct and indirect microbially-mediated bioreduction of Cr(VI) has been observed. Anaerobic bacterial strains with accelerated Cr(VI) reducing capabilities have been isolated from chromate-contaminated water and sludge. It is evident that anaerobic bacteria can effect preferential bioreduction of chromates under reducing conditions.

Toxic and mutagenic effects of Cr on microbes are well documented. Soil bacteria are inhibited with 10–12 mg Cr(VI) L^{-1}. Chrome-electroplating waste is toxic to saprophytic and nitrifying bacteria. However, bacteria that live in varied environments, where heavy metals occur naturally at high concentrations, evolve with resistance mechanisms, including the capacity to transform toxic species through processes such as:

• methylation, demethylation, oxidation, reduction, hydrogenation, hydroxylation, dehydroxylation,
• changes in uptake or transport of metals, and
• anaerobic growth with acetate, ethanol, malate, succinate, or glycerol, that favour Cr reduction.

There is a need to search for innovative methods for minimising the pollution. What is needed is a practical method that can be implemented to curtail the impact of Cr, the foul smelling sulfides and the level of common salt in tannery effluents. Many Indian tanning industries are small-scale, and hence the construction of waste water treatment plants is not economical for them, while treatment of the waste waters chemically is also a costly affair. It is necessary at this stage to work out an economical treatment process which will effectively alleviate the problem.

One alternative could be biological waste water treatment processes. It is known that all biological processes work faster in tropical conditions. By employing microorganisms, it could be possible to degrade pollutants and work out their fate in the natural environment. Tannin, the biggest pollutant in vegetable tanning effluents, is a phenolic and basically organic compound. Hence microbial degradation of this compound is a possibility.

Table 4. Distribution of chromium, sodium, electrical conductivity (EC) and pH in soil, water and groundwater

Sample	pH	EC (dS m^{-1})	Na (mg L^{-1})	Cr (µg L^{-1})
Raw effluent	6.17	11.4	2280	26 200
Treated effluent	8.17	13.4	2040	8800
Soil: Ambur	7.81	15.5	40 698	5728
Vaniyambadi	8.16	5.5	10 125	1314
Pernampet	7.70	20.8	29 239	16 158
Water	7.8	6.0	780	59
Borehole water	8.2	6.9	1600	511

Anaerobic treatment

Anaerobic digestion

Anaerobic digestion of vegetable tan liquor brings about a reduction in biochemical oxygen demand (BOD) of 95%, but this is reported at a low loading of 0.8 kg m^{-3} of volatile solids. Retention period is high. Our group has isolated and characterised an anaerobic bacterium, *Bacteroides* sp., capable of degrading tannin from the combined effluent. We have also characterised the intermediary compounds formed by this bacterium and developed a treatment strategy to remove residual tannin from composite effluent from tanneries. Reduction of Cr(VI) by anaerobes, and specific sorption by aerobes, could be possible factors controlling the treatment through bioremediation.

Anaerobic lagoon

The anaerobic lagoon employs the principles of anaerobic digestion with no gas collection. The capacity of a lagoon can be about 15 to 20 days storage. These lagoons can be operated at high loadings of 100–250 kg ha^{-1}d^{-1}. Biochemical oxygen demand of tannery waste is reduced by 70–80%. Once the lagoon stabilises and methane fermentation sets in, it becomes self-sustaining. Studies have found that the BOD of settled tannery waste reduces from 1500 mg L^{-1} to 190 mg L^{-1}. This process involves low capital and running costs.

Aerobic treatment

Oxidation pond

In an oxidation pond, the depth varies from 1.0 m to 1.5 m and BOD loading is 250 kg ha^{-1}d^{-1} with a retention period of 40 days. The BOD of the settled and diluted waste mixed with sewage in the ratio of 3:1 can drop to 218 mg L^{-1} from 802 mg L^{-1}.

Activated sludge process

Studies of the activated sludge process have found that at a mixed liquor suspended solid (MLSS) concentration of 3000–4000 mg L^{-1}, the BOD of the pretreated effluent comes down to 34 mg L^{-1} from 988 mg L^{-1} within 24 hours of aeration. Generally a BOD removal of 85–95% can be expected from this system. We have isolated and characterised several floc-forming bacteria associated with the sewage sludge digestion. The same cultures as those adopted to deal with agro-industrial wastes have performed well in association with other heterotrophic bacteria to reduce the protein concentration and metals. Most of the metal removal is by sorption and sedimentation.

Trickling filtration

With trickling filtration, the BOD of pretreated vegetable tannery effluent can fall to 158 mg L^{-1} from 900 mg L^{-1}. When the filtered effluent settles, the BOD drops to 56 mg L^{-1}. In the case of chrome tanning waste, the BOD can be brought down to 88 mg L^{-1} from 129 mg L^{-1}, and a further reduction in BOD, to 56 mg L^{-1}, can be obtained after setting the effluent from trickling filtration.

Aerated lagoon

With the aerated lagoon system, a BOD removal of 70–90% has been demonstrated.

Oxidation ditch

The oxidation ditch is an extended aeration system with a low organic loading and a high mixed liquor suspended solids concentration of the order of 400 mg L^{-1}. A BOD removal of 90–95% can be expected with this system.

Constructed wetlands

The use of constructed wetlands using native water plants and floating macrophytes is catching the imagination and attention of the pollution abatement system. Some macrophytes (such as water hyacinth) accumulate heavy metals at higher rates and are suitable candidates for the tertiary treatment sites. A constructed wetland provides an aerobic and microaerophilic environment, so it could be suitable for reducing the heavy metal contamination and organic loading in waste water.

Microbial reduction of chromium

Traditional techniques for remediating chromate-contaminated tannery effluent involve reduction of Cr(VI) to Cr(III) by chemical or electrochemical means at pH >5, followed by precipitation and finally filtration or sedimentation. These processes are intensive, and present costs for disposal are very high. The discovery of microorganisms that preferentially reduce Cr(VI) has led to applications in the bioremediation field which are potentially more cost-effective than traditional methods.

Table 5. Tolerance limits for industrial effluent discharged into surface waters or sewers or onto land

Important characteristics	Into inland surface waters	Into public sewers	On land for irrigation
Colour, odour	absent	–	absent
pH	6.0 – 9.0	6.0 – 9.0	6.0 – 9.0
Suspended solids (mg L^{-1})	100	600	200
BOD (mg L^{-1})	30	350	100
COD (mg L^{-1})	250	–	–
TDS (mg L^{-1})	2100	2100	2100
Chlorides as Cl$^-$ (mg L^{-1})	1000	1000	600
Total chromium as Cr (mg L^{-1})	2	2	2
Hexavalent Cr (mg L^{-1})	0.1	0.1	0.1
Sulfide as S (mg L^{-1})	2	2	2
Sodium (%)	–	60	60
Boron as B (mg L^{-1})	2	2	2
Oil and Grease (mg L^{-1})	10	20	10

Biosorption or reduction

Russian researchers first proposed the use of Cr(VI)-reducing bacterial isolates in the removal of chromates from industrial effluents. Since then, various reduction parameters have been evaluated for a diverse group of microorganisms that accelerate Cr(VI) reducing capabilities, with the prospect of developing commercially viable bioremediation techniques exploiting these organisms. Bioreactors are used which basically consist of a reduction phase with Cr(VI)-reducing bacteria immobilised on inert matrices within the reactor, followed by a settling or filtration phase to remove Cr(III) precipitates. Chromate-contaminated effluent is pumped into the reactor and supplemented with various carbon sources and nutrient additives; the Cr(VI) is then reduced, precipitated and removed. A disadvantage here is that the lowest achievable effluent concentration of Cr is probably around 1 mg L^{-1} and considerably higher than the national Environment Protection Authority drinking water standard of 0.05 mg L^{-1}. Also the reaction rate is slow.

A land-application method for remediating Cr-containing effluent has been investigated. It consists of passing the effluent through an organic matter-enriched soil where reduction, precipitation and immobilisation take place. Another application of direct reduction has been demonstrated using anaerobic Cr-reducing bacteria. The cultures, in dialysis tubes, are submerged in contaminated water. Chromate diffusing into the tubes is reduced and precipitated and thus is unable to diffuse out. Laboratory studies using this system have found that 90% of the Cr is removed from water.

Gaseous bioreduction

Gaseous bioreduction involves microbial reduction of Cr(VI) by a metabolic byproduct which is produced in anaerobic environments by sulfate reducing bacteria. An anaerobic bioreactor is used, containing marine-derived sulfate-reducing bacteria, immobilised as a biofilm on gravel. By this method, effluent Cr levels as low as 0.01 mg L^{-1} are attainable. An advantage of this system over biosorption or bioreduction is that the CrO_4^{2-} need not come into contact with the cells for reduction to occur. Hydrogen sulfide (H_2S) diffuses out into the medium, and this can increase the reduction rate and protect the cells from the toxic effects of Cr(VI). This could promote faster reduction rates and may explain the lower effluent concentrations achieved.

Minimum National Standards for the quality of tannery waste water have been established and the Ministry of Environment and Forests, Government of India, has stipulated the pollution control standards in Table 5. Compliance to these standards has been a problem for the tanners. Because of the nature of the tannery waste waters, it is a major problem to treat waste water to a consistent quality. Solutions cannot be easy and piecemeal.

Treatment and Disposal Arrangements in India

The degree and type of treatment vary greatly from tannery to tannery. In most of the units, initial treatment takes place in effluent sedimentation tanks to settle the solids. Some of the units have mechanical or chemical treatment systems. It is reported that in the important tanning centres, 82% of tanneries in Pernampet and 57% in Ambur are treating effluents. The tanneries at Vaniyambadi, Ranipet and Chennai are treating the effluents at primary level.

In Tamil Nadu, tanneries have set aside part of their own land for the accumulation of effluents and subsequent solar evaporation. Even the agricultural lands are being used for this purpose. From half of the units in Ranipet and Chennai and its neighbourhood, where some type of effluent treatment system is being followed, the effluents are let out into the adjoining areas. About 33% of the units have earmarked their own lands specifically for disposing of the effluents. In Erode, only one unit is treating the effluents and it runs the treated water onto its agricultural lands. It may be noted that during the rainy season, along with the drain and rain water, the effluents ultimately find their way into the rivers, drainage canals and sometimes flood the fertile agricultural lands as well.

Challenges Ahead for Indian Tannery Industries

The global market for leather products is competitive. 'Value adding' through design innovations is possible, but this needs to be done at the output end of the process rather than being linked to the input stages, unlike many other manufacturing sectors. In other words, knowledge of the market and of consumer needs for fashion products is essential if manufacturers are to realise value from finished leathers of identical qualities. Control on raw material and skill base as inputs is not adequate.

The tanning industry is a challenging sector which demands entrepreneurial skill and innovative management systems suited to small industries. Since fashion changes frequently, it is necessary to be able to respond to rapid change in the market's needs. Small-scale production systems permit flexibility. There is also a need for constant technological innovation in the sector, for

economic gain from leather processing. This is a challenge to a tannery owner. Material, method, money, men and market management form the fundamental needs for a tanner. If all these challenges are met then there remains a need to ensure that industrial practices are such that they have minimum impact on the environment. Indeed the environmental impact of tanning industries poses the greatest threat to the human resources employed within the industry, and to the land and water bodies. Despite these challenges, the tanning sector is rapidly emerging as one of the largest foreign revenue earners in India.

Legal Measures On Environmental Protection

On August 28th 1996, the Supreme Court delivered a historic judgment on pollution in India. In a series of comprehensive measures aimed at minimising the environmental impact of the tannery industry in Tamil Nadu, the Supreme Court directed the Government of India to establish within 30 days an independent authority on each of the tanning polluting units. During this process the high court also levied a penalty of Rs 10 000. The polluting tannery units were to pay the fees by October 30, 1996 and this money was to be deposited, with the compensation amount for the affected families to be assessed by the authority, in an Environmental Protection Fund.

The compensation paid by the polluting industries would be computed by the authority according to the loss caused, or damage done, by the reversal of the ecology and failure subsequently to set this right. The amounts so computed by the authority were to be forwarded to District Collectors, and they could recover them as arrears of land revenue. The court directed the district authorities to close down any polluting units whose owners refused to pay the compensation amounts arrived at by the authority.

In the recent judgement the judges, while suspending the closure of all tanneries in five districts of Tamil Nadu, gave one last opportunity to the tanneries to set up common effluent treatment plants or put up individual pollution control devices before 30 November 1996. This was in addition to the primary pollution control devices already functioning in the tanneries.

The court ordered that by 15 December 1996, all the tanneries should obtain a consent order from

the State Pollution Control Board. Moreover establishment of new industries within a 1 km wide area along the river bank was prohibited. The court directed that pollution standards should be operative in all the cases. All these measures resulted in the establishment of 11 common effluent treatment plants (CETPs) and a few more are being considered.

Conclusion

The present overview provides an appreciation of tannery industries in India and also of the adverse environmental impact of waste disposals. Despite the tannery industries' major economic contribution to the country, it is now estimated that the adverse impact of their wastes may cost the country billions of dollars in lost production. Research during the last four years, together with the recent ruling by the Supreme Court indicates that implementation of better waste management practices, together with new industrial processes, may lead to significant economic benefit to the country. Given that many tannery industries are located in close proximity to each other it may be better to combine the treatment systems, thereby minimising costs. It may also be reasonable to combine the anaerobic and aerobic treatments through different steps and use macrophytes for tertiary treatment for toxic effluents. Such a combination will ensure safe disposal to receiving ecosystems because as the effluent passes through the treatment plants, microbial processes may enhance the removal of toxic substances. Unfortunately, the industry has so far only attempted to precipitate the colour and organic colloids, by adjusting the pH or through the use of coagulants. The introduction of chemicals during the treatment process may further limit the use of treated effluents for land-based production systems.

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Critical Environmental Issues Relating to Tanning Industries in Bangladesh

S.M. Imamul Huq[1]

Abstract

Industrialisation has been rapid in Bangladesh during the last decade, particularly in the sectors of leather, pharmaceuticals and industrial chemicals. However, these industries are discharging and dumping their wastes and effluents without treatment into nearby water bodies. Tanning — one of the oldest industries in the country — contributes to a great extent. Most tanneries are in Dhaka, beside the River Buriganga into which they flush their waste water. Studies have found high levels of pollution at several points in the river. Macrophytes in the river absorb various amounts of nutrients and pollutants, but the macrophytes are then eaten by livestock or humans. Other studies have measured heavy metal species in soils and plants in the tannery areas that have been affected by tannery waste. In grasses, Cr accumulates to concentrations exceeding the limits set by health authorities, and the yields and performance of rice and wheat are reduced.

THERE are at present 214 tanneries in Bangladesh: 200 of them in the city of Dhaka and 14 others scattered all over the country. Covering an area of 25 ha, Hazaribagh in the heart of Dhaka city is the centre of the entire leather industry of Bangladesh. Nearly 149 tanneries of the 200 producers of leather and leather products are located in the Hazaribagh area. Fifty three of these 149 operate all year round (Enamul Haque et al. 1997).

Tanneries in Hazaribagh were started in 1960 by Punjabi traders from what was then Pakistan. The industries grew and, after the independence of Bangladesh in 1971, became a 'cash cow' to earn foreign currencies. In terms of foreign exchange earnings, hides and leather are among the five leading commodities in Bangladesh (Khatun and Huq 1994; Enamul Haque et al. 1997). It has been estimated that about 13 500 000 pieces of hides and skins from all over the country are brought to Hazaribagh every year for processing. The peak time of collection is during the Muslim festival of animal sacrifice, the Eid-ul-Adha. These industries influence local and foreign exchange and also the environment of Bangladesh.

Effect on Economy

The leather industry sector is the fourth largest foreign exchange earner of the country, contributing about 6% of total export earnings. Export earning from the leather industries sector in 1995–96 was US $237.79 million, of which US $211.70 million was from leather exports, and US $26.09 million from export of finished leather products. The leather sector provides about 10 000 jobs in Dhaka alone. It has been reported in a survey that manufacturing industries in and around Dhaka city provide about 270 000 jobs, which is around 25% of the total employees in the city (Emranul Huq and Hossain 1996), and the leather industry provides about 4%.

Processing

Tanning—the making of raw hides and skins into leather—converts the putrescible protein in hides and skins into a stable, non-putrescible material. The tanning process in Hazaribagh involves chrome tanning, vegetable tanning and combined

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chrome and vegetable tanning. Chrome tanning is used for light leather, and vegetable tanning for heavy leather for shoe soles, handbags, straps and belts, for example. Except for a few big leather-producing firms that produce nearly 80% of the total daily output, most of the firms use vegetable tanning processes. In vegetable tanning, raw hides and skins are treated in water containing extracts from plant leaves, barks, fruits, and roots. In chrome tanning, raw hides and skins normally go through a process called pickling, with sulfuric acid and common salt, after which they are treated with solutions of basic chromium salts. In the Hazaribagh area about 260 t of hides and skins are processed each day. The processing uses nearly 35 L water kg^{-1} raw material, so the volume of water used is about 9100 kL or 9100 m^3. The quantity of raw hides and skins increases to about 426 t during the peak period which extends to two or three months after the Eid-ul-Adha festival.

Various chemicals are used during the soaking, tanning and post-tanning processes of hides and skins. About 2000–3000 t of sodium sulfide and nearly 3000 t of basic chromium sulfate, in addition to other chemicals, are used each year for leather processing and tanning (DOE 1992). These other chemicals include non-ionic wetting agents, bactericides, soda ash, calcium oxide, ammonium sulfate, ammonium chloride, enzymes, sodium bisulfate, sodium chlorite, sodium hypochlorite, sodium chloride, sulfuric acid, formic acid, sodium formate, sodium bicarbonate, vegetable tannins, syntans, resins, polyurethane, dyes, fat-emulsions, pigments, binders, waxes, lacquers and formaldehyde. Various types of process and finishing solvents and auxiliaries are used as well.

Wastes

The process of tanning produces both liquid and solid wastes. The solid wastes are predominantly from the initial and final stages of processing while the effluents are produced mostly during tanning and dying. The 149 operating tanneries produce 14 910 m^{3}d^{-1} of effluents or waste water during the peak time and about 9100 m^{3}d^{-1} waste water during the off-peak period. The effluents contain dissolved lime, hydrogen sulfide, acids, chromium dyes, oils, organic matter and suspended solids. The waste water is discharged into open drains and ultimately finds its way onto land surfaces and into natural waters in the vicinity. About 150 Mt of solid

waste is produced per day, of which 59% comes from the hides and skins processed. Part of the solid waste is collected by the Dhaka City Corporation and taken to landfill sites but most of it accumulates in the swamp-sludge.

Below is a schematic representation of the solid and liquid waste disposal system in the tannery area of Hazaribagh:

Soaking and Liming $\Rightarrow$ Chemicals, wastes $\Rightarrow$ salt, dirt, blood, hair, flesh, lime, sulfide, etc. $\Rightarrow$ **Solid and Liquid wastes**

Tanning $\Rightarrow$ Chemicals $\Rightarrow$ Chromium oxide, ammonium sulfate, formic acid, sulfuric acid, sodium chloride, etc. $\Rightarrow$ **Solid and liquid wastes**

Post tanning and processing $\Rightarrow$ Chemicals, synthetic oil, bleaching agents, dye, phenol $\Rightarrow$ **Solid and Liquid wastes**

Treatment Facilities

In tannery industries, treatment methods that must be used to combat pollution include segregation of process waste water, sedimentation, neutralisation and biological treatment. Unfortunately, except for two modern tanneries, BATA and Dhaka Leather Complex, none of the tanneries has a treatment plant. Few leather industries reuse any of the liquid wastes. Most of the wastes and effluents are subjected to natural decomposition in the environment, causing serious pollution problems affecting soil, water, air and human life. Currently, about 90% of the finished trimming wastes are used by local shoemakers. About half the tanneries apply some kind of solid waste reuse. The government of Bangladesh made an attempt to relocate the tanneries from the present area to a proposed site outside Dhaka and offered a compensation of US $1.4 million for this purpose. An Asian Development Bank study concluded that US $18.4 million would be needed to develop an area with waste treatment facilities; but because of lack of funds, the relocation scheme has been abandoned. Instead, the Government has decided to establish a common effluent treatment plant with the assistance of the United Nations Industrial Development Organization (UNIDO) for the 200

Table 1. Water quality in the Buriganga River near, or away from, the outfall of the tannery effluents, during two seasons

Parameter	Wet Season (April – September)		Dry Season (October – March)	
	Near	Away	Near	Away
pH	7.2	6.7	7.2	7.7
Water temperature (°C)	29.5	29.5	24.5	24.5
Electrical conductivity (μS)	1650	730	2460	750
Dissolved oxygen (mg L^{-1})	1.3	3.4	0	6.1
Nitrate (mg L^{-1})	163	75	168	82
Chloride (mg L^{-1})	266	71	763	71
Bicarbonate (mg L^{-1})	244	122	854	153
Sodium (mg L^{-1})	83	19	184	53
Calcium (mg L^{-1})	4.2	2.7	5.8	3.5
Zinc (mg L^{-1})	0.05	0.04	0.06	0.05

tanneries in Hazaribagh. A preliminary study on the discharge of wastewater from Hazaribagh is being carried out by UNIDO.

Effects on Soil, Water and Crops

It has been mentioned earlier that most of the tanneries in Bangladesh are located in the city of Dhaka. Dhaka has three interconnected river systems, the Turag to the north-west, the Buriganga to the south-west and the Sitalakhya to the south-east, with the Turag flowing into the Buriganga. The Hazaribagh tanneries are located on the south-west periphery of Dhaka alongside the river Buriganga. On each side of Dhaka, a flood protection embankment has been constructed to make Dhaka flash-flood free. As stated earlier, the tanneries discharge the effluents and wastes into the river system. Consequently, there is a large area of acid sludge alongside the flood protection embankment, and the liquid wastes are dumped in the river through a flood-control regulator-cum-sluice near Hazaribagh. During monsoon months, the flood protection embankments protect Dhaka from heavy flooding while making it difficult to flush-out the waste water, thereby creating a great environmental hazard in the neighbourhood of the tanneries. On the other hand, during the dry season the waste water is flushed out into the river, causing pollution of the river water and ultimately affecting the aquatic flora and fauna. Likewise the dumping of the solid wastes is seriously affecting the soil and plants, besides vitiating the air, groundwater and human health. The impact of waste disposal

on water, soil and plants is briefly elaborated in the following paragraphs.

Water pollution

A study on the water quality of the river Buriganga near the discharge point and at a point in mid-river during April–September (wet season) and October–March (dry season) revealed that tannery effluents heavily pollute the river water, so much so that the dissolved oxygen in the river water was found to be nil during the dry season and no fish or other aquatic animals were found living, up to 500 m downstream of the sluice gate (Chowdhury et al. 1996); see Table 1.

Concentrations of Fe, Mn, Cu and Pb were determined. Only trace quantities were found, indicating that they remain precipitated on the riverbed because of the pH of the water. Values for electrical conductivity (EC), chloride, bicarbonate, nitrate and dissolved oxygen indicate high pollution, even in the middle of the river where the water is not stagnant.

Effect on aquatic plants

Various types of aquatic plants, particularly macrophytes, are present in the Buriganga River (Table 2). Macrophytes absorb macro- and micronutrients from the ambient water for their growth and nutrition. The macrophytes also absorb pollutants from the river water and store them in their cells. When biota further up the food-chain, such as humans, animals and fish, eat the macrophytes the biota is also affected by some of

Table 2. Distribution of macrophytes in the Buriganga River

Location	Source point	Aquatic macrophytes	
		Wet season	Dry Season
Hazaribagh	1	*Hydrilla verticillata*	*Polygonum glabrum*
		Ceratophyllum demersum	*Cyperus platystylis*
	2	*Alternenthera philoxeroide*	*Ipomea aquatica*
		Ipomea aquatica	*Cyperus platystylis*

these undesirable substances. In this way, various pollutants enter the food chain, and are likely to cause degradation of the natural system.

Macrophyte samples were collected from two source points: the first was along the Hazaribagh tannery sluice gate; the second was about 50 m downstream of the first point (Table 2). Water samples at the same two points were analysed and the results are summarised in Table 3.

Table 4 shows the concentrations of ions determined in the wet and the dry seasons in the macrophytes and the water of the Buriganga River at the two source points. Table 4 shows that the concentrations of P, Fe, Cu, Zn and Pb tend to be higher in the macrophytes at source 1 of the Hazaribagh location during the dry season than during the wet season. However, different macrophyte species absorb different amounts of pollutants. At source point 2, the concentrations of K, P, Mg, Fe, Cu, Mn, Zn, Na and Pb in the macrophytes were higher during the dry season than was observed during the wet season. At this location, the extent of pollution during the dry season was greater than at source point 1.

The concentrations of Na, Zn and Pb in all the macrophytes, and Fe in *Hydrilla verticillata* (Kurali), *Ceratophyllum demersum* (Jhangi), *Polygonum glabrum* (Bishkatali) and *Cyperus platystylis* (Burunga) are toxic. Only three macrophyte species, viz., *Alternenthera*

philoxeroide (Sechi sak), *Cyperus platystylis* (Burunga) and *Ipomea aquatica* (Kalmi lata) were abundant in both seasons.

These macrophytes are consumed either by humans and their animals or by various fishes. Particularly, human beings eat Kalmi and Sechi 'saks' as leafy vegetables. Macrophytes growing in the Buriganga are used as a source of animal fodder as well. So, the pollution that is occurring in the Buriganga River water is slowly entering the food chain and is likely to cause degradation or disruption of the natural ecosystem.

Effect on soils and plants

Very scanty data are available about the spatial distribution of the pollutants from the sources, their extent and concentrations, and their effects on natural vegetation and cultivated crops. Research has been conducted in the Department of Soil Science at the University of Dhaka on the effects of wastes and effluents on soil properties adjacent to the tanneries and other industries. In these studies, the intensity of pollution in the soil, on field crops and on water bodies has been measured. In some cases, the effects on crop performance, physiology and metabolism have also been studied. Compositions of effluents and waste water collected from locations adjacent to the tannery industries in the Hazariba7gh area are as follows:

pH = 7.9; EC = 8.0 S cm^{-1}; Ca = 62 mg L^{-1};

Table 3. Ionic species in the Buriganga river during the dry season (tr = trace)

Location	Concentration (mg L^{-1})										
	NO$_3$	P	K	Ca	Mg	Na	Zn	Fe	Cu	Mn	Pb
Hazaribagh											
Source 1	115	0.50	13	4.2	17	96	0.05	tr	tr	tr	tr
Source 2	110	0.25	9	3.5	1.5	53	0.03	tr	tr	tr	tr

Table 4. Comparison of ionic species and pollutants among six macrophytes species and ambient water in wet and dry seasons at two sources

	K	Ca	P	Mg	Fe	Cu	Mn	Zn	Na	Pb
			Ionic species and pollutant contents (mg L^{-1})							
A. At source 1										
				Wet season						
Hydrilla verticillata	27457	395	3952	6088	2433	26	361	81	33	3
Ceratophyllum demersum	45014	21	2756	3493	2389	30	679	78	33	21
Water	34	3.3	0.45	10	tr	tr	tr	0.05	40	tr
				Dry season						
Polygonum glabrum	19900	78	5096	5261	2611	41	683	87	17	24
Cyperus platystylis	47609	238	4940	5013	2405	37	295	141	133	17
Water	13	4.2	0.5	17	tr	tr	tr	0.05	96	tr
B. At source 2										
				Wet season						
Alternenthera philoxeroide	40052	359	3172	2324	823	7	76	23	100	21
Ipomea aquatica	27457	250	3588	2112	836	9	39	43	50	3
Water	18	2.4	0.2	6.7	tr	tr	tr	0.02	14	tr
				Dry season						
Ipomea aquatica	57685	384	4784	3652	1128	18	584	187	100	24
Cyperus platystylis	32495	160	4056	3113	1955	32	240	123	117	17
Water	9	3.5	0.25	15	tr	tr	tr	0.03	53	tr

Mg = 25 mg L^{-1}; K = 12 mg L^{-1}; PO$_4$ = 26 mg L^{-1};
SO$_4$ = 815 mg L^{-1}; Cl = 2470 mg L^{-1};
Cu = 0.04 mg L^{-1}; Fe = 0.4 mg L^{-1};
Mn = 0.17 mg L^{-1}; Zn = 0.13 mg L^{-1};
Cr = 0.28 mg L^{-1} (Pb and Cd not determined).

These values are averages of between three and five samples taken at various sampling times (Nuruzzanman 1995; Kashem 1996). The Cr level has been found to vary from 0.02 to 0.28 mg L^{-1} in the waste water and from 0.34 to 1.3 mg L^{-1} in the effluents, the highest value being for material collected at the source and the minimum value for material collected farthest from the source.

Studies on the properties of soils collected from the tannery area revealed that soluble salts, particularly Ca and Mg from tannery effluents, enhanced the soil cation exchange capacity which adversely affects seedling establishment. More than 505 mg L^{-1} of Cl was found in the soil solution at the disposal point of the tannery wastes, but this decreased the total and available N, P and S in the surface soils. High accumulation of N was observed even at 120 cm depth. This is a source of groundwater contamination. Excessively high concentrations of N and S appear to be hazardous in the tannery waste disposal areas.

Of the heavy metals, tanneries have been found to discharge not only Cr, which is an inherent product of the tanning proces, but also significant amounts of Zn, Mn, Cu and Pb. High levels of Cr (29 402 mg L^{-1}) with Zn, Cu and Pb have been observed at the main waste disposal point, exceeding the toxic level range in soils. The extractable fractions of heavy metals (Table 5) give some indication of their phytoavailability and mobility in soils of that area. Many of these heavy metals are being carried down to the groundwater and are causing severe environmental concern. The season of the year is not reflected in any substantial fluctuation in the values of heavy metal contents. Cr appears to be concentrated more in the surface 0–15 cm. There is a decreasing trend in the spatial distribution of Cr from the point of discharge.

Mineral N was found to increase both in the effluents (521–1089 mg L^{-1}) and in the waste water

Table 5. Total and extractable contents (mg L^{-1}) of heavy metals in soils of the tannery area

Ionic species	Total (HNO$_3$-HClO$_4$)	DTPA extractable	NH$_4$OAc extractable
Cd	1.26	0.04	—
Cr	20845	—	51.5
Cu	115.5	8.0	2.7
Fe	21086	226.4	20.2
Mn	425.2	53.2	2.9
Ni	89.8	3.0	—
Pb	68.1	7.7	—
Zn	290	23.4	3.0

Source: Nuruzzanman 1995; Kashem 1996

Table 6. Metal contents (mg kg^{-1} dry matter) in plants collected from the tannery waste-affected area

Metal species	Water hyacinth	Grass	Paddy
Cd	—	0.83	0.58
Cr	161	595	12
Cu	5.3	16.7	48
Mn	116	229	372
Ni	—	14	7
Pb	—	45	13
Zn	139	158	107

Source: Nuruzzanman 1995; Kashem 1996

(23–261 mg L^{-1}). Total organic carbon in the tannery waste water (850 mg L^{-1}) and effluents (520–1050 mg L^{-1}) were found to be above limit values. The phosphate and sulfate contents in the effluents and waste water showed toxic limits even 1.5 km downstream from the main disposal point.

Analysis of the standing field crops and aquatic plants showed that the concentrations of N, P, K, S, Fe, Cu, Mn, Zn, Cr, Cd, Pb were correlated with total contents of these elements in the soil. Grass accumulated more Cr than paddy and water hyacinth, and exceeded toxic limits (Table 6). Transfer coefficients for Zn, Cu and Mn into rice, water hyacinth and grass were higher in rice plants than in grasses and water hyacinth. Transfer of Cr into grasses was higher than into rice. These concentrations generally exceed the permissible levels (ranging from 0.05 mg kg^{-1} to 0.1 mg kg^{-1} depending on the crop) set by the Australian National Health and Medical Research Council.

Rice and wheat were grown in a pot experiment in soils from the tannery area with high contents of Cr. The wheat showed delayed maturity and stunting of growth, and the rice showed late flowering and maturity with dark green colour; Cr was found to have accumulated more in roots than in shoots or grains (Table 7).

In another experiment it was observed that application of tannery effluents to soils of differing textures resulted in reduction of yield of rice, with enhanced uptake of Na, Mn, Zn, Cd and Pb. The adverse effect was more pronounced in light soils than in heavy soils. The effluent was also found to negatively affect performance, nodulation and growth of mung beans (Nazmul Islam 1994).

Regulatory Measures

Toxicities of chemicals used in Bangladesh are not generally tested, except for some formulated drug items. The Department of Environment (DOE) is responsible for ensuring the safe use and disposal of toxic chemicals or effluents from various industries, including the tanning and leather industries. The existing industries in most cases do not have any effluent treatment plants for neutralising the toxicity and harmful effects of their pollutants. Those industries have now been directed to build appropriate waste treatment plants for neutralising harmful chemicals before disposal of the waste into the environment. The government has recently fixed a legal limit value for discharge of tannery effluent to surface water but this has yet to be enforced.

For new industries, an environmental impact assessment has made it mandatory for them to set up appropriate procedures at the planning stage,

Table 7. Metal contents (mg kg^{-1}) in wheat and rice grown on soils contaminated by tannery wastes

Metal species	Wheat root	shoot	grain	Rice root	shoot	grain
Cr	376	5.4	<5	4702	112	<5
Cu	9.9	4.2	9.7	4.0	6.3	4.3
Mn	19	10	15	161	125	34
Zn	129	57	118	276	121	3

Source: Nuruzzanman 1995

so that development can be safe and sustainable. These activities of DOE are backed up by an Ordinance promulgated in 1977, which is still in force as an act of law.

Future Research to Manage Tannery Waste-contaminated Land

The available information on the nature and extent of contamination of soil by tannery wastes is not sufficient. Further research is needed to:

a) assess the effects of tannery wastes on soil quality with respect to physical, physico-chemical and biological properties, and more particularly nutrient dynamics and microbiology;

b) investigate in situ the uptake of various heavy metal species by the existing crops and by various economically important crops under experimental conditions;

c) determine the threshold limits of various heavy metals for various crops;

d) determine the extent of pollution of surface and groundwater by the wastes;

e) study the ameliorative effects of various organic manures and materials;

f) find an acceptable strategy for the disposal of wastes to the agricultural system — alternative uses of the treated wastes for agriculture and/or other purposes;

g) study the transfer of polluting agents to humans and animals via the food chain.

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Critical Environmental Issues Relating to Tanning Industries in Nepal

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Abstract

In comparison to neighbouring countries, the leather industry sector in Nepal is very small. Tanneries in Nepal are still in a pre-industrial stage. The leather industry is the third major export earner of the country, but, because of the absence of a value-added leather conversion sector, it is providing limited employment opportunities. Regulatory measures have been lax, so the use of poor quality water and chemicals and the uncontrolled disposal of waste water and solid waste are damaging the environment. Pollution preventative techniques such as cleaner technology, effluent treatment facilities, recycling and waste reuse are not being practised in this country. The environmental Act and Regulation on pollution control are not yet effective due to lack of a strong implementing mechanism. So far, no work has been initiated to assess the impact on soil and agriculture. A study program is needed immediately.

COMPARED to other south-east Asian countries, the industrial sector in Nepal is still in an early stage of development. Industrialisation started late—after 1950—and for most of the fifties and sixties it concentrated on the building up of basic infrastructure for industrial development and the establishment of import substitution industries. It was only after 1970 that the industrial sector started to have an impact on the national economy and to provide employment. Major industries established during this period were agricultural and forest-based, producing products for export and domestic consumption. There has been a widening of the industrial base in recent years with the establishment of several modern industrial enterprises.

The history of the leather sector in Nepal is not very old; the tanning industry was only established during the mid-1960s. According to recent sectoral analysis, the leather and leather product industries are the third major export earner of the country and have good development potential (Table 1).

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Compared to neighbouring countries, the production capacity of Nepalese tanneries is very small. Industrial production of leather in Nepal is carried out by 16 tannery units, most of them in the southern lowland of the country adjoining Bihar and Uttar Pradesh, the northern states of India. Though the basic leather manufacturing process is the same, none of the tanneries is able to run at full capacity. In some tanneries the capacity utilisation is very low, ranging from 64% to 36%. The availabilities of raw materials, technology and machinery govern the production capacity of these tanneries.

The basic raw materials for leather manufacture in Nepal are buffalo hides and goatskins (Table 2).

Table 1. The five main industrial exports from Nepal

Major export commodity	Export value (in '000 Rs)	Percentage of total exports
Woollen carpets	7 715 000	53
Ready-made garments	5 130 200	35
Hides and skins	516 500	3.55
Gold and silverware	164 500	1.13
Handicrafts	115 500	0.8

In terms of leather production processes, technological improvement is still very slow. Leather processing knowledge and skill—both traditional and modern—are neither evenly nor widely disseminated. Further, certain technologies that are well established and widely used in other countries have not yet reached the Nepalese leather industries. For these reasons the bulk of leather is exported in the form of semi-processed wet blue leather (Table 3).

Of the total export of 11 million square feet of leather in 1995–96, about 59% was exported to European countries; Indian tanneries bought 31%.

Very few value-added leather goods are produced and there are few craft industries in Nepal, mainly because of the lack of skilled workers and finished leather. The absence of a leather conversion sector to produce value-added finished leather and leather goods is clearly reflected by the number of workers currently employed in the leather sector. A survey of all operating tanneries shows that they employ less than 1000 skilled and semi-skilled workers. The absence of leather technical support centres for skill development and technical advisory services is the main reason behind this low employment.

To promote the production of value-added finished leather and leather goods, in 1996 the Government gave tanneries 10 years to switch over from wet blue to finished leather. The operating tanneries are required to export a minimum of 15% of their production in the first year in the form of crust or finished leather. This percentage will be increased proportionately each year, and after ten years export of wet blue will be completely stopped.

As mentioned above, there are 16 tannery units in Nepal; only 13 of them are in operation at present. The majority of these are processing wet salted hides or skins into wet blue leather. The processing capabilities, water consumption and effluent volume generated by these tanneries are shown in Table 4.

Environmental Considerations

The rapid growth in exports of leather, mainly in the form of wet blue, combined with an increase in the number of tanning industries in the country has caused serious environmental degradation by water pollution and land pollution, particularly in areas where most of these tanning industries are

Table 2. The basic raw material base for leather manufacture in Nepal

Livestock	Population (million head)	Production of hides/skins (million pieces)
Bovine	9.3	1.2
Goat	5.4	2.7
Sheep	1.3	0.9

located. The open disposal of untreated waste water and solid waste onto land or into water bodies not only pollutes surface and groundwater, it equally degrades the surrounding environment, posing a great threat to the population.

Water use

All tanneries are using underground bore water. The untreated raw water is conveyed either to storage tanks or directly used in the production process. As there is no restriction on water use an unlimited volume of water turns into polluted waste water. The workers and tanners have no sense of water conservation, and there is no incentive to conserve water. Systems of recycling and reusing waste water do not exist. Some additional reasons contributing to this are:

• water sources are not metered;
• there is no tax on use of underground water;
• there is no effluent treatment plant to control the volume of waste water discharged and the load of pollutants in it.

It is therefore difficult to estimate the actual volumes of water used and waste water generated by a tannery. They can be estimated only on the basis of the weight of raw material processed and the discharge of a corresponding volume of waste water.

Water pollution

In Nepal, the tanneries are not clustered in one location as in other south-east Asian countries. The tanneries are widely separated from each other and

Table 3. Proportions of types of leather exported

Type of leather	Product percentage
Wet blue	70
Crust	20
Finished	10

Table 4. The processing capabilities of tanneries

Tannery	Production capacity (kg hide or skin day⁻¹)	Water consumption (m^3 day⁻¹)	Effluent volume estimated from process (m^3 day⁻¹)
Narayani Manufacturing Ind.	5700	91	54
Everest Leather Ind.	3600	57.6	35
Standard Leather Ind.	3000	48	29
Annapurna Leather Ind.	3000	48	29
Universal Leather Ind.	7200	115	69
Nepal Tanning Ind.	7500	120	72
Pioneer Tanning Ind.	6000	96	58
United Tanning Ind.	3000	48	29
Bagmati Tanning Ind.	600	9.5	5.7
Mankamana Leather Ind.	600	9.5	5.7
Birat Leather Ind.	3000	48	29
National Leather Ind.	3000	48	29
Marim Leather Ind.	1200	19	11
Total		757.6	455.4

Weight of raw skin ~6–8 kg per piece; weight of raw hide ~30 kg per piece

operate mostly in non-residential areas. The cumulative effect of pollutants from tanneries on the environment is therefore not apparent. However, in real terms it is very serious.

In most of the Nepali tanneries the following characteristics contribute to pollution.

1. Green weight after fleshing is not determined, so chemicals and water are added in surplus and these unnecessarily pollute the environment, particularly with sodium sulfide.
2. There is a lack of control on the production process which leads to unnecessarily excessive use of chemicals, resulting in a high pollution load, e.g. an incomplete liming process leads to poor chrome fixation, resulting in:
- lower leather quality,
- unnecessarily high cost of chemicals, and
- high chrome content in effluent.
3. There is no recycling of floats.
4. Washing is carried out continuously, creating large volumes of unwanted waste water.
5. Tannery machinery as well as drums need improvements.

These characteristics mainly result from a lack of:
- critical sense towards chemical use and technical know-how,
- well equipped testing facilities and experienced leather technologists,
- R&D service in all tanneries,
- technical know-how about cleaner technology,
- process quality control and quality improvement of the end product,
- total quality management (TQM).

All tanneries directly discharge their waste water into inland rivers or streams. Some tanneries, especially large tanneries, have small multi-chambered (3) settling tanks and/or ponds. These treatment facilities are not very effective in reducing pollutants, perhaps because:
- there is no mixing and intermediate neutralisation of effluent which would improve precipitation;
- the tanks are seldom cleaned or maintained so they are mostly filled with the solid waste and sludge from the tannery and they are not functional;
- sludge removal from the tanks (ponds) is very difficult since it should be done manually.

Waste waters from beam houses and tanyards are not separated, so they contain high concentrations of dissolved solid fibrillar materials, chemicals and chromium salt. The effect of such polluted water can be easily seen in and around discharging water bodies and land.

Solid waste

Tanneries are major sources of highly toxic and hazardous solid waste. They produce animal

residues from such operations as cleaning, fleshing, splitting, trimming, shaving and buffing. Each of these operations generates waste products, which must be either reused or disposed of. Solid wastes of animal origin are powerful pollutants in water and produce odour when they decompose.

Some factories sell or give away the solid waste to farmers who use it as fertilizer or process it in small quantities into chicken feed. Otherwise tanneries in Nepal have no organised solid waste disposal system or by-product manufacturing units.

A critical study is needed, to evaluate the quantity of solid waste generated, its disposal and the implications of that for water and the surrounding environment.

Problems and Possibilities for Cleaner Technologies

Various factors, among them the very small size of tannery units, and absence of adequate technical know-how and motivation, are the major obstacles preventing cleaner technology in Nepali tanneries. However, as the tanneries in Nepal are still in many respects in a pre-industrial stage, care is needed to ensure that the necessary modernisation goes hand in hand with a gradual introduction of low pollution and cleaner technology.

Environmental legislation and administration

Concern has already been expressed in the Constitution of the country about increasing environmental degradation and its effect on the environment. The Constitution proclaims that: 'The State shall give priority to the protection of the environment'. To meet the spirit of the Constitution and to control environmental degradation, His Majesty's Government of Nepal has set up a new ministry, Ministry of Population and Environment (MOPE). This ministry is solely responsible for formulating policy and plans to safeguard the environment from pollution. With this aim, the government has already promulgated the Environmental Act and Environmental Regulation. It will be the responsibility of the line ministries and departments to implement the provisions of the Act and Regulation in establishments that come under their administrative control.

Pollution control from industries is also regulated by the Industrial Enterprises Act (1992) and administered by the Department of Industry. Similarly there are a number of other laws which can deal with environmental pollution, especially to protect against water pollution, e.g. the soil and water conservation Act, the canal (irrigation), electricity and related water resources Act, etc.

In the control of industrial pollution, the Nepal Bureau of Standards and Metrology (NBSM) also holds a very important position. It is the responsibility of the Bureau to monitor industrial waste water and atmospheric emissions to ensure compliance with the provisions of the Act and Regulation, including compliance with standards as and when they become available and are incorporated into the Regulation. For the implementation of the industrial pollution control management strategy, the NBSM has formulated general standards on 'Waste water discharge into inland surface waters (NS: 229)' and industry specific standards on 'Effluent discharge from the tanning industry (NS: 229: Part 1)'. All these standards are of a voluntary nature; it is up to the Ministry of Population and Environment to implement and enforce them.

Waste water treatment facilities

Environmental and quality awareness are present among the staff of the tanneries but seem to be limited to individual tanners. So far, the tanning industry in the country has shown very little interest in controlling pollution, minimising waste and improving quality. In order to overcome the pollution problem and initiate the participation of tanners in pollution control, a non-governmental organisation has been subsidising 50% of the cost of making simple multi-chambered effluent treatment systems in tanneries whose tanners wish to construct this pre-treatment system.

Only recently, a project sponsored by the United Nations Industrial Development Organization, UNIDO/NEP/92/120, has started construction of one effluent treatment plant and a common effluent treatment plant as demonstration effluent treatment facilities in Nepal. These establishments will be used only for primary treatment of tannery effluent. The treated discharged water from these treatment plants will be sent to municipal waste water treatment facilities for biological treatment. This project has also established one chrome recovery unit as an effective option for

cleaner technology, and at present three tanneries are using this facility.

Future Institutional and Research Needs

At present, tanneries in Nepal are characterised by low levels of technology and the production of low-grade leather from low-grade raw hide and skins. System innovation and enhancement in industrial efficiency are necessary for quality improvement as well as reduction in pollution. To be motivated towards process modification, the tanners need clear and consistent evidence to support it.

In the present situation, to introduce cleaner technology, it is necessary to build an experimental tannery consisting of one or two small drums with the necessary equipment. This could be used to study and demonstrate new methods and test chemical recipes. In addition to this, there is a need for technical expertise in Nepali tanneries. Consultants and trainers from countries well advanced in this field could be useful in the short term for solving specific problems, establishing quality experiments, and implementing cleaner production technology. They are not and should not be an alternative to developing a sustainable Nepali tanning industry.

In order to assess the impact of tanning waste on soil, first a critical baseline study program in this direction is needed and only after this should further research work be organised to manage the tannery waste-contaminated soils.

Tanning Industries in Sri Lanka:
Review of Status

Azeez M. Mubarak[1]

Abstract

During the past decade the economy of Sri Lanka has shown a slow but steady shift from an agricultural to an industrial base. In the early 1960s the share of agriculture in GDP was around 40%. It declined to 28% by 1980 and further to 18% in 1996. On the other hand the rapid growth of the manufacturing sector in Sri Lanka has been a recent phenomenon, a direct result of the liberalisation of the economy which started in the late 1970s. The share of the manufacturing sector in GDP rose from 15% in 1980 to 21% in 1996. The industry and services sectors assume critical importance in the economic development of the country when one considers the limited land resources available to support the increasing population at a reasonable standard of living. The challenge of development in the broadest sense is to improve the quality of life, raising incomes and standards of health, and cleaning the environment. This paper describes current industrial pollution management in Sri Lanka and then focuses on the tanning industries and their impact on the environment.

THE industrial development that has taken place so far in Sri Lanka has been mainly at small and medium scale. The urban sector is dominated by small and medium size manufacturing industries including tanneries, textiles, garments, food processing, paints, varnishes, cosmetics and other chemical products, glass, asbestos products, rubber products, etc. Industries in the rural area are small cottage-scale units using traditional technologies. These include foundries, hand looms, handicrafts, bricks and tiles, the agro-based industries such as rubber processing, rice milling, coir and coconut processing, and essential oil extraction. Cement, paper, steel, petroleum refining, sugar, ceramics and textiles represent large manufacturing industries. They are few in number and, for the most part, are outside the main urban areas.

In Colombo the Gampaha districts form the most developed regions, accounting for nearly 80% of the industrialisation in the country. Morotuwa/

Ratmalana and Jaela/Ekala have the highest concentration of industries and are characterised by mixed, unplanned land use with a large number of industrial and other complexes intermixed with residential and commercial establishments. Development over four decades has created environmental problems in these two areas: water pollution is the predominant form of environmental degradation.

A recent survey in the Western Province revealed that approximately 46% of the industries classified as highly polluting have installed some type of pollution control systems (ERM 1994). Industries established after 1990 routinely install pollution control systems to treat their effluent before discharge, but the problem lies with those industries that came into operation before environmental laws came into force.

Industrial solid wastes are increasingly becoming a major problem in the country. A recent survey estimates that at least 40 000 t y^{-1} of hazardous wastes are generated in the country (ERM 1996). With moderate industrial growth it is predicted that hazardous waste generation could rise to around

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90 000 t y^{-1}. At present most of the hazardous wastes are either dumped within the site or collected by private contractors but the final destiny of these wastes is unknown.

Apart from localities where a few industries such as cement-making, quarrying or refining are located, air pollution from industrial emission is relatively small at present. However vehicular air pollution is significant in urban areas, particularly in the Colombo Metropolitan Area.

Current Strategy for Management of Industrial Pollutants

Any national management system for the control of industrial wastes should comprise the following four elements: legislation, implementation and enforcement, facilities, and infrastructure and support services. For an effective management system it is important that all four elements are in place; legislation cannot be enforced satisfactorily without facilities and support services. Nor has it been found possible to implement a waste management system nationally in the absence of suitable legislation.

Successful industrial pollution management (IPM) is a cooperative as well as coercive exercise, which ultimately relies on contributions from a range of ministries, industrial bodies and individual companies. Implementation and enforcement programs must be practical within the limits of resources and skills.

Technological actions

The IPM strategy adopted by the Government includes short-term actions for immediate implementation and a phased approach to implement longer-term actions. One of the more important actions of the IPM strategy is to actively promote Source Management and Control. At present there is a little evidence of application of source management and control procedures by industry. The reasons are both technical and financial; as well, there is a lack of awareness among industrialists of the advantages. The potential benefits both to industry and to the environment are substantial when disciplined procedures are adopted for the implementation of source management and control.

Several initiatives are already underway to promote the concept of cleaner production/waste minimisation in Sri Lanka. The Pollution Control and Abatement Fund (PCAF) operated by the National Development Bank provides financial assistance to industry engaged in cleaner production/pollution control activities. The Industrial Pollution Reduction Programme (IPRP) sponsored by UNIDO (United Nations Industrial Development Organization) aims to identify and implement financially viable waste minimisation options in textile, metal finishing, distillery and tannery industries. It is setting up site-specific demonstration projects to promote clean technologies. Local tanneries are now being assisted by UNIDO/CLRI (Central Leather Research Institute) in cleaner production activities, including water management, chrome recovery and reuse, technology upgrading and environmentally friendly processes.

To minimise the environmental degradation of water bodies in the Ratmalana and Ekala industrial areas where there is a relatively high concentration of industries, common waste water treatment systems are to be constructed with World Bank funding to treat combined industrial and domestic waste water. There are technical, commercial and economic benefits if new industry, particularly industry in the high-pollution category, is located in estates or zones that have been provided with common waste water treatment facilities. The Ministry of Industrial Development has short-listed several areas suitable for development as industrial estates. Construction of an industrial estate at Sithawaka is already underway while environmental impact assessment is being carried out on several sites in other parts of the country.

Industrial waste water treatment plants (physical–chemical and/or biological) produce sludge that requires safe disposal off-site in accordance with the specific nature of sludge generated. This requirement applies both to individual industry-based treatment plants and to combined industrial/domestic waste water treatment plants. Currently, viable outlets are limited for the disposal of this sludge. This forces industry to adopt a range of uncontrolled procedures for sludge disposal, such as spreading it on land within factory premises, with an associated risk of groundwater pollution, or having it disposed of by private contractors at unknown sites. A solid-waste disposal site is to be established with World Bank assistance in the Western

Province for municipal waste and non-hazardous industrial solid waste.

The problem of hazardous waste generation and its safe disposal has become a major concern in the country. A pre-feasibility study carried out under the Metropolitan Environmental Improvement Programme (MEIP) recommends a low technology central treatment facility for the chemical treatment and stabilisation of hazardous wastes with a landfill site for the stabilised wastes (ERM 1996). It also proposes the use of an existing cement kiln to burn pumpable organic wastes.

Support measures

Policy and legislation

The National Environmental Act (NEA) was passed in 1980. Then the Central Environmental Authority (CEA) was created in 1981 as a policy making and coordinating body. Amendments in 1988 transformed the CEA into an enforcement and implementing agency. Until recently, all industries—whether they were classified as low pollution, medium or high pollution—were required to obtain an environmental protection licence (EPL). In view of the thousands of industries scattered around the country and the regulatory burden placed on the relatively few CEA staff, it became very difficult to issue EPLs to all industries. To relieve this constraint the issue of licences to low pollution industries has been delegated to the relevant local authorities since 1994. The NEA is also being amended to prescribe that industries which are highly polluting require a licence. This will allow the CEA to more closely monitor the activities of the major polluters.

Under the environmental impact assessment (EIA) regulations, certain prescribed projects are required by law to undergo EIA. Large-scale and hazardous industries such as iron and steel industries, chemical industries, petroleum refineries, sugar, cement and paper mills, tanneries above a certain production capacity, and others, have been listed as prescribed projects which require an EIA study prior to commencement. In addition, all industrial estates exceeding 10 ha will also be required to undergo EIA.

The existing discharge standards for industrial effluent on land or in surface waters and marine coastal areas are being reviewed by the Sri Lanka Standards Institute (SLSI). National ambient air quality standards and noise control standards have been gazetted based on World Health Organization guidelines. Stack emission standards for stationary sources have been formulated and will be implemented soon. A National Definition on Hazardous Wastes, and regulations to control the collection, storage, transport and disposal of hazardous wastes, have been gazetted.

In 1996 a National Industrial Pollution Management Policy Statement was signed jointly by the ministers of Industry, Environment and Science and Technology which advocates the following principles: pollution prevention at source; polluter pays; clustering of industrial units in estates or parks; incentives and enforcement; and interaction between the community, the private sector and the government .

Institutional development

It is very difficult to build a control system for industrial pollution without strengthening the institutional capacity for monitoring pollution and enforcing the regulations. Some of the powers of the CEA have been delegated to the Board of Investment and other local authorities to help in the implementation and enforcement of the legislation. It is also envisaged that an Environmental Consultants and Consultancy Scheme will be developed to help industry.

It is important to build up indigenous capacity to develop cost-effective pollution control systems, to select and assimilate imported technology, and to provide access to foreign technical information for industry. Several state organisations such as the CISIR (Ceylon Institute for Scientific and Industrial Research), NBRO (National Building Research Organisation), RRI (Rubber Research Institute) and the universities offer testing and consulting services to industry to solve their pollution-related problems. In addition many private sector companies and consultancy firms have mushroomed to serve the growing demands. However, to provide a more effective and reliable service to industry, the expertise and facilities available in these laboratories need strengthening and accreditation to international norms.

Training and awareness

Several environment-related courses at post-graduate level have been initiated by Colombo,

Moratuwa, Peradeniya and Kelaniya universities to cater for the growing demand for environmental engineers and scientists in the country.

The ministries of Science, Technology and Human Resources Development will be implementing a comprehensive science and technology manpower development program sponsored by the Asian Development Bank next year which will enhance, among other things, the quality and R&D capability of the environmental science and technology capacity in the country.

Tanning Industry

The tanning industry in Sri Lanka is relatively small. There are about 16 private tanneries in Sri Lanka, most of which are situated in and around Colombo. These tanneries process raw hides or skins to semi-finished leather and crust or to finished leather using traditional vegetable and chrome tanning, for the domestic and export markets. Finished leather is further processed to leather goods and footwear mainly for export markets. The installed capacities of these tanneries are generally low, ranging from 15 000 kg month^{-1} to 12 000 kg day^{-1}. Some of the tanneries producing finished leathers are equipped with modern machinery, most of it imported.

The total availability of raw hides and skins per month has been estimated as 50 000 cow hides (10–12 kg each), 25 000 buffalo hides (18–20 kg each) and 45 000 goat skins (1–2 kg each). This amounts to a total supply of 1092 t of hides and skins per month or 43.7 t day^{-1} using an average of 25 working days per month (Table 1). Since the current production ceiling has been fixed at 28 t day^{-1}, a direct loss of 15.7 t of valuable raw material per day is estimated (RPPC 1997). There is, however, a shortage of good grade rawhides and skins and the tanneries have been importing some raw hides and skins as well as semi-processed leather (wet blue and crust) for processing into finished leather. The locally available raw hides and skins are not of good quality, mainly due to branding and improper flaying and preservation methods.

Impact on economy

In 1996, the textile, wearing apparel and leather sectors' contributions to industrial production were as high as 41% (1124 SDR million) (CBSR 1996).

Table 1. Profile of 15 tanneries in the tanning sector

Number of establishments	15
Raw material availability	
cow hides	50 000 (10–12 kg each)
buffalo hides	25 000 (18–20 kg each)
goat skins	45 000 (1–2 kg each)
total	43.7 t day^{-1}
Total waste water volume	1614 m^3 day^{-1}
based on production statistics (1.1 x 10^6 ft^2 month^{-1})	
1 tonne of hides = 1492 ft^2	
emission factor = 52 m^3 waste water t^{-1} hides	
number of working days = 286 per year	
Estimated pollution load	
BOD	3229 kg day^{-1}
COD	8070 kg day^{-1}
Total toxic metals	161 kg day^{-1}
Size (water use m^3 day^{-1})	No. of establishments
6–75	9
76–150	4
151–350	1
351–750	1

Sources: ERM 1994; RRPC 1997

Even though wearing apparel is the major contributor to this sector the leather industry's contribution was significant. Export of leather products has achieved a growth of 25.76% during 1990–1996. The highest growth has been seen in the travel goods and bag category. In 1996 the total export value from the leather sector was 16.4% (82.71 SDR million) of total manufacturing exports (EPI 1990–1996).

The Ministry of Industry has estimated direct employment generated by the tanning industry at 500. Employment is expected to be much higher in downstream leather processing—footwear and leather goods.

Environmental issues

Almost all the tanneries are located in urban areas that have a mixture of residential, commercial and industrial establishments. Of the 16 tanneries, only one has a treatment plant, but even this does not function optimally. Hence all the tanneries discharge their untreated effluent to inland waterways or marshy land, causing considerable pollution. In addition, solid wastes are either dumped within the site or transported outside for

Table 2. Pollution discharge standards for tannery effluent in Sri Lanka[a]

Parameter	Inland waters	Marine coastal waters
pH	5.5–9	5.5–9
Suspended solids (mg L^{-1})	100	150
BOD (mg L^{-1})	60	100
COD (mg L^{-1})	250	300
Alkalinity (CaCO$_3$) (mg L^{-1})	750	NA
Chloride (mg L^{-1})	1000	NA
Cr^{+6} (mg L^{-1})	0.5	0.5
Cr (total) (mg L^{-1})	2	2
Oil & grease (mg L^{-1})	10	10
Phenolic compounds (mg L^{-1})	1	5
Sulfide (mg L^{-1})	2	5

[a]All efforts should be made to remove colour and unpleasant odour as far as possible.
These values are based on dilution of effluent by at least eight volumes of clean receiving water. If it is less, the permissible limits are multiplied by 1/8 of the actual dilution.

dumping in marshy areas by contractors. The growing public awareness of the nuisance caused by the discharge of untreated effluent, and the visible accumulation of tannery solid wastes coupled with the obnoxious odour arising from tannery operations, have attracted increased attention to this sector. In response to objections from the public and in view of the existing tannery effluent discharge standards, the CEA has fixed the production levels of the tanneries at the 1991 level, until a more permanent solution is found.

Pollution load and water use

Based on production figures, water use of the tanneries has been estimated (Table 1) (ERM 1994). Small-scale units consume 6–75 m^3 day^{-1} while the largest unit uses 351–750 m^3 day^{-1}. Similarly, total waste water volume from tanneries has been estimated at 1614 m^3 day^{-1} using an emission factor of 52 m^3 waste water t^{-1} hides. The estimated pollution load is 3229 kg day^{-1} BOD (biological oxygen demand), 8070 kg day^{-1} COD (chemical oxygen demand) and 161 kg day^{-1} total toxic metals. Estimates are not available for the solid wastes generated: salt, hair, fleshing, trimmings of untanned leather, buffing, shavings, etc.

Discharge standards for tannery waste water

Table 2 gives the National Standards for discharge of tannery effluent into inland surface waters and marine coastal areas.

Impact on soil, water and crops

Most of the tanneries have been operating for more than 30 years, discharging untreated effluent to the nearby waterways and marshy land, and the impact on soil, water and crops grown on these marshy lands appears to be quite high. Apart from one research study that revealed the presence of chromium in leafy vegetables grown in marshy land adjacent to a tannery, there are hardly any data on the impact of tanneries on soil, water and crops.

Although the tanneries are to be relocated in an industrial zone in the Southern Province, the present locations of tanneries may require rehabilitation, depending on the extent of contamination. Rajagiriya, where some of the tanneries are located, is a priority area for further investigation because of its close proximity to the administrative capital of the country, Sri Jayewardenepura. The following actions are suggested:

i) a detailed study to estimate the impact of tannery industries on soil, water and crops in the Rajagiriya and Hendala/Wattala area;

ii) if contamination is extensive, short-term and long-term solutions should be identified, for managing contaminated land.

Relocation

A site with an area of 105 acres (42 ha) at Bata Atha in the Hambantota District (approximately

320 km south of Colombo) has been identified for relocation of all tanneries. Based on the EIA study the CEA has given provisional clearance subject to: (i) availability of sufficient water, and (ii) a dispersion model study in the event of effluent being discharged into the sea without adequate treatment. Meanwhile a proposal (RPPC 1997) has been submitted to UNIDO for technical assistance to set up the Common Effluent Treatment Plant at Bata Atha.

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Fate of Chromium in Soils

Chemistry of Chromium in Soils: an Overview

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Abstract

Chromium, a transition group metal, enters the soil environment both through natural processes and as a result of human activities. Natural processes generally include weathering of Cr-containing parent materials similar to the serpentine mineral soils. In such soils Cr concentration is generally high and often exceeds 1000 mg kg^{-1}. However, such soils rarely pose a risk to human or ecosystem health because of the low bioavailability of Cr. In its most stable elemental state, Cr has a $3d^5$ and $4s^1$ electronic configuration. Therefore Cr can exist in a number of oxidation states, the two most stable states in soils being Cr(III) and Cr(VI). Of these, the Cr(III) species forms stable tetrahedral complexes because of its much larger crystal field splitting energy. Consequently Cr(III) is often the dominant form in the soil environment. The chemistry of Cr in soils is controlled by Eh–pH interactions through its effect on soil and solution factors. Thus in soils with pH < 4.0 and at Eh values ranging from 400 to 200 mV, Cr(III) is the dominant species. In contrast, Cr(VI) is the predominant species in soils with high pH and with Eh ranging from 200 to 600 mV. Both Cr(III) and Cr(VI) concentrations are also controlled by naturally occurring reductants such as Fe(II) and organic matter, and oxidants such as Mn(IV). Chromium interacts with colloid particles both through specific and through non-specific adsorption reactions. However, a recent EXAFS study by Ferndorf (1995) indicates that Cr(VI) can bind to oxidic surfaces via either a monodentate (single) or a bidentate mechanism. The chemistry of Cr in waste material is complex and is controlled by the redox coupling reactions and pH. This paper provides an overview of Cr chemistry in soils and its implications for the dynamics of Cr at tannery waste-contaminated sites.

MANY industrial activities, including electroplating, electric power production, the leather and pulp industries, and ore and petroleum refining generate waste products that contain solid and aqueous forms of chromium (Cr) (Förstner and Wittman 1981). Due to lax regulatory measures, land disposal of such wastes has led to extensive contamination of soils and groundwater in many countries throughout the world. Following the introduction of legislation in the late 1970s and 1980s, landfills were considered as possibly suitable disposal options. However, disposal of wastes in landfills can also lead to potential release of Cr(VI) species to surface and subsurface waters. Since Cr(VI) is both toxic and mutagenic (Adriano 1986) many researchers have been working on techniques for remediating water and soils contaminated with Cr.

Following its entry into the soil environment, Cr is partitioned between the mineral, organic and solution phases. Many bacteria have charged external surfaces, so it is likely that Cr(VI) may also bind to those surfaces which have positive charge. The chemistry of Cr, however, is not as simple as that of many heavy metals. Firstly, Cr exists in both anionic and cationic state and the

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nature of the species may vary with changes in the soil environmental conditions. Such conditions may be those that occur following the disposal of wastes, with fluctuations in soil moisture levels, pH, redox potential, etc. Of the two forms or species commonly detected in nature, Cr(VI) is of concern because of its high mobility and toxicity.

Hexavalent Cr species are anionic (i.e. $HCrO_4$ and CrO_4^{2-}) and are generally mobile in most neutral to alkaline systems. Under acidic conditions, Cr(VI) is generally removed from the solution phase by adsorption reactions involving positively charged sites on oxidic surfaces (Bartlett and James 1988). Trivalent Cr follows the general reactions of cationic heavy metals, i.e. complexation with humic matter, cation exchange on humic acids or clay minerals, and formation of hydroxy compounds by hydrolysis. Although many studies have been conducted on the behaviour of Cr in the aquatic environment (James and Bartlett 1983a,b,c; Stollenwerk & Grove 1985; Richard and Bourg 1991; Anderson et al. 1994), limited effort has been directed towards studies involving the behaviour of Cr at contaminated sites. This paper presents an overview of the behaviour of Cr in the soil environment.

Position in Periodic Table

Chromium, which is a transition element, belongs to group VIB of the periodic table. It is the seventh most abundant element on Earth. The crustal concentration ($100 \, \mu g \, g^{-1}$) of Cr is much lower than the concentration in the mantle ($5000 \, \mu g \, g^{-1}$). It exhibits variable oxidation states that can range from $-II$ to VI. However, Cr is commonly found in oxidation states 0, III and VI; oxidation state III is the most stable. Hexavalent Cr is extremely soluble in water and forms divalent anion species (CrO_4^{2-}) which can rapidly reduce to Cr(III) under redox conditions and acidic pH. Chromium can exist in four oxidation states within the range of pH and redox potentials commonly found in soils: they are Cr^{3+}, CrO_2^-, and two hexavalent forms, $Cr_2O_7^{2-}$ and CrO_4^{2-} (Bartlett and Kimble 1976a,b).

Background Concentrations in Soil

The concentrations of Cr in soils are largely determined by the nature of parent material. For example, surface soils of gabbroic origin from Scotland (West 1979) typically contain Cr at

Table 1. Chromium abundance (mg kg^{-1}) in ultramafic rocks (from Sumner and Naidu 1997)

Rock type	No. of samples	Average Cr	Range
Ultramafic rocks	113	2980	205–15 300
Dunites	15	3440	1190–10 700
Pyroxenites	8	2690	920–4730
Periodites	20	2410	410–4550
Serpentinites	44	3560	670–15 300
Kimberlites	3	1200	690–1720

approximately $100 \, \mu g \, g^{-1}$ soil while in Scottish soils of granitic origin Cr concentrations are usually tenfold lower. On the other hand, soils derived from serpentines usually contain high concentrations of Cr. Birrel and Wright (1945) reported Cr concentrations ranging from 4.89% in surface soils to 3% in a subsurface soil from New Caledonia. Kilpatrick (1969) studied the distribution of nickel, Cr and cobalt in tropical soils over serpentines in the north-west district, Guyana. The Cr concentrations of soils in this area range from 100 to 38 000 mg kg^{-1} with a mean content of 1200 mg kg^{-1}. Analyses of serpentinite and of soils over serpentinite showed considerable enrichment of Cr. Similarly, high Cr concentrations ranging from 2500 to 4000 mg kg^{-1} were also reported by Proctor (1971) for British and Swedish serpentine soils. Table 1 lists the abundances of Cr in ultra-mafic rocks.

Soil Solution and Extractable Chromium

Despite the high concentrations of Cr in serpentine rocks, the concentrations of Cr in the soil solution and on the soil exchange phase are generally low. For this reason, data on the total Cr content of soils are of little relevance to plant Cr content because the Cr minerals present in soils are extremely insoluble. Chromium ion concentration in the soil is likely to be governed by the presence of insoluble $Cr(OH)_3$ which has a solubility product of 1.0×10^{-30}. Breeze (1973) reported that the solubility of Cr ion decreases 1000 fold (from 1660 mg kg^{-1} to 1.66 mg kg^{-1}) in the pH range 4.5 to 5.5. This suggests that in serpentine soils which have a pH greater than 6.0, Cr ion concentrations in the soil solution will be extremely low. The low solubility of Cr was illustrated by Soane and

Saunder (1959) who compared Cr extractability from serpentine soils using cation and anion resins at about pH 6. They found that only the cation exchange resin extracted appreciable quantities of Cr over a two month incubation period.

Soil solution concentrations of Cr in relation to uptake by oats in a wide range of soils formed on ultrabasic rocks were investigated by Anderson et al. (1973). They found concentrations ranging from 0.01 to 0.02 mmol L^{-1}. These investigators also found that Cr was not detected in neutral molar ammonium acetate solutions (NH$_4$OAc). This contrasts with the studies of Birrel and Wright (1945) who found 0.026 mg kg^{-1} extractable Cr in normal NH$_4$OAc from a soil derived from serpentine in New Caledonia. Robinson et al. (1935) noted much lower levels in a number of serpentine soils, where Cr ranged from 0.001 to 0.006 mmol kg^{-1} soil. Also Cr was undetectable in 2.5% acetic acid. These results were similar to those of Lyon et al. (1968) for a range of soils developed on serpentine in the South Island of New Zealand. Shewry and Petersen (1976) studied the distribution of Cr in soils from serpentine and other sites in Scotland and Austria. The pH values and concentrations of Cr in soil samples from these studies are presented in Table 2.

Shewry and Petersen found that exchangeable Cr comprised <0.005% of the total Cr and that nitric acid dissolved 30–50% of the total Cr. They attributed the insoluble fraction of Cr mineral to chromite. Wild (1974) studied the relationship between 2.5% acetic acid extractable Cr and Cr contents in indigenous plants growing on Cr-bearing soils. He found that 2.5% (by volume) acetic acid extracted <2 mg Cr L^{-1} from most soils and therefore concluded that Cr may be scarcely available for plant uptake. Bertrand (1969) determined M NH$_4$OAc extractable Cr in 83 soil samples from various parts of France, and found

that in 44.6% of the soils examined the available Cr ranged from 0 to 20 µg kg^{-1} of air dried soil, while 26.5% contained 20–40 µg Cr kg^{-1} and 7.2% contained >100 µg Cr kg^{-1}; results much higher than those reported above for serpentinite soils.

Behaviour of Cr in Sludge-treated Soils

It is apparent from the behaviour of Cr in soils that the amount of extractable Cr is controlled by the nature of extractants and Cr species and also by soil properties. Among the soil properties, soil pH has a controlling influence both on the nature of the soil surface and on the oxidation state of Cr. Consequently an increase in soil pH can change Cr species from cationic to anionic forms. Grove and Ellis (1980) evaluated the effects of pH on the soil chemistry of added Cr(III), Cr(VI) and sludge Cr to an Entic Haplorthod of initial pH 4.7. Concentrations of Cr ranged from 0 to 500 mg kg^{-1} as either CrCl$_3$ and CrO$_3$ or sludge at a rate of 1400 mg kg^{-1}. Following a time-dependent incubation of 1 day to 16 weeks, soils were extracted with M NH$_4$Cl, 0.1M CuSO$_4$, 0.3M (NH$_4$)$_2$C$_2$O$_4$ and citrate-dithionite-bicarbonate. Both water soluble Cr(III) and Cr(VI) decreased with time and increasing pH, although the decrease in Cr(VI) with pH was less pronounced. Exchangeable Cr (M NH$_4$Cl) and organically bound Cr (0.1M CuSO$_4$) were negligible; similar observations were also reported for natural soils developed on serpentinites by Anderson et al. (1973). Oxalate and dithionite extractions removed extremely large concentrations of Cr from all the treated soils. This suggests that the water soluble Cr compounds were rapidly transformed into highly immobile forms with ageing of the sludge- and Cr-treated soils.

The rapid immobilisation of Cr in sludge-treated soils is also evident from the recent investigations

Table 2. pH values and concentrations of chromium (mg kg^{-1} air dried soil) in soil samples from various sites in Europe (data from Shewry and Peterson 1976)

| Location	pH	Exchangeable Cr	HNO$_3$-soluble Cr	Total Cr
Unst Island	7.05–7.45	<0.1	500–1200	>1800
Aberdeen Shire	6.95	<0.1	660	>1600
Austria	7.10	<0.1	480	n.d.

n.d. = not determined

on tannery-waste-amended soils by Milacic and Stupar (1995). These investigators carried out detailed studies on the behaviour of Cr in clays, sand and peat soils for a period of two years. The final concentration of total Cr was between 1500 and 2000 mg kg^{-1}. They fractionated Cr into a water soluble fraction, an exchangeable fraction (ammonium chloride), an organic-bound fraction (tetrasodium diphosphate), a carbonate-bound fraction (sodium acetate/acetic acid), an oxide–hydroxide-bound fraction (hydroxylamine hydrochloride), and a residual (nitric acid) fraction. Fractionation of Cr in these soils indicated that five months after the start of the experimental study up to 1.1% of total added Cr was oxidised in clay, 0.45% in sand and only 0.03% in peat soils. The concentration of the water-soluble Cr and Cr(VI) decreased with further continuation of the study because Cr was redistributed to more sparingly soluble fractions of soils. The degree of Cr oxidation in these soils was found to be proportional to their concentrations of Mn(IV) oxides and water soluble Cr.

Most of the added Cr was found to be in the sparingly soluble hydroxylamine hydrochloride extractable fraction (~70%) in the clay soil. In the peat soil the Cr distribution was primarily in the organic (about 35%), hydrochloride extractable (about 25%) and mineral fractions (about 20%). These results indicate that the behaviour of Cr in soils varies considerably depending on the nature of soil type, minerals and organic matter.

Processes Controlling Cr Solubility and Transformation in Soils

The chemistry of Cr in the soil environment, including the adsorption–desorption reactions, is controlled both by factors that control the surface chemistry of soils and by the composition of the soil. Unlike most metal ions, the chemistry of Cr fluctuates with the redox chemistry of soils. Factors that favour an oxidising environment assist with the transformation of Cr(III) to toxic Cr(VI) while redox conditions favour the reverse process. However, the extent of transition is controlled by a series of complex interactions between soil and solution factors. The following sections summarise the oxidation–reduction processes controlling Cr chemistry, and the adsorption processes.
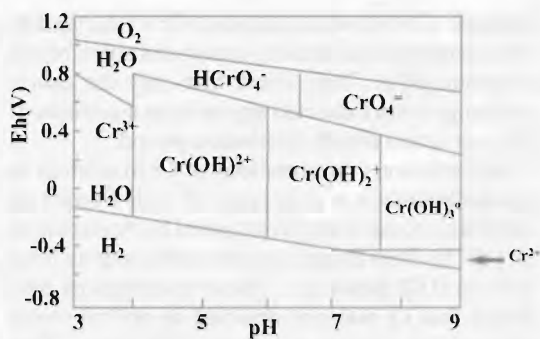

Figure 1. Thermodynamic stability of aqueous Cr species over a range of Eh and pH values (Rai et al. 1989)
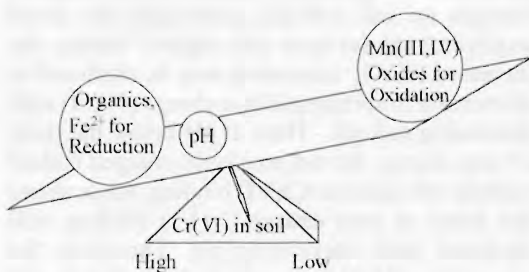
Oxidation–reduction processes

Rai and co-workers (e.g. Rai et al. 1989) studied the processes that control the environmental chemistry of Cr, and concluded that oxidation–reduction reactions, precipitation–dissolution reactions and adsorption–desorption exchanges play major roles in controlling soil solution concentrations of Cr. They found that the solubility of Cr was generally very low and limited by the formation of several oxide and hydroxide species at the pH values typical of most soils. The Eh–pH stability phase diagram in Fig. 1 illustrates the Cr species predominant under equilibrium conditions and their potential for oxidation or reduction.

With increasing pH and under reducing conditions Cr^{3+} rapidly forms metal–hydroxy species that change to anionic $Cr(OH)_4^-$ above a pH of 11. Between pH 6 and 11, the insoluble $Cr(OH)_3$ is the dominant form. In contrast to Cr^{3+}, Cr(VI) is anionic in nature under oxidising conditions at pH > 2. Above pH 6.5, $HCrO_4^-$ dissociates to CrO_4^{2-} as the dominant form of Cr(VI) in dilute aqueous systems (Deltcombe et al. 1966). These polynuclear hydroxy species condense to polymers, which initially precipitate as Cr(III) hydroxide (Spiccia and Marty 1986). Naturally occurring reductants, such as Fe(II) compounds, S(II) compounds and organic matter, transform Cr(VI) compounds to trivalent Cr compounds (Bartlett and Kimble 1976; Eary and Rai 1989). According to Sass and Rai (1987) mixed hydroxides, such as Fe(III)–Cr(III) hydroxide of solubility even lower than Cr(III) hydroxide, are the most likely forms of the precipitate under geologic or hydrologic settings.

Thus, soil pH and Eh control the form of Cr species reacting with soil colloids. Reduction rates are often pE–pH dependent (Saleh et al. 1989). Because of the differences in charge and the nature of ionic species, sorption of Cr(III) and Cr(VI) vary considerably in soils. While under normal soil pH conditions sorption of Cr(III) increases with increasing soil pH, Cr(VI) sorption decreases. Bartlett and James (1979) demonstrated that Cr(III) is oxidised to Cr(VI) in fresh soil samples only; dried soils had lost all capability of oxidising Cr(III) to Cr(VI). They found that a variable fraction (typically <15%) of Cr(III) added to soils oxidised to Cr(VI) in laboratory tests. When they added Cr(III), the extent of oxidation was proportional to the level of easily reducible Mn(III,IV) hydroxides and oxides in the soils. They also reported that presence of Mn served as the electron link between the Cr(III)–Cr(VI) redox couple and atmospheric oxygen. However, Eary and Rai (1987) found that oxidation was essentially independent of dissolved oxygen. This indicates a direct reaction between Cr(III) and β-MnO$_2$ for the production of Cr(VI), suggesting that the presence of β-MnO$_2$ in soils can catalyse such oxidation reactions (equations (1) and (2))

$$MnO_2(s) + 4H^+ + 2e \iff Mn^{2+} + 2H_2O \qquad (1)$$

$$2Cr^{3+} + 7H_2O \iff Cr_2O_7^{2-} 7H^+ + 3e . \qquad (2)$$
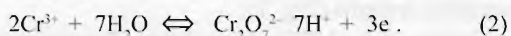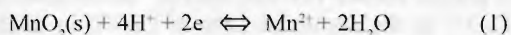
However, the extent of oxidation was also dependent on the form of added Cr(III) (soluble vs. insoluble; organically complexed vs. inorganic


Figure 2. The role of pH in Cr oxidation–reduction in soils. The extent of Cr(III) oxidation in soils by Mn(III,IV) hydroxides is a result of interaction between the oxidation reaction and the simultaneous reduction process effected by organic compounds and Fe^{2+} (James and Bartlett 1984).

forms). Subsequent studies by James and Bartlett (1983a,b,c) showed that the extent of oxidation was substantially less if Cr(III) was added to the soils as aged, more crystalline precipitates or as tannery wastes.

While the presence of Mn(IV) oxides can oxidise Cr(III), both Fe(II) and organic matter containing minerals can reduce Cr(VI) to Cr(III). Eary and Rai (1989) demonstrated that even the small amounts of Fe(II) contained in haematite and biotite can reduce aqueous Cr(VI) species to Cr(III), resulting in the precipitation of (Fe,Cr)(OH)$_3$atm. These results suggest that soil conditions that enhance release of Fe(II) from silicate (see equation (3)), or oxidic minerals, may enhance the reduction of Cr(III). Thus the release of Fe(II) from silicate minerals in acidic solutions (Eary and Rai 1989) or the reductive dissolution of Fe(III) silicates or oxides by organic acids (Hering and Stumm 1990) can introduce Fe(II) in soil solution:

$$[FeO]_{min} + 2H^+ \iff Fe^{2+} + H_2O . \qquad (3)$$
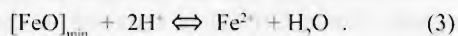
In solutions with pH <10.0, the Fe(II) species rapidly oxidise (equation (4)), the nature of hydrolysis species depending on the pH of the solution (Eary and Rai 1987):

$$3Fe^{2+} + HCrO_4^- + 3H_2O \iff CrOH^+ + 3Fe(OH)_2^+ . \quad (4)$$
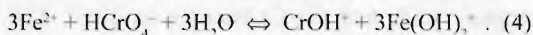
There are many reports in the literature that show that residual organic material, soluble or insoluble, has the capacity to reduce Cr(VI) to Cr(III) (Bartlett and Kimble 1976b; James and Bartlett 1983c). Thus in soils high in organic matter, Cr(VI) reduction is rapid regardless of the soil pH, while less degraded organic matter such as cow manure has a more limited influence on Cr(VI) reduction (Bartlett and Kimble 1976b). Using soil incubation studies with cow manure, Bartlett and Kimble (1976b) demonstrated that Cr(VI) reduction was only appreciable when the pH of the soils was decreased below 3. Soluble low molecular weight organic acids have also been shown to be effective reductants of Cr(VI). In addition to reducing Cr(VI) to Cr(III), many low molecular weight organic acids form Cr–organic complexes which can eventually complex with manganese oxides (James and Bartlett 1983a). These results indicate that the relationship between Cr(III) and Cr(VI) depends on a balance between oxidation and reduction processes (Fig. 2) (Bartlett and James 1984).
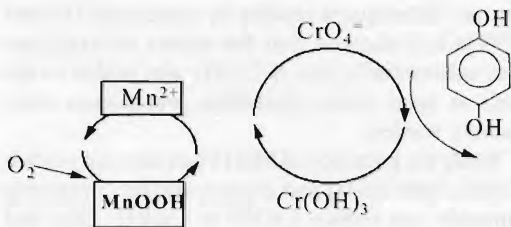
Figure 3. The role of factors other than pH in Cr oxidation–reduction in soils

Reviewing the mobility and bioavailability of Cr in soils, Bartlett and James (1984) concluded that the coupling and reduction reaction of Cr in soils may be viewed as a cycle (Fig. 3) in which Cr(III) and Cr(VI) are interconverted by a manganese redox cycle and the oxidation of organic matter. However, both these processes are controlled by pH and the presence of chelating agents. Once Cr(VI) is reduced in the soil environment, Cr(III) is then bound by a variety of ligands that render it insoluble, immobile and unreactive. Complexes between soluble Cr(III) and low molecular weight organic acids can deliver Cr to manganese oxide surfaces where both the organic acids and the Cr become oxidised. The whole cycle is dependent on the concentration of organic acids. Where organic acids are excessive in relation to small amounts of Cr(III) held, the surplus organic sites have been found to induce dismutation of MnO_x by binding the Mn(III) (Bartlett and James 1988).

Adsorption reactions

Adsorption of Cr by soils and standard minerals has been studied extensively. Results from such investigations suggest that sorption reactions are controlled by the nature of Cr species, soil and soil solution factors. Some of these factors include pH, ionic strength of the soil solution, composition of the soil solution (competing anions and index cations) and soil mineralogy.

As discussed above, Cr ion can exist both in cationic Cr(III) and in anionic Cr(VI) forms. Therefore, depending on the nature of the species, the effect of pH may be to increase or reduce adsorption onto soil colloid particles. Generally, Cr(III) adsorption increases with increasing pH
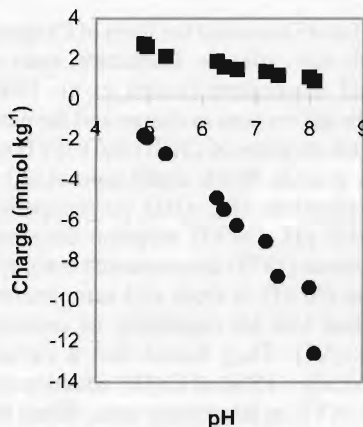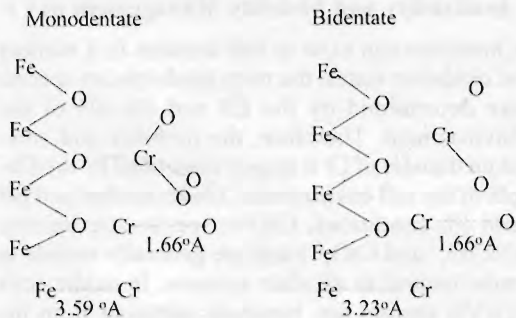

Figure 4. Effect of soil pH on net surface negative and positive charge of an Oxisol (after Naidu et al. 1990) (● negative charge; ■ positive charge)

while Cr(VI) adsorption increases with decreasing pH. Since the nature of Cr species varies with varying pH, the extent of adsorption is also strongly dependent on pH. Soil pH determines both the speciation of Cr(VI) and the charge characteristics of the colloidal surface with which it reacts. Above pH 6.4, $HCrO_4^-$ dissociates to CrO_4^{2-} as the dominant form of Cr(VI) in dilute aqueous systems (Fig. 1).

Griffin et al. (1977) showed that adsorption of Cr(VI) by kaolinite and montmorillonite increased with decreasing pH. Similar results were obtained by James and Bartlett (1983a,b,c) for adsorption of Cr(VI) by various soils and $Fe(OH)_3$. Since soil pH affects the quantities of positive and negative charges on soil colloids, especially the metal oxyhydroxide surfaces and organic matter, the increased $HCrO_4^-$ adsorption may be attributed to an increase in surface positive charge (Fig. 4) with decreasing soil pH. Thus, at pH below the point of zero charge, the net positively charged colloid surface will enhance Cr(VI) binding, while above the point of zero charge Cr(VI) binding will decrease with increasing pH. Therefore the adsorption of Cr(VI) in soils is dependent on soil mineralogy and on the relation of soil pH to the pH of zero point of charge.
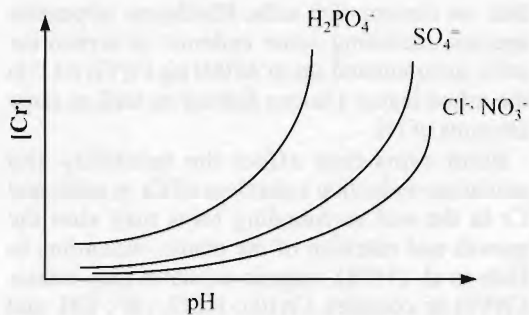
Stollenwerk and Grove (1985) investigated the adsorption and desorption behaviour of Cr(VI) in an alluvial aquifer near Telluride, Colorado. They showed that Fe oxide and oxyhydroxide coatings

Figure 5. The surface complexation structure of goethite

Figure 6. Effect of pH and inorganic ligand ions on equilibrium solution Cr(VI) concentration

on the alluvial particles were principally responsible for the adsorption of Cr(VI). These investigators also reported that changes in net surface positive charge on oxidic surfaces with increasing pH were predominantly responsible for reduced sorption of Cr(VI). Numerous reasearchers have postulated that Cr(VI) forms an outer-sphere complex on hydrous oxides of Fe and Al (Benjamin and Bloom 1981; Zachara et al. 1987, 1989; Ainsworth et al. 1989). These postulates are based on macroscopic data that cannot definitively ascertain microscopic information, so Fendorf (1995) studied the surface reactions that influence Cr chemistry in soils using EXAFS spectroscopy and Al and Fe hydrous oxides. The extended portion of the Cr K-edge spectra was used to determine the type, number and distance of the atoms coordinating Cr(VI) in the Al and Fe hydrous oxide samples. It was found that Cr(VI) forms an inner sphere complex on goethite with bidentate and monodentate complexes (Fig. 5). This is in agreement with the ion displacement studies of Bartlett and Kimble (1976).

Adsorption of Cr(VI) generally decreases as the ionic strength of a particular solution increases (James and Bartlett 1983c). Stollenwerk and Grove (1985) studied the effect of inorganic ligand ions on the adsorption of Cr(VI) by soils. They found that while all anions retarded sorption of Cr(VI), the effect was most pronounced for SO_4^{2-} and HPO_4^{2-} and $H_2PO_4^-$. A similar effect of inorganic ligand ions on Cr(VI) adsorption was recorded in our laboratory (Fig. 6). This was attributed to direct competition for sorption sites between the added ligand ions and Cr(VI). Although NO_3^- and Cl^-

were not effective competitors for sorption sites because of their lack of specificity, the decreased sorption in the presence of these ions was attributed to their effect on the electrostatic potential on the plane of adsorption.

Plant Uptake

Plant response to varying levels of naturally occurring and applied Cr has been studied extensively and these studies reveal that Cr can be toxic to plants. However, the toxicity level may vary with the nature of plant species and soil types. For instance, using solution culture studies, Turner and Rust (1971) showed that 5 µg Cr(VI) mL^{-1} caused toxicity in soybeans, while Mortvedt and Giordano (1975) reported that 20 µg Cr(VI) mL^{-1} applied to soils reduced the dry matter yield of corn. Zaccheo et al. (1982) investigated Cr ion toxicity on the membrane transport mechanisms in segments of maize seedling roots, and concluded that both Cr(VI) and Cr(III) caused changes in the pH of the medium and inhibited potassium uptake by segments of maize seedling roots which retarded plant growth. However, in these studies, the concentrations of Cr used were several percent lower than those found in some soils developed on serpentinites.

Soils derived from ultrabasic (serpentine) rocks contain several percent Cr. Brown *et al.* (1972) observed that vegetational differences clearly mark serpentine soils in which some plants called 'serpentinophytes' grow well. Shewry and Petersen (1974) claimed that Cr could be essential to the growth of serpentine species. Wild (1974) found

that, on chrome-rich soils, Rhodesian serpentine species, including some endemic to serpentine soils, accumulated up to 48 000 µg Cr(VI) mL^{-1} in the ashed leaves (*Sutera fodina*) as well as large amounts of Ni.

Plant roots may affect the solubility and oxidation–reduction behaviour of Cr in soils, and Cr in the soil surrounding roots may alter the growth and nutrition of the plants. According to Hale et al. (1978), organic exudates may reduce Cr(VI) or complex Cr(III); HCO$_3^-$, H$^+$, OH$^-$ and other exuded ions may alter the pH and pE of the rhizosphere. The effect of Cr on the roots will depend on its forms in soils: oxidised, reduced, chelated, precipitated or adsorbed. Numerous studies have failed to show absorption and translocation by plants of cationic Cr(III) and have concluded that anionic Cr(VI) is rapidly reduced in roots of most plants (e.g. Lahouti and Peterson 1979). Cary et al. (1977) also reported that Cr(VI) may be the source of plant-available Cr.

Wallace et al. (1977) reported that EDTA added to soil increased the toxicity of Cr(III) to bush beans although very little Cr was translocated to the leaves. Shewry and Petersen (1976) also observed little translocation of Cr in barley seedlings grown in nutrient solution. They suggested that most of the root-Cr was held in water soluble form in root cell vacuoles. Indirect effects on plant growth have been observed at sub-toxic levels of Cr. Yamaguchi and Aso (1977) reported decreased root elongation of rice and wheat growing in soils amended with 200 mg Cr(III) kg^{-1}, while shoot elongation was unaffected. James and Bartlett (1984) studied plant–soil interactions of Cr to investigate the nature of Cr species absorbed by plant roots using the A horizon of a Typic Eutrochrept soil, field moist and freshly amended with Cr(OH)$_3$ and tannery wastes. They found that soils supporting plant growth contained less soluble Cr(VI) and more soluble Cr(III) than unplanted soil receiving the same Cr(III) treatment, and the beans and tops in this treatment had higher Cr than did plants grown in unamended soils. The level of Cr in bean roots after 46 days correlated well with Cr(VI) in unplanted soils 1–3 days after seeding. Addition of citric acid to the soils significantly increased Cr levels in bean shoots and roots grown in the Cr(OH)$_3$ treatment.

Availability and Mobility Management of Cr

Chromium can exist in soil solution in a number of oxidation states; the most predominant species are determined by the Eh and the pH of the environment. Therefore, the mobility and soil–plant transfer of Cr is largely controlled by the Eh–pH of the soil environment. Under normal soil pH and Eh conditions, Cr(VI) species are anionic (HCrO$_4^-$ and CrO$_4^{2-}$) and are generally mobile in most neutral to alkaline systems. In acidic soils Cr(VI) species are, however, removed from the solution by adsorption onto positively charged sorption sites (Zachara et al. 1989). The Cr(VI) species is also rapidly reduced to the Cr(III) species by Fe(II) minerals and organic compounds under acidic conditions. This indicates that in most surface soils Cr(VI) will rapidly be converted to the insoluble Cr(III) compounds by organic matter thus inhibiting Cr(VI) mobility. However, where surface soils are excavated exposing subsurface horizons, Cr(VI) mobility is less likely to be retarded in the absence of organic matter unless similar reactions occur, involving Fe(II) minerals.

The mobility of Cr(III) in soils may also be controlled by processes similar to podzolisation (Bartlett and James 1988). In their studies they found accumulation of native Cr in spodic horizons, similar to aluminium. Levels of Cr extracted were significantly greater in 46 Typic Haplorthod Bhs or Bs horizons than in the Ap or C horizons of the same soils (3.7 ± 0.46 versus 2.38 ± 0.36 versus 2.09 ± 0.24 mg kg^{-1}), respectively. The E horizons contained only 0.4 ± 0.23 mg kg^{-1}. Although levels of extractable Al were orders of magnitude higher, the aluminium relationships among horizons were similar to Cr distribution patterns. If the podzolisation process involves translocation of metals as metal-dissolved organic complexes, then studies by James and Bartlett (1983a) support this hypothesis. For instance, they demonstrated that presence of citric acid, DTPA, fulvic acids and a water soluble extract of an air-dried soil all formed soluble Cr(III) complexes. These complexes remained soluble as the pH was increased above pH 5.5, at which pH all the uncomplexed Cr(III) was precipitated. Since many of these organic acids are produced at the soil–root interface and also by decaying plant material, the mobility of Cr(III) as dissolved

organic complexes may be enhanced under cropping systems that contribute to the dissolved organics in soil solution.

The soil–plant transfer of Cr is generally independent of the concentration of Cr in soils. Sheppard et al. (1984) found that, independent of Cr applied, plants took up a similar fraction, about 0.007, and this was not influenced by placement depth in loamy soils but was highly dependent on placement in sandy soils. Thus the phyto-availability of Cr added to soils is generally low (Bartlett and James 1988) with little Cr translocated to plant tops and edible plant parts.

Guidelines for the re-use of sludge in agriculture in USA, developed by the USEPA (503 regulations, US EPA 1993), have identified that plant phytotoxicity is the major limiting pathway for regulation of Cr applications to soil, and that risk to human or animal health is minimal. A cumulative threshold of 3000 kg ha^{-1} has been suggested, although the regulations have been mostly on studies of municipal sewage sludges. On the basis of this, Cr-contaminated soils could be used for crop growth provided Cr phytotoxicity is minimised. This may be achieved by either ameliorating soils to minimise plant-available Cr or by using Cr accumulator plants such as those commonly found in serpentinite soils.

Implications for the Chemistry of Cr in Tannery Waste-contaminated Soils

Since Cr(III) is the major Cr species added during the tanning process, leather technologists and many scientists argue that disposal of tannery waste sludge is not an issue as long as the salt content is kept below the level of concern. It is generally believed that the thermodynamics of the reduction process, i.e. Cr(VI) to Cr(III), are the dominant processes in the soils and any Cr added through waste disposal will remain in the non-toxic Cr(III) form. However, there are now numerous studies that demonstrate the high mobility of Cr(III) in the presence of organic acids. Harter and Naidu (1995) report that low molecular weight organic acids and soluble fulvic acids are commonly present in soil solution and these acids can modify the chemistry of metals in the soil environment. Moreover, presence of oxidising agents such as Mn(III,IV) can catalyse the oxidation process. Bartlett (1985) studied the potential for Cr(III) oxidation by

incubating a 1% Cr tannery sludge with Typic Eutrochrept A horizon samples (2 g kg^{-1}). He maintained the samples at field moisture capacity inside polyethylene bags. Analyses of the samples using the standard Cr oxidising test (Bartlett and James 1988) showed the presence of Cr(VI) that increased from 1 mg kg^{-1} after three weeks to 2–3 mg kg^{-1} after four months. The presence of Cr(VI) was attributed to oxidation by manganese oxides. They found that formation of manganese oxides, optimal for Cr(III) oxidation, was favoured by a somewhat restricted oxygen supply and moderate levels of organic reducing substances. These results have implications for the Cr oxidation processes in tannery waste sludge which is often contaminated by MnSO$_4$ to reduce odour. Presence of MnSO$_4$ together with organic matter may initiate the Cr(III) oxidation process. Low molecular weight organic acids increase solubility and mobility of Cr(III) and thereby may facilitate its oxidation. James and Bartlett (1983b) studied the initial oxidation rates of different species of Cr(III) added to an Aquic Udorthent. They found that the maximum Cr(VI) observed decreased in this order: freshly precipitated Cr(OH)$_3$ > Cr-citrate > aged Cr(OH)$_{3+}$ in citrate > aged Cr(OH)$_3$. Organic acids present in the tannery waste material may facilitate such an oxidation process.

During their continued investigations with Cr, James and Bartlett (1983b) studied the oxidation of Cr(III) in tannery sludge and in tannery effluent added to Typic Eutrochrept samples in a continuously aerated slurry, as a function of time and loading rate. Amounts of Cr(VI) increased with increasing additions of Cr(III) added as high Cr sewage sludge or tannery effluent. The increased Cr(VI) in the sludge-treated soils may be attributed both to the presence of organic matter and to Mn^{4+} formed through the oxidation of Mn^{2+} in the presence of air. Manganous ions generally rapidly oxidise in air and do not form complexes due to the generally low ligand field stabilisation energy of the Mn^{2+} ion.

Role of Microbes in Cr(III) Oxidation

Although much research has been conducted on the factors controlling Cr(III) oxidation in sludge materials and contaminated soils, limited attempts have been directed towards investigations on microbe-facilitated oxidation of Cr(III). While the

presence of Cr(III) oxidising microbes is yet to be demonstrated, Mn^{2+} oxidising bacteria have been reported. Current investigations in our laboratory focus on the role of Mn-oxidising bacteria on Cr oxidation in sludge and contaminated soils.

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Distribution and Fate of Chromium at Sites Historically Contaminated with Tannery Waste: Case Studies from Australia and India

Fate of Chromium at Tannery Waste-Contaminated Sites at Mount Barker, South Australia

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Abstract

In Australia, tannery wastes were commonly discharged onto agricultural land before the introduction of regulations prohibiting such disposals. This has resulted in extensive contamination of localised areas of agriculturally productive land. Major contaminants associated with tannery wastes include chromium (Cr), salt and increased biological oxygen demand. This study investigated the extent of surface and subsurface Cr contamination of soils at an old tannery waste disposal site near Adelaide, and measured the salt and total Cr contents of a range of tannery effluents and sludge. Total Cr in the surface and subsurface soils ranged from <100 mg kg^{-1} to ~70 000 mg kg^{-1}. At all sites where Cr exceeded 1000 mg kg^{-1} an appreciable concentration of Cr was detected in the surface and subsurface water samples in the lysimeters and piezometers. Speciation of Cr showed there was a large proportion of hexavalent Cr in all samples except those with pH <4.0, in which the bulk of the Cr was in trivalent form. Detailed studies on seasonal variation in solutes at the contaminated sites showed marked increases in the concentrations of Cr and salt in the piezometer water samples and in subsurface and groundwater samples during and after the wet winter months, confirming our hypothesis that there is high mobility of Cr and salt in the high pH soils at the contaminated sites.

HEAVY metals (chromium (Cr), cadmium, lead, copper, zinc) are major constituents of various industrial effluents, phosphate fertilizers, municipal sewage sludges, and city composts as well as emissions from power generation plants and smelters. Increased industrialization in the last 50 years together with the expanding world population have led to extensive degradation of the environment in many countries throughout the Asia–Pacific region through disposal of sewage and industrial wastes. Lack of appropriate guidelines for waste disposal has culminated in extensive pollution of productive agricultural land, surface water and groundwater in these countries. This is evident from the many contaminated sites that are now being identified.

In Australia, tannery wastes were commonly discharged onto agricultural land, before the introduction of regulations prohibiting such disposals. This has resulted in contamination of localised areas of agriculturally productive land. Major contaminants associated with tannery wastes include chromium (Cr), salt (NaCl) and increased biological oxygen demand (BOD). One example of such contamination is at the old tannery waste disposal site at Mount Barker, South Australia. Preliminary investigations of contaminated soils at this site show that total Cr concentrations exceed 5% in the surface soils. Parts of this site are also highly saline. According to Mount Barker City Council, liver biopsies of animals feeding on pasture grown on contaminated sites show elevated levels of Cr. Consequently, productive land in Mount Barker has been declared contaminated and fenced. Consultancy reports organised by the city council health

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officials show Cr contents in excess of 6% in soils around waste disposal storage ponds and Cr(VI) concentration in runoff water often exceeds 0.015 µg mL^{-1}. However, there is no report on the Cr and salt status of subsurface soils and water in the unsaturated zone and groundwater. In this study we examined the Cr concentration of surface and subsurface soils including the subsurface soil waters in soils contaminated with tannery waste at Mount Barker.

Materials and Methods

Composition of effluent and sludge

Samples of sludge and effluent materials were obtained from two tanneries in southern Australia. Following centrifugation of the effluent samples, the pH and electrical conductivity (EC) were measured and the total composition was analysed using a combination of atomic absorption and inductively-coupled plasma emission spectrometry. The sludge samples were freeze-dried, ground to a fine powder, digested in aqua regia (HNO$_3$: HCl) and analysed as described above.

Soils

Soil profiles representative of contaminated sites were sampled to 70 cm depth, air dried and crushed to pass through a 2 mm sieve. The sieved samples were randomised using the quartet technique and then kept in polyethylene bags for subsequent laboratory study.

Routine analyses

Soil pH, EC and soluble cations and anions were determined in 1:5 soil:water extracts following overnight saturation (Table 1). The soil suspension was then centrifuged for 90 min at 15 000 rpm and the supernatant passed through 0.2 µm millipore nylon filter to minimise colloidal contamination before all analyses. All major cations and anions except Cl were estimated using inductively coupled plasma emission spectrometry (ICPES) with an ultrasonic nebuliser. Chloride in the extracts was estimated with an autoanalyzer using mercuric thiocyanate indicator. The proportions of clay, silt and sand in the soils were estimated by the sedimentation procedure using a hydrometer following saturation of soils with calgon (Jackson 1969).

Total Cr

Surface soil samples (0–10 cm) and subsurface soil samples (10–70 cm at 10 cm intervals) were collected, passed through a 2 mm sieve and air dried in fanforced ovens. The samples were homogenised and then subsamples were taken for pH and EC (1:5 soil:water) and total Cr. Total Cr was determined on extracts following the microwave digestion of contaminated soils using aqua regia. Cr in the digest was determined by atomic absorption spectrophotometry and air acetylene flame.

Fate of salt and chromium

Soils in southern Australia are typically texture contrast soils with a sandy A horizon overlying a clayey subsurface B horizon. In these soils, both lateral water flow — at the interface between the clayey B horizon and sandy A horizon — and throughflow control the transport of pollutant materials. Studies by Naidu et al. (1993) suggest that lateral movement of salt and colloid particles in association with dissolved organic compounds and metal ions is prevalent in texture contrast soils. For these reasons, the fate of salt and Cr in effluent and sludge discharged into dams and landfills were investigated at the Mount Barker old tannery sites. Movement to subsurface waters in the unsaturated zone and also to groundwater was assessed at selected sites.

To investigate the effect of long-term tannery waste disposals on the fates of salt and Cr in subsurface waters in the unsaturated zone, simple lysimeters made with PVC pipes were installed at contaminated sites. For their construction, a design similar to that adapted by Naidu et al. (1993) was used (Fig. 1). Soil water was sampled immediately after each rainstorm and also every fortnight and analysed for salinity, total chemical composition and dissolved organic carbon. The colloid fraction of subsurface waters was also separated and its Cr content determined.

Nested piezometers were installed to depths of 50 cm, 100 cm and >6 m to monitor salinity and Cr concentrations of groundwater. Soil water was periodically sampled from the lysimeters and the piezometers during the winter rains when moisture saturation allowed subsurface flow. The sampled water was transported on ice to the laboratory and subsamples were analysed for pH and EC. Aliquots

Table 1. Ranges of EC, pH, total Cr and Cl in surface and subsurface soil samples at the contaminated site at Mount Barker, South Australia (see Appendix Table A1 for details)

Sample depth (cm)	EC (dS m^{-1})	pH (1:5 soil:water)	Cr (mg kg^{-1})	Cl$^-$ (mg L^{-1})
0–10	0.03–0.85 (0.27)	6.51–8.43 (7.77)	249–69500 (26452)	9–126 (33.6)
10–20	0.02–0.92 (0.21)	6.54–8.61 (7.96)	52–59271 (7244)	7–184 (19.0)
20–30	0.03–1.24 (0.15)	6.25–8.98 (8.13)	45–66312 (3400)	7–200 (15.0)
30–40	0.04–1.54 (0.13)	5.90–8.82 (7.80)	34–32126 (350)	6–317 (22.4)
40–50	0.02–2.18 (0.14)	4.58–8.96 (7.69)	19–34500 (639)	5–396 (17.4)
50–60	0.02–1.74 (0.15)	4.15–9.06 (7.72)	16– 8805 (197)	6–434 (14.1)
60–70	0.01–1.76 (0.13)	3.90–8.50 (8.04)	12– 6697 (100)	6–595 (16.0)

Numbers in parentheses are median values

of the soil water were also centrifuged at 12 000 rcf and passed through a 0.20 μm millipore filter before all chemical analyses. Total Cr and Cr(VI) were analysed in the filtered samples using atomic absorption spectrophotometry and the colorimetric method, respectively. Total Cr in the soil water samples (i.e. including colloid particles) was determined following aqua regia digest of replicate aliquots of the sampled water.

Results and Discussion

Soil characteristics

The pH and EC of the 1:5 soil:water extracts varied considerably among the study soils (Table 1). In general, soil pH ranged from ~6 to 9 in the surface and the subsurface samples from all except the soil profile SL17 (Appendix Table A1) in which pH of the soils exceeding 40 cm decreased to <4. Repeated sampling of soils at this site showed that the acidic zone was genuine. It was not possible to explain the low pH given the presence of calcareous materials throughout much of the

Subsurface Water

Soil profile

1 m depth

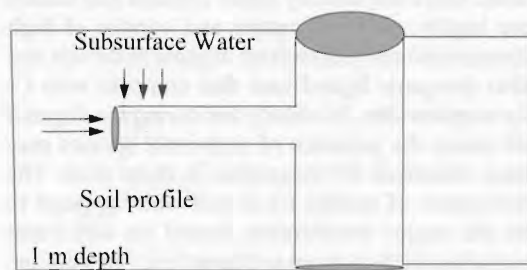**Figure 1.** Diagram of the lysimeter design

contaminated site. Further work on this sample is in progress to determine the reasons for the acidic pH. A wide range of EC values and soluble cation and anion concentrations were also recorded. In general the EC and the sodium absorption ratio of the 1:5 soil:water extracts were higher than those expected in normal soils and generally fell in the sodic soil category. This is also apparent from the dispersive nature of the subsurface clayey soil which sets hard during the dry summer months.

Total Cr

The total Cr data in surface and subsurface soils of 31 soil profiles (Table 1) indicate extensive contamination of soils at the Mount Barker tannery waste disposal sites. With the exception of profile SL7, the total Cr concentration in the surface soil samples ranged from ~400 to >5000 mg kg^{-1}. At many of the sites the total Cr concentration exceeded 40 000 mg kg^{-1}. In profile SL7, the total Cr concentration was 249 mg kg^{-1} in the top 10 cm and 183 mg kg^{-1} in the 10 to 20 cm layer (see Table A1).

According to the Australian National Health and Medical Research Council guidelines (NHMRC 1992), the maximum permissible concentration of Cr in the general environment is 50 mg kg^{-1} before investigation is required. No guideline for health investigation is currently available in the Australian literature. On the basis of this regulation, all sites sampled at Mount Barker exceed the NHMRC environmental guideline and therefore require further investigation.

The ANZECC/NHMRC environmental health guidelines are based on threshold contaminant levels for (i) phytotoxicity, and (ii) uptake of contaminants that may result in impairment of plant

growth or unacceptable residue levels. The NHMRC considered worst case scenarios during the development of these guidelines. They define 'Investigation level' as the concentration of a contaminant above which further appropriate investigation and evaluation are required. Thus investigation levels are intended to ensure that a detailed investigation of a site is done whenever necessary, to ascertain:

• the optimum and extreme concentrations of the contaminants on the site;
• the horizontal and vertical distribution of the contaminants on the site;
• the physico-chemical forms of the contaminants;
• the bioavailability of the contaminants.

Further investigations indicate that the Cr in surface soil samples is highly soluble in the 1:5 soil: water extracts and is present at from 1 to 10.5 µg mL^{-1}. Presence of soluble Cr also indicates the potential for Cr contamination of groundwater. In South Australia, winter rains are usually slow and because most of the native vegetation in these catchments has been removed and replaced by annual pastures and crops which are inefficient in their use of rainfall, most of the water percolates into the soil. Such slow percolation of water may enhance Cr mobility in these soils. Indeed, Cr was detected in all the soil profiles sampled at the contaminated site. Typical trends are presented in Fig. 2. The concentration of Cr decreased with increasing depth at all sites except profile 7 (Table A1). At this site with increasing depth the Cr concentration increased to 3700 mg kg^{-1} at 35 cm and then decreased slowly to <100 mg kg^{-1} at a depth of 65 cm.

Considerable inconsistency exists in the literature on the distribution of Cr in soil profiles. Chromium has been found to increase, decrease or show no pattern with depth. Bleeker and Austin (1970) found that some soil profiles displayed accumulation of Cr in the surface horizons and depletion with depth. The mobility of Cr was addressed by Lund et al. (1976) who found Cr enrichment to depths as great as 3 m under some sewage disposal ponds. These investigators hypothesised that the metals move as soluble metal–organic complexes. If this mechanism is predominant, then organic complexation of Cr(VI) would be the major mechanism for Cr transport in these soils.
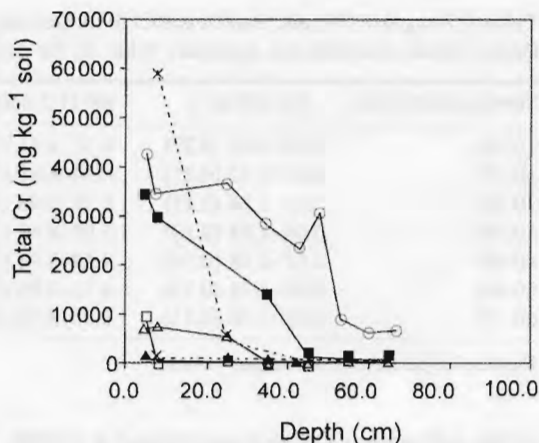
Figure 2. Typical distribution of Cr: six of the 31 soil profiles sampled at Mt Barker contaminated sites (see Appendix for data)

Total Cr content ranged from 45 mg kg^{-1} to 66 300 mg kg^{-1} in the 10–30 cm layer of the soil and from 12 to ~6200 mg kg^{-1} at 60 cm depth. These values exceed the current NHMRC (1992) limits of 100 mg Cr kg^{-1} soil. The presence of Cr in the subsurface horizons indicates translocation through movement of the contaminant either in solution or in association with colloid material. Analyses of Cr in the subsurface water and suspended matter indicate that both mechanisms are operating in the environment at Mount Barker. However, these mechanisms per se do not explain the large concentrations of Cr at depths greater than 60 cm. Another reason for the high Cr could be the disposal of Cr-rich wastes as landfill at these sites. However, examination of soil cores to 3 m depth at selected sites does not show any discontinuity with soil type, indicating that landfill may not be the reason for the high Cr in subsurface soils. Since the tannery waste effluent and wastes are highly saline in nature and consist of high concentrations of dissolved organic materials and also inorganic ligand ions that compete with Cr for sorption sites, it is likely that during the disposal of wastes the presence of such ionic species may have enhanced Cr movement in these soils. The movement of mobile Cr in soil water appears to be the major mechanism, based on soil:water extracts which show up to 10 mg Cr L^{-1} in solution. Further work is being conducted to explain the presence of Cr in the subsurface soil horizons.
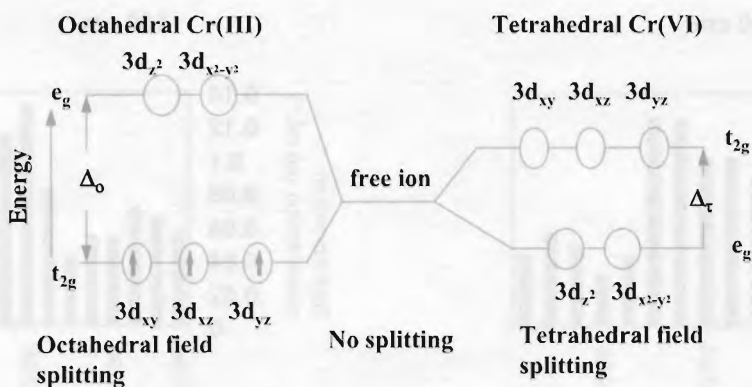
**Figure 3.** Crystal field splitting of Cr(III) and Cr(VI)

Fate of salt and metals

Chromium in subsurface waters

Subsurface flow occurred only at some of the sites and therefore Cr data are available only for selected samples. The diphenylcarbazide analyses showed the presence of Cr(VI) in all the subsurface water samples in the Mount Barker area. Presence of Cr(VI) in the subsurface water samples and also in selected deep water piezometers indicates high Cr mobility at the Mount Barker site. High Cr content in groundwater has been reported by several workers. Davids and Lieber (1951) reported an average of 450 µg Cr L^{-1} in groundwater, whereas Förstner and Wittman (1983) reported a mean value of >10 000 µg Cr L^{-1} in groundwater near Tokyo. They suggested 0.5 µg Cr L^{-1} as the background content of Cr in surface water. Drinking water standards have been set at 0.05–50 µg L^{-1} for total Cr because of the toxic effect of Cr(VI) and the possibility of oxidation of Cr(III) to toxic Cr(VI) (USEPA 1976).

The presence of Cr(VI) in subsurface waters is surprising given that Cr(III) was used during the tanning process. Historical documents from the old tannery sites were not available although retired tannery workers said that both Cr(III) and Cr(VI) salts were used by the industry.

Thermodynamic considerations, however, suggest that Cr(III) is the stable form in the soil environment. According to crystal field splitting theory, the splitting energy Δ_o is much greater for Cr(III) than for Cr(VI) and this allows Cr(III) to form stable octahedral complexes (Fig. 3).

This indicates that Cr(III) is the stable form in the soil environment particularly in the presence of electron donor groups such as soil organic matter. Indeed, James and co-workers report rapid transformations of Cr(VI) to Cr(III) in sludge and Cr(VI)-treated soils although such transformations may be retarded by Mn(IV) oxides (James and Bartlett 1983a,b,c, 1984). Since Cr(III) binds strongly to soil colloid particles it is extremely immobile and is not considered a threat to subsurface and groundwater contamination. However, leaching studies in our laboratory using sludge material from tanneries show both Cr(III) and Cr(VI) in the leachates. This suggests that sludge Cr(III) is mobile and also is transformed to Cr(VI), although the precise nature of the oxidation process is not clear. Such transition may be possible at the oxide–solution interfaces that often influence redox reactions by allowing accelerated redox pathways, e.g. by oxygenation of metal ions (Wehrli and Stumm 1989) or by acting as an oxidant or reductant of species present in soils and waters (Stone 1991). Manganese oxide is the only naturally occurring oxidant of Cr(III) at pH < 9 (Eary and Rai 1987) and readily oxidises this species (Bartlett and James 1979; Eary and Rai 1987). However, many of these studies were conducted using pure systems. More recently, Ferndorf et al. (1993) investigated the effect of competing ions on Cr(III) oxidation by δ-MnO_2 concluding that aluminium ions influenced the extent of Cr(III) oxidation. However, this effect was pH dependent. At pH ≥ 4 and at pH 5, Al decreased the extent of oxidation of Cr(III).

50 cm
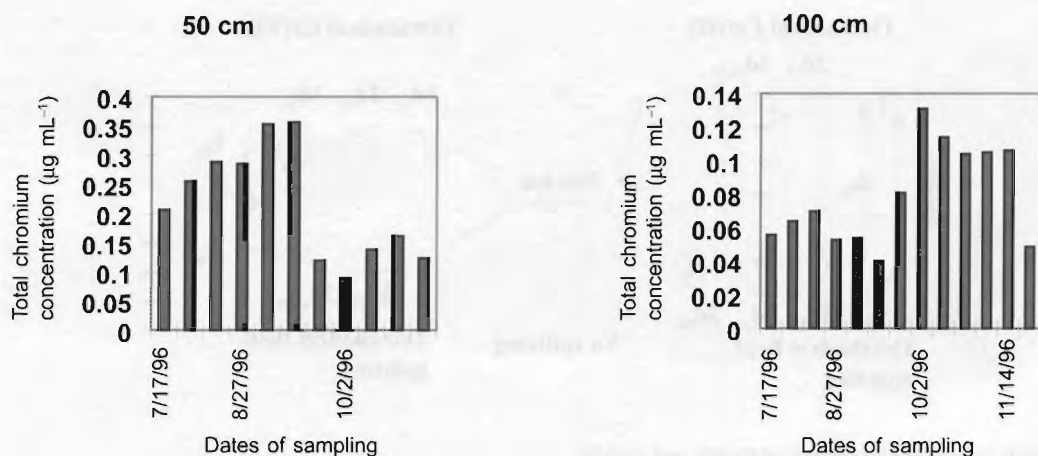
100 cm

Figure 4. Total Cr concentrations in the piezometer water samples at 50 and 100 cm depth in July–November 1996

Analyses of soil samples from the Mount Barker site show the presence of significant amounts of extractable Mn. Soil water also showed the presence of Mn(II). Currently we are investigating the role of Mn-oxidising bacteria on Cr(III) oxidation through indirect processes. Such a process may occur in soils containing Mn^{2+}. Microbial oxidation of Mn^{2+} to MnO_2 may catalyse the oxidation of Cr^{3+} as shown here:

$$MnO_2(s) + 4H^+ + 2e \Leftrightarrow Mn^{2+} + 2H_2O$$
$$2Cr^{3+} + 7H_2O \Leftrightarrow Cr_2O_7^{2-} + 7H^+ + 3e$$
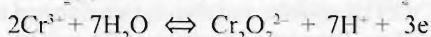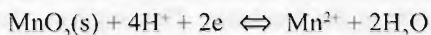
where (s) means solid.

Chromium movement through the soil profile

The data on total Cr from the piezometer samples at the site suggest that Cr was quite mobile through the soil profile, particularly at locations where the total Cr in surface soils was high (Table A1). A typical distribution of Cr in water samples collected from different depths during the winter–spring season of 1996 is shown in Fig. 4. The figure shows that Cr concentrations in the water samples varied both with depth in the soil profile and with time. The highest concentrations were noted in the piezometer installed to a depth of 50 cm in which water samples ranged from 0.35 μg Cr mL^{-1} during the dry period (July–August) to 0.10 μg Cr mL^{-1} after substantial rain (September–October). The

concentration of Cr in samples from 100 cm depth ranged from about 0.05 μg mL^{-1} during July and August to 0.10–0.15 μg mL^{-1} during the September –October sampling period. The samples from groundwater had much lower concentrations, around 0.02 μg mL^{-1} at this site, which shows a very small degree of contamination (Fig. 5).

Speciation of Cr in the subsurface water samples indicated that the concentration of Cr(VI) decreased with increasing depth (Fig. 6a), with a concomitant increase in Cr(III). This was particularly evident in the soil profile with acidic pH at depths approaching 50 cm.

Chromium concentrations in water samples collected during July–August were consistently different from those collected during September– October (Fig. 4). The concentrations in the water samples from the piezometers installed to a depth of 50 cm decreased during September–October but increased in the samples from 100 cm depth. This suggests that Cr present in the surface (0–50 cm) contaminated soil was probably moving rapidly and contaminating water at 100 cm depth. The data also indicate that during August, because of lower volumes of water flowing through the soil (see rainfall pattern in Fig. 6b), adsorbed Cr from soil was enriching the Cr in water, and with the incidence of rain the released Cr in soil water was flushed down the profile, resulting in lower concentrations at the surface but relatively high
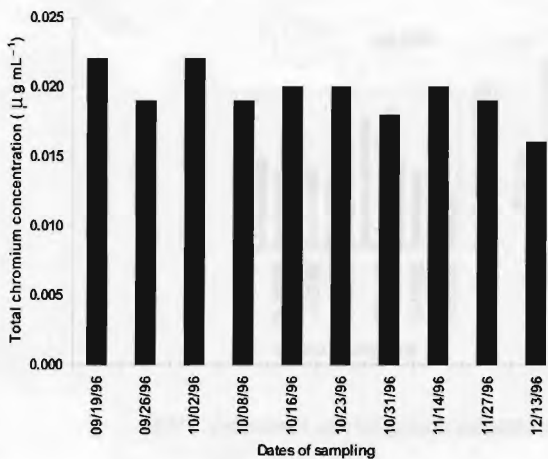
Figure 5. Total Cr concentrations (µg mL⁻¹) in the groundwater samples in September–December 1996

concentrations in the subsurface layers of the soil profile. However, this hypothesis needs to be investigated further.

Movement of sodium

The sodium (Na) concentrations in the samples for the period July to November 1996, at two depths in the soil profile (50 cm, 100 cm) and at the water table are presented in Fig. 7. The trend

in Na concentration in the water samples differs from that observed for Cr. The concentrations of Na in soil water at 50 cm depth were much lower than those at 100 cm depth, throughout the sampling period. The concentration of Na varied from 20 to 40 µg mL⁻¹ at 50 cm depth and from 60 to 140 µg mL⁻¹ at 100 cm depth. This suggests that, with continuous leaching over a sustained period of time after the disposal of effluent, Na had moved deeper than Cr in the profile. The concentrations of Na in the water table were found to be very high (1400–1600 mg L⁻¹).

The effect of precipitation received during the sampling period was noticeable in the Na concentrations of the water samples, particularly at 100 cm depth. There was higher rainfall during September–October (Fig. 6b), and the Na concentration in the water samples decreased at 100 cm depth during this period, suggesting either a leaching of Na or a dilution of Na with the larger volume of water. However, it is noteworthy that this trend was in sharp contrast to that observed for Cr, where the Cr concentration decreased in samples from 50 cm depth but was enriched at 100 cm. Clearly Cr is not as mobile as Na, although considerable movement of Cr is occurring during the wet period. In contrast to the water in the unsaturated zone, the groundwater samples showed an appreciable increase in concentration of Na over the same period indicating enrichment of groundwater with respect to salt (Fig. 8).
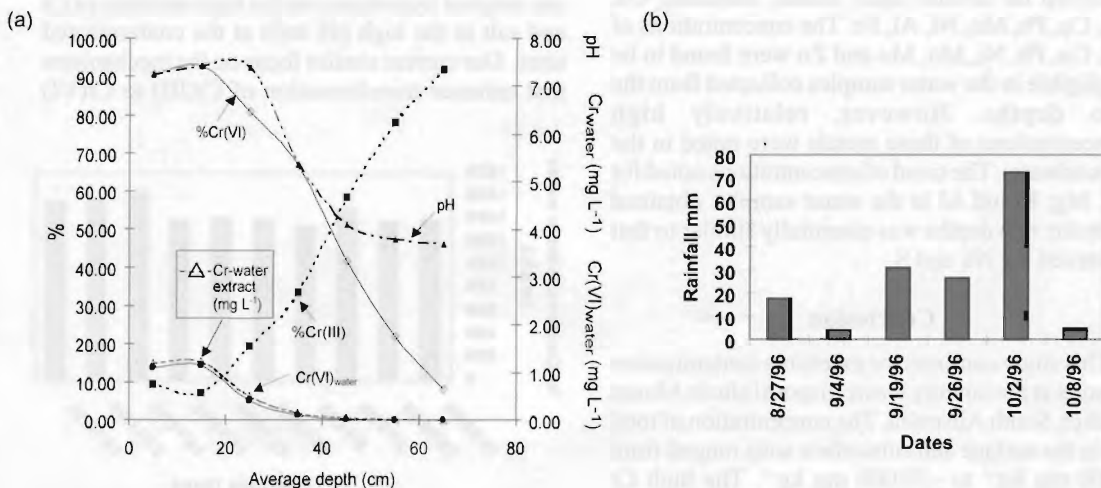
Figure 6. Nature of Cr species in subsurface water samples (from lysimeters) at various pH (left) at sites at Mount Barker, and total rainfall during the sampling period (right)

Figure 7. Total sodium concentrations in subsurface water samples during July to November, 1996

Movement of sulfur down the profile at the Mount Barker site

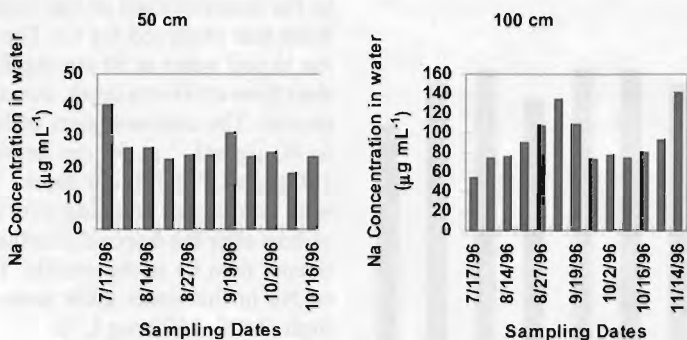The data for sulfur (S) concentration in the water samples at the site (Fig. 9) show that there is a similarity between the movements of Na and S. As with Na, the concentrations of S in the water samples at 50 cm depth were lower than those at 100 cm depth. The amount of rainfall had similar effects on the leaching of S from 100 cm depth. This suggests leaching of Na as Na:S ion pairs and the dominance of Na_2SO_4 salt at the site.

Fate of other metals at the site

The water samples collected from the site were analysed for several other metals, including Cd, Co, Cu, Pb, Mo, Ni, Al, Fe. The concentrations of Cd, Cu, Pb, Ni, Mn, Mo and Zn were found to be negligible in the water samples collected from the two depths. However, relatively high concentrations of these metals were noted in the groundwater. The trend of concentrations noted for Ca, Mg, K and Al in the water samples obtained from the two depths was essentially similar to that observed for Na and S.

Conclusion

This study confirms the extensive contamination of soils at the tannery waste disposal site in Mount Barker, South Australia. The concentration of total Cr in the surface and subsurface soils ranged from <100 mg kg^{-1} to ~70 000 mg kg^{-1}. The high Cr concentration in subsurface soils at depths greater than 50 cm indicates high Cr mobility, because the sites showed neither buried horizons nor mixing of surface and subsurface soils. At all sites where Cr exceeded 1000 mg kg^{-1} an appreciable concentration of Cr was detected in the surface and subsurface water samples in the lysimeters and piezometers. Speciation of Cr showed the presence of a large proportion of hexavalent Cr in all samples except those with pH <4.0. In these samples the bulk of the Cr was present in trivalent form. Detailed studies on seasonal variation in solutes at the contaminated sites showed a marked increase in the concentration of Cr in the piezometer water samples following wet winter months. A similar and much more marked increase in salt levels was also recorded in subsurface and groundwater samples during the wet winter months confirming our original hypotheses on the high mobility of Cr and salt in the high pH soils at the contaminated sites. Our current studies focus on the mechanisms that enhance transformation of Cr(III) to Cr(VI)
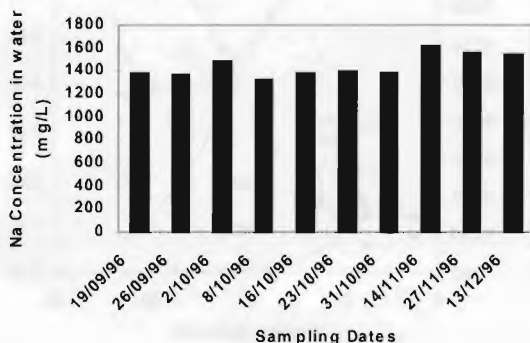

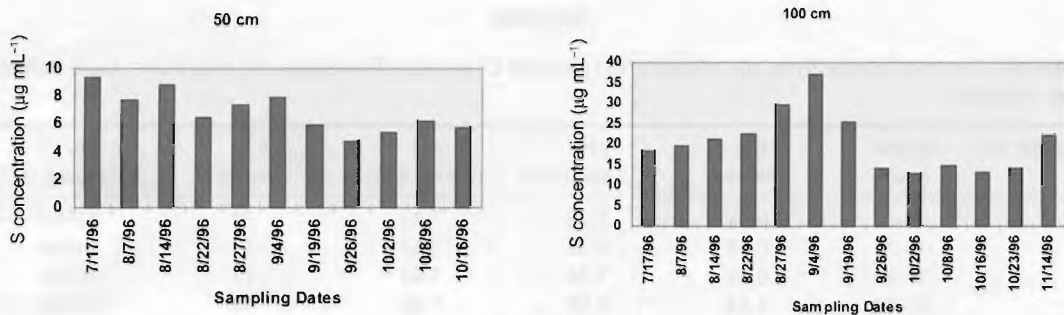**Figure 8.** Concentrations of Na in the groundwater piezometer samples

Figure 9. Total sulfur concentrations in subsurface water samples during July to November, 1996

in the soil and water environments. This study demonstrates that long-term tannery waste disposals have severely contaminated soil and groundwater at the site under current investigation.

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Appendix

Table A1. Electrical conductivity, pH, chloride (Cl) and total Cr content of contaminated soils from Mount Barker, near Adelaide

Sample ID	Depth (cm)	EC (dS m⁻¹)	pH (1:5 soil:H₂O)	pH (0.01M CaCl₂)	Cl (mg kg⁻¹)	Cr (mg kg⁻¹)
SL 1	0–10	0.38	7.76	7.34	20	42701
	10–20	0.48	7.79	7.40	17	34500
	20–30	0.69	7.76	7.43	17	36911
	30–40	1.54	7.59	7.45	34	27944
	40–46	2.18	7.56	7.48	48	23091
	46–50	2.06	7.59	7.45	48	30754
	50–56	1.74	7.75	7.49	35	8805
	56–64	1.40	7.66	7.40	36	6182
	64–70	1.76	7.72	7.50	60	6697
SL 2	0–10	0.52	8.00	7.40	34	33903
	10–20	0.58	7.99	7.45	32	29606
	20–30	0.71	7.97	7.51	31	29719
	30–40	0.89	7.93	7.56	23	13740
	40–50	0.51	7.56	7.35	20	1063
	50–60	0.72	6.70	6.75	27	518
	60–70	1.48	4.70	4.80	63	603
SL 3	0–10	0.11	6.85	6.27	10	929
	10–20	0.08	7.40	6.29	8	354
	20–30	0.09	7.63	6.32	10	226
	30–40	0.13	7.66	6.33	13	289
	40–46	0.17	7.69	6.33	15	219
SL 4	0–10	0.20	7.67	6.72	9	7069
	10–20	0.20	7.81	6.77	7	7244
	20–30	0.19	8.12	7.10	8	5363
	30–40	0.08	8.27	7.04	7	346
	40–50	0.07	8.24	7.04	7	150
	50–60	0.09	8.25	7.05	7	169
	60–70	0.15	8.19	6.93	10	174
SL 5	0–10	0.59	8.05	7.18	119	8412
	10–20	0.48	8.61	7.46	184	462
	20–30	0.42	8.98	7.52	200	69
	30–40	0.64	8.82	7.52	317	48
	40–50	0.76	8.80	7.45	396	48
	50–60	0.69	8.64	7.42	408	28
	60–70	0.59	8.33	7.32	378	28
SL 6	0–10	0.85	7.63	7.35	17	59517
	10–20	0.92	7.68	7.28	8	4744
	20–30	1.24	7.43	7.12	15	2577
	30–40	0.53	5.90	5.82	14	458
	40–50	0.63	5.93	6.60	20	639
	50–60	0.48	5.60	5.40	25	339
	60–70	0.77	5.68	5.59	28	1107

Table A1 continued. Electrical conductivity, pH, chloride (Cl) and total Cr content of contaminated soils from Mount Barker, near Adelaide

Sample ID	Depth (cm)	EC (dS m^{-1})	pH (1:5 soil:H$_2$O)	pH (0.01M CaCl$_2$)	Cl (mg kg^{-1})	Cr (mg kg^{-1})
SL 7	0–10	0.03	6.51	5.53	9	249
	10–20	0.04	6.54	5.69	7	183
	20–30	0.14	7.29	6.15	8	3697
	30–40	0.14	7.68	6.55	6	2728
	40–50	0.13	8.10	6.97	7	1005
	50–60	0.10	8.24	7.14	7	71
	60–70	0.09	8.21	6.91	7	95
SL 8	0–10	0.24	7.91	7.05	17	17257
	10–20	0.18	8.07	7.17	9	11630
	20–30	0.14	8.13	7.40	8	2133
	30–40	0.09	8.31	7.50	7	297
	40–50	0.07	8.33	7.40	8	154
	50–55	0.07	8.20	7.30	8	76
SL 9	0–10	0.19	8.06	7.40	16	15804
	10–20	0.17	8.23	7.50	13	10300
	20–30	0.16	8.28	7.38	10	8571
	30–40	0.20	8.21	7.37	7	12400
	40–50	0.46	7.88	7.37	9	34500
	50–60	0.19	8.21	7.50	7	3300
	60–70	0.11	8.38	7.50	6	65
SL 10	0–10	0.31	8.05	7.44	26	69500
	10–20	0.51	7.97	7.40	36	51000
	20–30	0.26	8.18	7.49	13	5200
	30–40	0.34	7.80	7.41	7	70
	40–50	0.19	6.84	6.81	7	55
	50–55	0.32	6.20	6.30	8	225
SL 11	0–10	0.14	7.10	6.27	17	405
	10–20	0.06	7.43	6.53	11	400
	20–30	0.03	7.62	6.45	7	110
	30–40	0.04	7.69	6.65	6	94
	40–50	0.04	7.67	6.67	6	96
	50–60	0.03	7.75	6.64	6	30
	60–70	0.04	7.88	6.50	6	52
SL 12	0–10	0.22	7.64	6.67	18	17250
	10–20	0.13	8.06	6.73	9	1050
	20–30	0.08	8.26	6.85	7	45
	30–40	0.04	7.26	6.49	6	100
	40–50	0.04	7.59	6.47	5	28
	50–60	0.05	7.69	6.52	6	28
	60–70	0.05	7.89	6.45	6	22
SL 13	0–10	0.25	7.78	6.80	33	67500
	10–20	0.22	8.20	7.50	14	25000
	20–30	0.17	8.32	7.29	7	4400

Table A1 continued. Electrical conductivity, pH, chloride (Cl) and total Cr content of contaminated soils from Mount Barker, near Adelaide

Sample ID	Depth (cm)	EC (dS m⁻¹)	pH (1:5 soil:H₂O)	pH (0.01M CaCl₂)	Cl (mg kg⁻¹)	Cr (mg kg⁻¹)
SL 14	0–10	0.29	8.09	7.29	24	42000
	10–20	0.28	8.21	7.63	20	23500
	20–30	0.12	8.63	7.70	8	3800
	30–40	0.05	8.55	7.69	6	275
	40–50	0.05	8.41	7.63	7	220
	50–60	0.05	8.35	7.55	6	280
	60–70	0.05	8.34	7.55	7	146
SL 15	0–10	0.29	8.16	7.55	35	43000
	10–20	0.24	8.24	7.49	14	9250
	20–30	0.10	8.52	7.67	8	3400
	30–40	0.08	8.47	7.61	6	146
	40–50	0.06	8.38	7.58	5	60
	50–60	0.06	8.37	7.53	6	80
	60–65	0.04	8.44	7.59	6	22
SL 16	0–10	0.32	8.12	7.43	46	19000
	10–20	0.11	8.51	7.53	9	2300
	20–30	0.06	8.53	7.58	7	328
	30–40	0.06	8.49	7.54	10	108
	40–50	0.11	8.57	7.44	23	138
	50–60	0.18	8.57	7.40	43	40
	60–70	0.32	8.44	7.32	78	104
SL 17	0–10	0.43	7.71	7.26	45	59000
	10–20	0.53	7.86	7.44	23	57000
	20–30	0.69	7.83	7.40	13	16000
	30–40	0.84	6.32	5.36	14	1250
	40–50	0.61	4.58	4.10	16	310
	50–60	0.51	4.15	3.79	14	152
	60–70	0.51	3.90	3.69	14	128
SL 18	0–10	0.42	7.95	6.97	53	56000
	10–20	0.37	8.18	7.18	56	27500
	20–30	0.29	8.32	7.49	20	26633
	30–40	0.52	8.23	7.52	29	8612
	40–50	0.44	6.62	6.53	39	821
	50–60	0.29	6.42	6.45	14	600
SL 19	0–10	0.04	6.88	6.20	22	1092
	10–20	0.02	6.95	6.10	12	171
	20–30	0.04	6.74	6.06	26	62
	30–40	0.05	6.67	6.09	41	34
	40–50	0.02	6.20	6.11	16	19
	50–60	0.02	6.36	6.04	15	16
	60–70	0.01	6.04	5.98	11	12

Table A1 continued. Electrical conductivity, pH, chloride (Cl) and total Cr content of contaminated soils from Mount Barker, near Adelaide

Sample ID	Depth (cm)	EC (dS m^{-1})	pH (1:5 soil:H$_2$O)	pH (0.01M CaCl$_2$)	Cl (mg kg^{-1})	Cr (mg kg^{-1})
SL 20	0–10	0.26	7.66	6.93	95	9976
	10–20	0.09	7.86	6.98	38	1054
	20–30	0.08	7.70	6.90	38	1097
	30–40	0.07	7.58	6.78	34	350
	40–50	0.06	7.47	6.68	25	126
	50–60	0.07	7.43	6.65	32	122
	60–70	0.04	7.58	6.68	18	77
SL 21	0–10	0.25	8.32	7.68	75	1936
	10–20	0.08	8.38	7.06	21	52
	20–30	0.09	8.26	7.03	32	54
	30–35	0.10	8.02	6.96	40	65
SL 22	0–10	0.11	7.62	6.74	24	10667
	10–20	0.03	7.89	6.64	19	937
	20–30	0.03	7.85	6.58	15	826
SL 23	0–10	0.21	7.78	7.24	38	44355
	10–20	0.25	7.51	7.17	31	4900
	20–30	0.60	6.25	6.15	14	14708
	30–40	0.27	6.42	6.26	33	5566
	40–50	0.10	6.48	6.15	22	1350
SL 24	0–10	0.07	7.07	6.46	32	547
	10–20	0.07	7.29	6.55	42	553
	20–30	0.12	7.54	6.75	30	576
	30–40	0.28	7.65	6.95	75	13236
	40–50	0.14	7.94	7.08	46	3428
SL 25	0–10	0.37	7.86	7.24	63	48323
	10–20	0.28	8.00	7.38	19	18458
	20–30	0.22	8.24	7.41	19	3352
	30–40	0.20	7.50	7.04	22	833
	40–50	0.17	7.25	7.00	13	703
	50–55	0.17	7.44	6.93	17	330
SL 26	0–10	0.28	7.75	7.32	60	56952
	10–20	0.31	7.90	7.49	27	53933
	20–30	0.27	8.13	7.61	106	15612
	30–40	0.13	7.19	7.60	87	3311
	40–50	0.13	7.97	7.55	33	1881
SL 27	0–10	0.33	7.74	7.65	53	51934
	10–20	0.29	7.96	7.71	37	59271
	20–30	0.33	7.99	7.69	32	66312
	30–40	0.54	7.93	7.71	17	8119
	40–50	0.49	8.00	7.76	17	4351
	50–60	0.12	8.34	7.74	15	1113
	60–70	0.11	8.44	7.77	21	1458

Table A1 continued. Electrical conductivity, pH, chloride (Cl) and total Cr content of contaminated soils from Mount Barker, near Adelaide

Sample ID	Depth (cm)	EC (dS m⁻¹)	pH (1:5 soil:H₂O)	pH (0.01M CaCl₂)	Cl (mg kg⁻¹)	Cr (mg kg⁻¹)
SL 28	0–10	0.14	7.31	5.64	60	10892
	10–20	0.07	7.32	5.49	39	716
	20–30	0.04	7.57	5.59	17	191
	30–40	0.09	7.48	5.70	64	76
	40–50	0.05	7.92	5.84	17	50
	50–60	0.09	7.90	5.89	25	42
	60–70	0.15	7.86	6.02	48	35
SL 29	0–10	0.61	8.01	6.78	78	62621
	10–20	0.70	8.01	6.93	148	49734
	20–30	0.34	8.34	7.25	90	6408
	30–40	0.67	8.74	7.50	235	2523
	40–50	0.86	8.96	7.90	298	1450
	50–60	1.05	9.06	8.05	434	1405
	60–70	1.15	8.50	7.75	595	376
SL 30	0–10	0.27	8.43	6.51	126	34553
	10–20	0.24	8.45	6.95	56	16351
	20–30	0.44	8.16	7.13	42	35467
	30–40	0.56	8.16	7.37	62	32126
	40–50	0.65	6.87	6.86	26	4279
	50–60	1.03	5.76	6.20	58	3356
	60–70	1.19	3.96	3.97	57	1439
SL 31	0–10	0.27	7.05	6.73	22	41169
	10–20	0.13	7.41	6.88	12	5150
	20–30	0.09	7.61	7.76	15	1460
	30–40	0.10	7.78	7.76	26	891
	40–50	0.08	7.80	7.68	26	739
	50–55	0.07	7.81	7.57	14	459

Fate and Behaviour of Chromium at the Long-term Tannery Waste-contaminated Site Near Adelaide

P. Thangavel[1,2] and R. Naidu[1]

Abstract

Samples to 70 cm depth were taken at 10 cm intervals from three contaminated soil profiles at Mount Barker, near Adelaide. These samples were fractionated using the speciation procedure of Noble and Hughes (1991) with modifications to include the ionic nature of chromium (Cr) species. The modified procedure partitions Cr in the solution phase as soluble species, and as exchangeable hexavalent and trivalent forms. The extractants used in sequence were deionised water for the soluble fraction, 0.5M KNO_3 for the exchangeable and sorbed fraction, 0.5M NaOH for the organic fraction, 0.05M Na_2EDTA for the remaining organic compounds plus iron oxide, and finally digestion with 4M HNO_3 to extract the residual forms of Cr. Over 90% of the Cr was extractable by HNO_3 while the general order of the remaining extractants was EDTA > NaOH >> KNO_3 = H_2O. The water and KNO_3 fractions constituted < 0.5% of the total Cr. Speciation of Cr into Cr(VI) and Cr(III) using the diphenyl carbazide indicator technique showed the presence of appreciable concentrations of Cr(VI) in the surface soils. The Cr added to soils with tannery wastes is trivalent, and Cr(VI) is generally rapidly reduced to Cr(III) in the presence of organic matter and Fe, so oxidation of Cr(III) to Cr(VI) is not expected under the conditions that prevail in the soil environment at the contaminated site. Further studies are continuing to investigate the reasons for the presence of Cr(VI) in these soils.

LAND-based tannery waste disposals have led to extensive contamination of soil and groundwater resources in many parts of the Asian region. Recent studies in India demonstrate the presence of chromium (Cr) in excess of the World Health Organization guidelines in borewell water samples at sites in close vicinity to tannery industries in India (Mahimairajah et al. these Proceedings). These disposals have also led to degradation of thousands of hectares of productive agricultural land, with both Cr and salt exceeding the maximum permissible concentrations. Land-based disposal of tannery waste was permitted because

the non-toxic form of Cr is used during the tanning process. Numerous investigators promoted such disposals because of the thermo-dynamic stability of Cr(III) compared to Cr(VI) in the soil environment. Once it is in the soil environment, Cr(III) may interact with both the mineral and the organic components of soil colloid particles. Interactions with soil colloids modify the bioavailability of Cr(III) in the field, leading to changes in its mobility.

However, soil samples in the field are subject to periodic wetting and drying cycles during the wet and cool winter and hot and dry summer months. Such changes in soil conditions may induce a series of biological and chemical processes that may influence the stability of Cr species in the soils at the contaminated sites. Moreover, presence of even small concentrations of Mn(IV) oxides would induce oxidation of Cr(III) to Cr(VI) (Bartlett and Kimble 1976). In

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Table 1. Sequential fractionation of Cr in soils from the Mount Barker contaminated site using a modified Noble and Hughes (1991) technique

Extractant	Duration (hours)	Nature of Cr
Deionised water	2	soluble
0.5M KNO$_3$	16	exchangeable and sorbed
0.5M NaOH	16	organic
0.05M Na$_2$EDTA	6	remaining organics plus iron oxide
4M HNO$_3$	16 (at 80°C)	residual

Figure 1. Comparison of sum of Cr in various sequential fractions with the total Cr in soils extracted by the nitric:hydrochloric digestion technique

this study we investigated the transformation of Cr(III) in the soil at the long-term tannery waste-contaminated site at Mount Barker, near Adelaide.

Materials and Methods

Soils

Samples to 70 cm depth were taken from three contaminated soil profiles. These samples were air dried and crushed to pass through a 2 mm stainless steel sieve. Total Cr concentrations in these soils were determined in triplicate following extraction of 1 g soil subsamples with aqua regia for 16 hours at 105°C. Samples were allowed to reflux at constant temperature until all the soil was digested. The digest was then diluted with deionised water, and total Cr in the extract was estimated by atomic absorption spectrophotometry and acetylene nitrous oxide.

Sequential fractionation

Samples were selectively fractionated using the speciation procedure of Noble and Hughes (1991). This procedure was slightly modified to include investigation of the ionic nature of Cr species. The modified procedure partitions Cr in solution phase as soluble species, as exchangeable Cr(VI) and Cr(III). If the procedure is correct then the sum of these fractions should yield a near perfect agreement with the total Cr estimated by the nitric:hydrochloric method.

The procedure involved sequential extraction of duplicate 2.5 g subsamples of air dried soils (<2 mm) as shown in Table 1. Following end-over-end equilibration at 20 ± 2°C, the samples were centrifuged at 10 000 rcf, and the supernatant was

filtered using a 0.45 μm millipore filter. Before extraction and between each extraction the tubes plus contents were weighed to account for entrapped solution and transfer of Cr between extractions. The concentration of Cr in each of the extracts was estimated by atomic absorption spectrophotometry. Amounts of Cr (μg g^{-1}) extracted by each reagent were calculated by the following equation:

$$Cr \ extracted = C \times (25 + M) - (C' \times M),$$

where C is the concentration of Cr in the extraction solution, C' is the concentration of Cr in the extraction solution in the preceding step of the sequence, and M is the mass (g) of the entrained solution carried over from the previous extraction.

Chromium fractions in the water, KNO$_3$ and NaOH extracts were speciated to determine the proportions of trivalent and hexavalent forms. To ensure that the extraction procedure did not lead to transitions between Cr(III) and Cr(VI) we added known concentrations of Cr(III) and Cr(VI) to soil samples and subjected these soils to the sequential extraction described above. Results showed no change in the amounts and nature of added Cr during the extraction procedure.

Results

The concentrations of Cr measured in the sequential fractions are listed in Table 2. The sum of the various

Table 2. Cr (mg kg^{-1}) distributions in various fractions of three soil profiles from the contaminated site at Mt Barker

Sample	Depth (cm)	water 1	water 2	water 3	KNO$_3$	NaOH	EDTA	HNO$_3$	Total
SL2	0–10	5.80	4.53	3.15	5.05	406.20	338.10	35945	36708
	10–20	7.50	5.42	4.00	5.34	320.64	336.38	37523	33202
	20–30	23.71	15.55	12.96	13.87	183.01	162.93	31730	32142
	30–40	0.00	0.77	0.50	0.55	51.10	323.74	9979	10356
	40–50	0.00	0.57	0.39	0.02	28.28	33.55	1140	1172
	50–60	0.08	0.00	0.44	−0.02	11.33	15.33	296.5	323.6
	60–70	0.47	0.04	0.42	0.53	11.81	17.25	487.0	517.5
SL12	0–10	2.12	0.86	1.18	1.49	108.18	189.35	17226	17529
	10–20	0.40	0.24	0.95	−0.05	7.30	41.80	1128	1179
	20–30	0.29	0.01	0.83	−0.09	2.82	16.11	49.0	60.0
	30–40	0.34	0.12	0.02	0.06	0.57	5.22	60.8	67.1
	40–50	0.00	0.18	0.09	0.15	−0.01	3.00	44.6	48.0
	50–60	0.47	0.12	0.17	0.08	0.05	1.21	21.6	23.7
	60–70	0.38	0.15	0.23	0.06	0.00	1.82	56.6	59.2
SL29	0–10	4.70	2.72	3.13	3.47	332.26	270.91	61314	61931
	10–20	2.99	2.20	1.98	2.90	348.61	233.38	47166	47758
	20–30	0.31	0.07	0.22	−0.02	19.05	206.74	5673	5899
	30–40	0.29	0.10	0.06	0.00	3.70	64.02	1631	1699
	40–50	0.28	0.19	−0.01	0.00	4.36	50.75	1525	1580
	50–60	0.53	0.55	0.11	−0.01	3.42	61.83	1053	1119
	60–70	0.29	0.69	0.88	0.09	1.22	16.90	362	382

fractions is about 5% lower than the total concentration of elemental Cr obtained by the nitric : hydrochloric digestion technique (Fig. 1).

Over 90% of the Cr was extractable by HNO$_3$ while the general order of effectiveness of the remaining extractants was EDTA > NaOH >> KNO$_3$ = H$_2$O. The water and KNO$_3$ fractions constituted <0.5% of the total Cr. These results indicate that most of the Cr at the contaminated site is present in residual fractions. Further detailed studies using a combination of scanning electron microscopy and X-ray diffraction revealed the presence of Cr in association with calcareous material, although a small fraction also appeared to be present on iron–oxyhydroxide surfaces (Audinayagam et al. 2000). These results are consistent with the EDTA and NaOH extractable fractions that show the presence of an appreciable fraction of Cr in the organic and iron oxide mineral pools present in the soil. While Cr in these pools is not of concern, given its low bioavailability, the presence of Cr in the water and KNO$_3$ extracts is of concern, because these fractions represent the soluble and most mobile forms of Cr. The data in

Table 2 show that even at the end of three repeated extractions Cr was still released in water, so there is considerable potential for the leaching of Cr in these soils. Speciation of Cr into Cr(III) and Cr(VI) using the colorimetric diphenyl carbazide (DPC) indicator technique showed the presence of significant concentrations of Cr(VI) in the soils from profiles SL2 and SL12 (Table 3). In the third soil profile Cr(VI) was detected only in the subsurface soil samples. Further studies are continuing to find out why Cr(VI) is present in these soil water extracts. The results suggest that there is high mobility of Cr(VI) at the contaminated sites, and cause for concern about potential groundwater contamination. In general, Cr(VI) was not detected in the EDTA extracts.

As discussed above, the presence of Cr(VI) in the soil water extracts and the soil solid phase is surprising, given that the Cr salt that was being used was predominantly of the Cr(III) form. Most Cr added to soils is rapidly reduced to Cr(III) in the presence of organic matter (electron donor group), so oxidation of Cr(III) to Cr(VI) is not expected under the conditions that prevail in the

Table 3. Concentration (mg L^{-1}) of Cr(VI) in each of the sequential extracts

Depth (cm)	water 1	water 2	water 3	Total water	KNO$_3$	NaOH	EDTA
0–10	5.122	2.97	3.072	11.164	3.877	28.79	1.901
10–20	6.39	3.708	3.501	13.599	4.814	30.2	0.301
20–30	20.58	10.807	9.518	40.905	11.175	29.41	1.444
30–40	ND	0.146	0.079	0.268	0.128	8.59	ND
40–50	ND	ND	ND	ND	ND	0.222	ND
50–60	ND	ND	ND	ND	ND	ND	ND
60–70	ND	ND	ND	ND	ND	ND	ND
0–10	1.686	0.201	ND	1.887	0.985	15.31	ND
10–20	0.179	0.066	ND	0.245	ND	5.01	ND
20–30	0.127	ND	ND	0.127	ND	ND	ND
30–40	ND	ND	ND	ND	0.044	0.216	ND
40–50	ND	ND	ND	ND	0.039	ND	ND
50–60	ND	ND	ND	ND	ND	ND	ND
60–70	ND	0.151	ND	0.151	ND	ND	ND
0–10	3.308	2.673	2.593	8.574	2.953	22.665	4.69
10–20	3.043	1.912	1.541	6.496	2.317	29.34	2.52
20–30	ND	ND	ND	ND	ND	3.709	ND
30–40	ND	ND	ND	ND	ND	2.19	ND
40–50	0.104	ND	ND	0.104	ND	2.041	ND
50–60	0.329	ND	ND	0.329	ND	2.46	ND
60–70	0.083	ND	ND	0.083	ND	0.059	ND

soil environment at the contaminated site. Consequently we have been investigating the role of microbial processes in Cr(III) oxidation in these soils. Our limited optical microscopic studies, using both the contaminated soils and effluent samples, have indicated the presence of microbes similar to Cr oxidising bacteria (Gupta et al. these Proceedings) although the rate of oxidation was slow. Further studies are continuing to establish the effects of other factors, including the effect of Mn(IV) on Cr(III) oxidation at the contaminated site. The potential for indirect oxidation of Cr(III) by Mn(II) in the presence of Mn oxidising bacteria is also being investigated.

Conclusion

Solid phase speciation of soils contaminated over a long period with tannery waste at the Mount Barker waste disposal site shows the presence of significant amounts of Cr(VI) in the soil matrix, suggesting there is potential for Cr(III) oxidation in soils. These studies also reveal the presence of appreciable amounts of Cr(VI) that are soluble in water and KNO$_3$, suggesting that there is considerable potential for leaching and subsequent contamination of groundwater.

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Extent and Severity of Contamination around Tanning Industries in Vellore District

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Abstract

Long-term disposal of tannery wastes has led to extensive contamination of the soil environment in many parts of India. The major contaminants in the wastes include chromium (Cr) and high concentrations of dissolved salts. In this study the extent and severity of contamination of the soils around selected tanneries in the Vellore district was investigated. Samples of tannery effluents and sludge were collected. Surface (0–15 cm) and subsurface (15–60 cm) soils were sampled around the tanneries and analysed for total Cr, pH and electrical conductivity (1:5 soil:water), and salt content. The results showed that the effluents varied considerably in pH (6.17–8.17), EC (10.4–23.0 dS m^{-1}), Na (2040–9000 mg L^{-1}) and total Cr (620–26 200 µg L^{-1}). The sludge contained higher Cr (1179–16 158 mg kg^{-1}) than the effluent. Variation was also observed between tanneries. Though no definite pattern has been observed in the distribution of Cr at different depths, Cr accumulation ranged from 569–79 865 mg kg^{-1} in surface and subsurface soils and the reasons for subsurface accumulation are not clear. Soils around the closed (old) tanneries were particularly high in Cr relative to the existing tanneries. This may be attributed to the more stringent guidelines recently (last 15 years) imposed by the Tamil Nadu Pollution Control Board. The speciation of Cr, determined by a sequential fractionation procedure, indicated that over 85–99% of Cr was extractable by HNO_3. The Cr extractable by NaOH (organic) and EDTA (remaining organics plus iron oxide) constituted only 0.5–15%. Though no Cr (soluble) was detected in the water extracts, concentrations ranging from 5.5 to 128 µg kg^{-1} obtained in KNO_3 extract are of concern, because this fraction represents the exchangeable and sorbed Cr.

THE leather industry is among the major sources of pollution in the state of Tamil Nadu. The effluent and sludge discharged from these tanneries into rivers and onto land has led to extensive degradation of productive land. The tannery wastes typically contain high concentrations of salts (sodium, chloride and sulfates, etc.) and chromium (Cr) which threaten surface and subsurface soil and water resources. High concentrations of heavy metals in soil, due to effluent or sludge, are of concern because of possible phytotoxicity or increased movement of metals into the food chain (Chaney 1990) and the potential for surface and groundwater contamination. Even in cases where there is low or zero metal contamination, pollution of surface water and groundwater may also be of concern because of excessive N and P loading of potable water supplies.

Lack of scientific information on the potential environmental impact of tannery effluent and sludge in India has culminated in extensive pollution of productive agricultural land, surface

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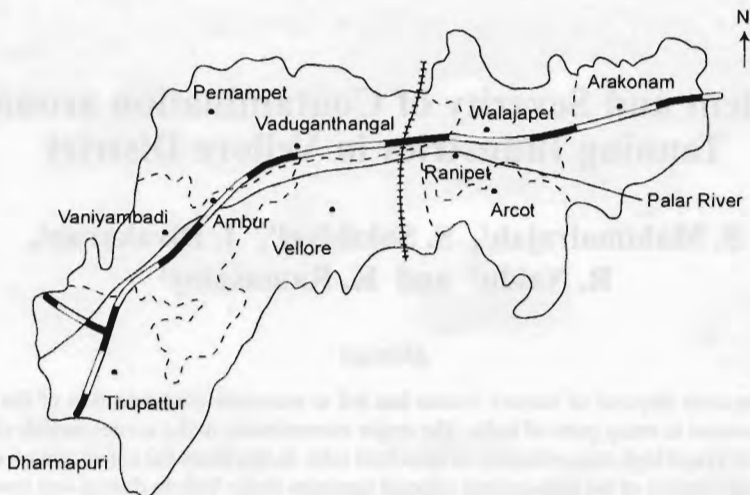
Figure 1. Locations of the sampling sites (dots)

and groundwater in Tamil Nadu. Moreover, information on the composition of tannery wastes (both effluent and sludge) is limited, particularly for Tamil Nadu where the environmental pollution due to tanneries is of serious concern. It is also not known to what extent the hazardous Cr has accumulated in the soil and water environment. This study was undertaken to characterise a range of tannery wastes available in Vellore district (North Arcot Ambedkar district) where many tanneries are located, and to assess the extent to which the soil and ground-water are contaminated with Cr from the disposal of tannery wastes.

Materials and Methods

Collection of samples

To characterise a range of tannery wastes, replicate samples of effluents and sludge were collected from selected tanning industries at Ambur, Vaniyambadi, Walajapet, Pernampet and Vaduganthangal in the Vellore district of Tamil Nadu. The locations of the sampling sites are depicted in Fig. 1. The effluents were collected in separate new 1 L polyethylene containers which were rinsed with effluent several times before filling. Samples of sludge were collected and stored in polyethylene bags.

Surface soils (0–15 cm) and subsurface soils (10–20 cm intervals to depths exceeding 60 cm) were collected, air dried at 25°C and passed

through a 2 mm sieve. The homogenised soils were stored in polyethylene bags for all laboratory studies.

Analyses

The pH of soil was measured both in water and in 0.01M $CaCl_2$ (1:5) suspension after one hour shaking, using a combination pH electrode. The electrical conductivity (EC) was measured only in soil:water (1:5) suspension. The effluent samples were acidified with concentrated HNO_3 to a pH of approximately 3.0 to stabilise the original valence state of Cr. The samples were stored at 4°C until further chemical analysis. Duplicate samples of sludge (1 to 2 g) or soil (1 to 2 g) were digested with 10–15 mL aqua regia at 110°C for 2 hours. The effluent samples were also digested using aqua regia at 1:2 ratio, because earlier observations showed that the determination of Cr in undigested and filtered effluent or water samples recorded a reduced level of total Cr content. Acid digestion recovers Cr both in solution as Cr(VI), and in colloidal particles as Cr(III). After filtration and appropriate dilution, Cr and other heavy metals including copper (Cu) and zinc (Zn) were determined using an atomic absorption spectrophotometer (AAS; Varian SpectrAA-200) and air-acetylene flame. A wavelength of 358 nm was used with a spectral slit width of 0.2 nm. The sodium (Na) content was also determined using a flame photometer.

Table 1. Mean pH, EC, total Na and Cr contents of tannery effluent

Effluent	pH	EC (dS m^{-1})	Na (mg L^{-1})	Cl (mg L^{-1})	Cr (µg L^{-1})
Ambur					
Raw effluent	6.17	11.4	2280	1805	26200
Treated effluent	8.17	10.4	2040	1644	8800
Vaniyambadi					
Treated effluent	7.02	23.0	9000	3674	900
Walajapet					
Treated effluent	8.17	13.5	2600	3143	2300
Pernampet					
Raw effluent	7.26	20.0	3150	3191	7200
Treated effluent	7.43	20.4	3250	2410	620
Vaduganthangal					
Treated effluent	7.56	13.0	2900	1720	760

Fractionation of Cr

To determine the nature of Cr in the contaminated sites, the Cr in soils was fractionated following a sequential fractionation procedure according to modified Noble and Hughes (1991) technique. Duplicate 1 g samples of air dried soil were shaken end-over-end with 25 mL of double distilled water (three times) at $20 \pm 2°C$ for 2 hours in a 50 mL polypropylene centrifuge tube. The tubes were centrifuged at 10000 rpm for 20 min and filtered through Whatman No. 40 filter paper. The soluble Cr in the water extract was determined using AAS as described above.

To the residue in the tube, 25 mL of 0.5M KNO$_3$ was added. The tube was shaken for 16 h and then centrifuged and filtered. This was followed by extraction with 0.5M NaOH for 16 h and 0.05M

Na$_2$EDTA for 6 h. The Cr in the respective extracts was determined by atomic absorption spectrophotometry. Before extraction and between each extraction the tube plus contents were weighed to calculate the volume of entrapped solution and transfer of Cr between extractions. The amounts of Cr (µg g^{-1}) extracted by each extractant were computed by the equation,

$$Cr \text{ extracted} = C \times (E + M) - (C' \times M),$$

where C = concentration of Cr in the extraction solution, E = mass (g) of the extractant, M = mass (g) of the entrained solution carried over from previous extraction, C' = concentration of Cr in the extraction solution of the preceding step of the sequence. The residue in the tube was carefully transferred to a 150 mL conical flask using a jet of water, and dried in an oven. Concentrated HNO$_3$

Table 2. Some important characteristics of tannery sludge

	pH		EC (dS m^{-1})	Na (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})
	H$_2$O	0.01M CaCl$_2$					
Ambur							
Site 1	7.81	7.65	16.0	62781	5728	58	106
Site 2	8.28	8.01	6.0	44875	1179	13	38
Site 3	7.76	7.65	15.5	40698	9312	54	218
Vaniyambadi							
Site 1	8.16	7.77	2.3	10125	1314	21	60
Site 2	8.05	7.85	5.7	9917	1895	16	48
Vaduganthangal	8.46	–	8.3	12231	8241	42	67
Pernampet	7.70	7.41	20.8	29239	16158	32	51

Table 3. Salt and heavy metal content in soils around tanneries at Ambur

	Depth (cm)	pH H₂O	pH 0.01M CaCl₂	EC (dS m⁻¹)	Na (mg kg⁻¹)	Cr (mg kg⁻¹)	Cu (mg kg⁻¹)	Zn (mg kg⁻¹)
Ambur								
Site 1	0–15	8.57	8.10	1.28	14216	924	23.6	924
	15–20	9.51	8.31	0.39	10265	813	12.1	813
	20–40	9.67	8.20	0.35	8838	543	9.3	543
Site 2	0–5	8.19	7.98	12.32	43301	1733	18.8	1733
	5–20	8.54	8.17	3.60	15150	2915	19.4	2915
Site 3	0–15	8.39	8.13	3.02	18445	949	29.2	949
	25–40	8.43	8.11	3.26	24959	5281	37.9	5281
	50–70	8.09	8.01	2.40	19900	4117	23.9	4117
Site 4	0–15	8.11	7.80	2.15	77711	1229	31.4	1229
	15–30	8.29	7.70	0.88	42102	1181	21.2	1181
Site 5	0–15	8.2	7.70	0.15	41936	1182	10.0	12.8
Site 6	0–5	8.20	8.10	1.28	42635	16731	35.9	89.3
Reference soil								
Site 1	0–15	7.96	7.49	0.55	1022	5.2	7.0	20.0
Site 2	0–15	8.24	7.86	0.32	2697	8.6	35.9	54.8
Site 3	0–15	8.23	7.16	0.59	1226	6.4	15.9	34.7

(10 mL) was added to the soil residue and it was digested at 110°C. The digest was diluted and filtered before the Cr was measured.

Results and Discussion

Tannery effluent and sludge

The effluent collected at different locations varied considerably in pH and EC (Table 1). The pH ranged from 6.17 (raw effluent) to 8.17. The EC was generally high and ranged between 10.4 and 23.0 dS m⁻¹. The effluent derived during the washing of preserved skin was highly saline, with concentrations of Na greater than 2000 mg L⁻¹ at all sites. The high salt content originated from the sodium chloride and sodium sulfide used in the washing process. Wide variation was also observed in the total Cr concentrations of the effluents (620–26 200 µg L⁻¹) collected at different locations (Table 1). These differences in the chemical constituents may be due to differing processing methods employed by the various tanneries.

The pH of sludge, measured both in water and in 0.01M CaCl₂, was relatively high (7.41 to 8.46) compared to effluent, but EC values were found to be lower in most sludge samples (Table 2). This

Table 4. Range in pH, EC, Na, Cl and Cr of surface soil

| Location	pH (1:5 H₂O)	EC (dS m⁻¹)	Na (mg kg⁻¹)	Cl (mg kg⁻¹)	Cr (mg kg⁻¹)
Ambur (n = 12 x 2)	8.11–8.57 (8.27)	0.15–12.3 (3.36)	14216–77711 (39707)	21.3–4587 (3240)	924–16731 (3791)
Vaniyambadi (n = 25 x 2)	7.68–8.87 (8.28)	0.43–20.6 (9.94)	2405–74398 (18952)	60.9–8175 (5165)	569–79865 (20164)
Reference soil (n = 3 x 2)	7.96–8.23 (8.14)	0.32–0.59 (0.48)	1022–2697 (1648)	45.4–84.0 (58.0)	5.2–8.6 (6.7)

n = number of samples; mean values given in parentheses

Table 5. Salt and heavy metal content in soils around tanneries at Vaniyambadi

	Depth (cm)	pH		EC (dS m⁻¹)	Na (mg kg⁻¹)	Cr (mg kg⁻¹)	Cu (mg kg⁻¹)	Zn (mg kg⁻¹)
		H₂O	0.01M CaCl₂					
Site 1	0–5	7.68	7.65	15.7	38501	41065	39	108
	5–15	8.13	7.87	4.9	44064	8450	66	116
	15–30	8.15	7.81	4.5	14786	69495	30	153
	30–50	8.15	7.86	5.1	46194	44838	29	152
	50–70	8.19	7.68	5.7	9719	10096	33	133
	> 70	8.26	7.89	5.2	50724	73111	30	125
Site 2	0–15	8.00	7.86	18.9	48870	79865	28	148
Site 3	0–15	7.94	7.74	11.1	59830	11464	31	146
Site 4	0–15	8.08	7.84	11.5	38592	14052	30	138
Site 5	0–15	8.00	7.78	12.4	29214	16790	32	151
Site 6	0–15	8.01	7.75	4.9	24705	13064	32	135
Site 7	0–15	7.94	7.67	7.9	34444	14116	33	122
Site 8	0–15	7.97	7.70	10.6	35391	11975	32	126
Site 9	0–15	8.11	7.59	9.3	74398	16858	28	125
Site 10	0–15	8.06	7.71	7.8	11644	37087	41	123
	15–30	7.83	7.62	2.9	5858	12341	31	39
Site 11	0–15	8.87	7.70	0.43	2405	28168	40	46
Site 12	0–15	8.13	7.65	3.08	10553	28952	40	78
Site 13	0–15	8.14	7.74	3.68	7563	8422	38	69
Site 14	0–15	7.91	7.65	10.3	15979	177539	44	89
Site 15	0–15	7.94	7.71	17.0	22833	18287	39	53
Site 16	0–12	8.10	7.61	20.6	29707	25664	67	161
	12–32	7.93	7.70	10.1	19218	33714	69	148
Site 17	0–15	7.73	7.49	2.65	5219	3646	43	72
Site 18	0–15	7.84	7.43	10.2	12120	8762	52	118
Site 19	0–15	7.83	7.27	7.26	7117	5827	35	83
Site 20	0–15	7.70	7.21	11.4	5793	1750	23	42
Site 21	0–15	7.81	7.46	5.86	4926	569	19	45
Site 22	0–15	7.81	7.54	6.59	4875	4252	31	82
Site 23	0–15	7.84	7.55	8.16	5450	9485	30	68
Site 24	0–15	7.86	7.65	13.0	18665	37036	109	207
Site 25	0–15	7.93	7.73	8.22	14068	49202	122	215

may be due to the nature of the salts present in sludge. The concentration of Na varied from 9917 to 62 781 mg kg⁻¹ and the total Cr content ranged from 1179 to 16 158 mg kg⁻¹. Other heavy metals such as Cu and Zn were also observed in the sludge (Table 2). Disposal of this effluent and sludge onto land is of concern since high salinity is linked to sodicity as well as to salt-associated land degradation and its related constraints to crop productivity. According to one estimate (Naidu and McLaughlin 1993), such disposals in the past have already degraded over 50 000 ha of agricultural land in Tamil Nadu.

Chromium Contamination in the Environment

Chromium in soil

The pH, EC and the distribution of Na and Cr in surface and subsurface soils around selected tanneries at Ambur and Vaniyambadi are presented in Tables 3, 4 and 5 and Figs 2 and 3. The pH (H₂O) of surface and subsurface soil at Ambur ranged from 8.11 to 8.57 and 8.09 to 9.67, respectively, and the EC from 0.15 to 12.32 and 0.35 to 3.60 dS m⁻¹, respectively. At Vaniyambadi, the pH and EC varied from 7.68 to 8.87 and 0.43 to 20.6 dS m⁻¹, respectively, over all depths. The
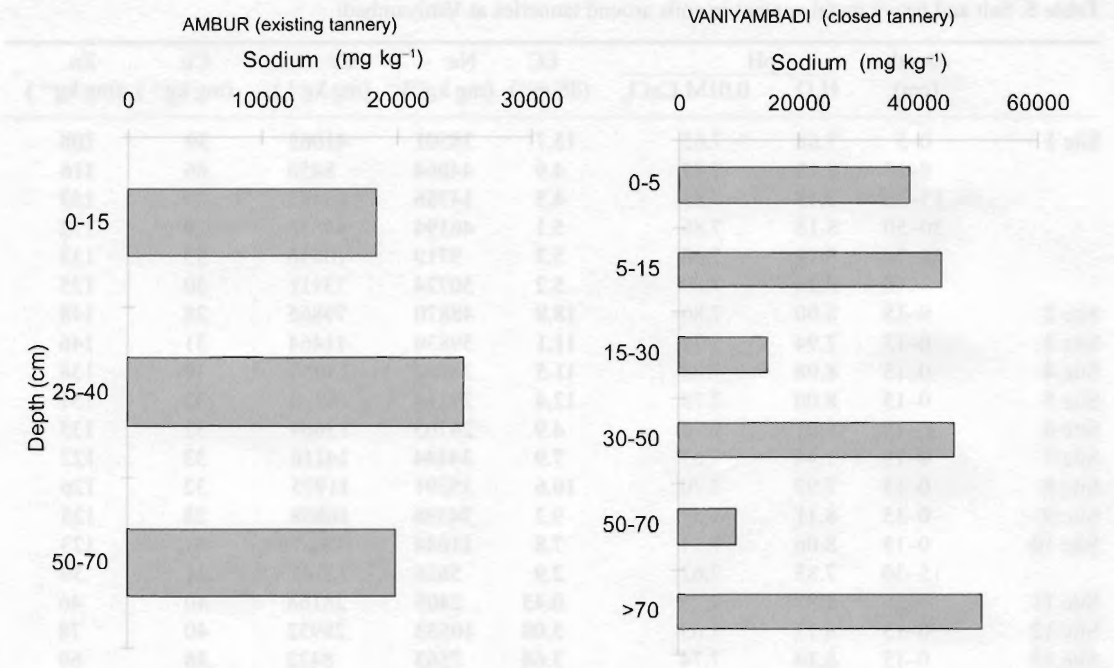
Figure 2. The distribution of sodium within two different soil profiles at contaminated sites in Ambedkar district
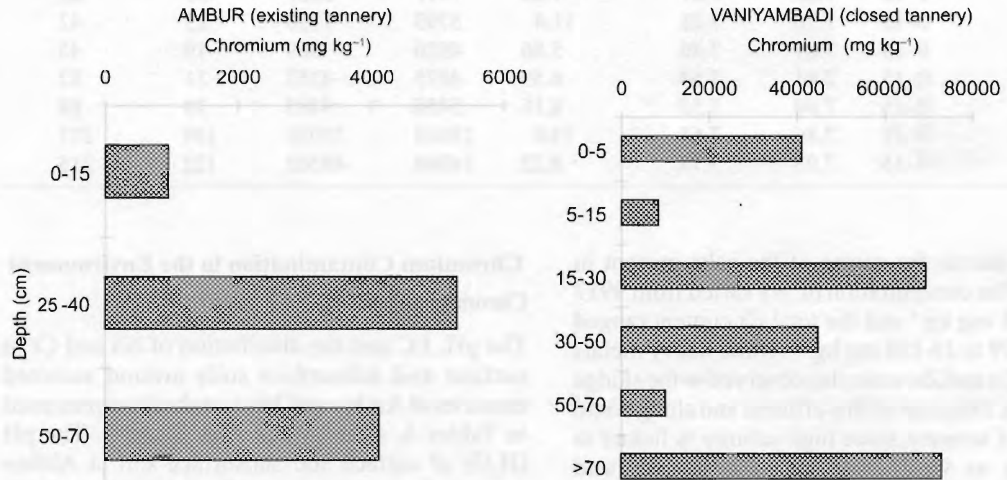
Figure 3. Distribution of chromium within soil profiles typifying Cr contamination at the contaminated sites

Table 6. Threshold levels of Cr permissible in soils of some developed countries (mg kg^{-1})

	Australia[a]	New Zealand[b]	UK[c]	Canada[d]	USEPA[e]	Germany[f]
Cr III	50 (Total)	600	600	250	1500	200
Cr VI		10	25	8	–	–

[a] ANZECC / NHMRC (1992)
[b] Ministry of Environment / Ministry of Health (1995)
[c] UK Department of Environment (1987)
[d] CCME (1990)
[e] USEPA (1993), Alloway (1995)
[f] Marshall (1994)

surface and subsurface soils both at Ambur and at Vaniyambadi had very high Na: 8838–77 711 mg kg^{-1} and 2405–74 398 mg kg^{-1}, respectively. The salt-rich effluent and sludge discharged at the sites are thought to cause the Na accumulation in the soils.

At both locations, the Cr content showed no definite pattern with soil depth, but tended to accumulate in disproportionate amounts within the soil profile (Fig. 3). This may partly be due to the varying texture of soil and hydrological features of the sampling sites which may have influenced the mobility of Cr, resulting in differential accumulation in the soil profile. Nevertheless, at Vaniyambadi the Cr level exceeded 70 000 mg kg^{-1} at depths exceeding 70 cm. The different chemical compositions of effluent and sludge also contributed to the variation in Cr accumulation.

The data clearly show that the soils around tannery industries are severely contaminated with

Cr. However, the nature and speciation of Cr has not been determined. In nature, Cr can occur both in hexavalent forms, as Cr(VI), and in trivalent forms, as Cr(III), depending on the nature of the soil environment. The Cr(VI) which exists primarily as CrO_4^{2-} and $HCrO_4^-$ in natural systems (Richard and Bourg 1991) is of particular concern because it is toxic, even at low concentrations, to both plants and animals (Bartlett and Kimble 1976) and it is more soluble and more mobile in the environment than Cr(III). The Cr accumulation in soils of Ambur and Vaniyambadi exceeded the maximum threshold limits prescribed in various developed countries (Table 6).

Speciation of Cr

The speciation of Cr as determined by a sequential fractionation procedure indicated that 85–99% of Cr was extractable by HNO_3 (data not presented here).

a) Ambur

b) Vaniyambadi
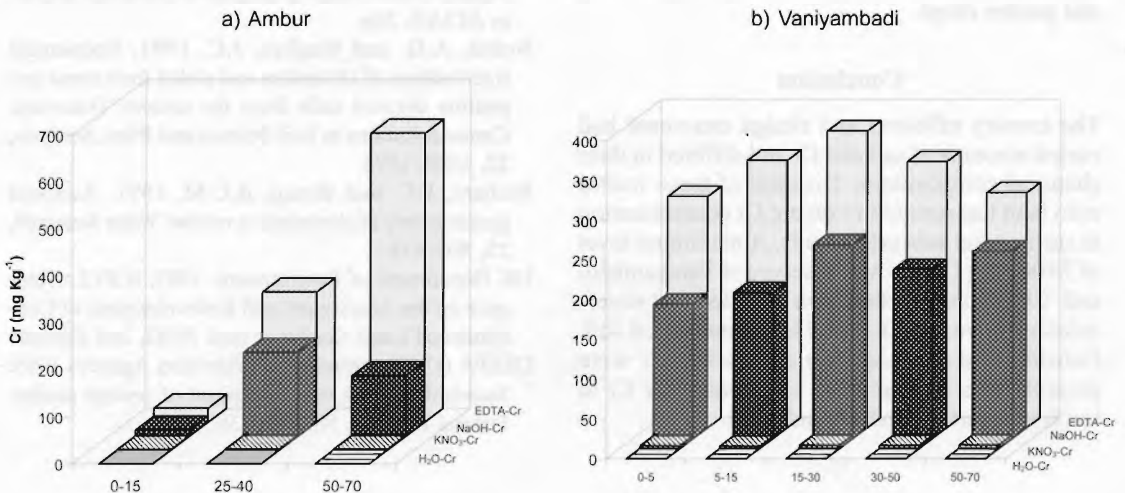
Figure 4. Nature of Cr in the surface and subsurface horizons in two of the contaminated soils

The Cr that was extractable by NaOH (organic) and EDTA (remaining organic compounds plus iron oxide) constituted only 0.5–15% (Fig. 4). Though no Cr (soluble) was detected in the water extracts, Cr concentrations of 5.5–128 µg kg^{-1} obtained in KNO$_3$ extract are of concern since this fraction represents the exchangeable and sorbed Cr that has the potential to leach. This study demonstrates that long-term disposal of tannery wastes has severely contaminated the soils around the tanning industries in Vellore district.

Implications of Tannery Waste Disposals to Environmental Quality

The long-term disposal of tannery wastes has implications both for environmental quality and for animal and human health issues. The salinisation of the soil and groundwater has implications for crop production in this district. While salt per se is not of major concern to human health, high salt content has been shown to have an impact on micro- and macrofaunal activities in soils. Of major concern is the presence of Cr(VI) in the soils as well as the groundwater; the latter is the major source of water for local consumption. Many people also grow food in backyard gardens and raise poultry for local consumption. With both of these activities there is the potential for Cr transfer from soils to animals and human beings. Thus there is an urgent need for the environmental scientists to assess the Cr contents of backyard soils and garden crops.

Conclusion

The tannery effluents and sludge examined had varied amounts of salt and Cr and differed in their chemical compositions. Disposal of these wastes onto land has resulted in severe Cr contamination in surface and subsurface soils. A maximum level of 79 000 mg Cr kg^{-1} was observed in Vaniyambadi soil. Chromium fractionation revealed that water-soluble Cr was not detected in contaminated soil. Considerable exchangeable and sorbed Cr were present, showing that there is potential for Cr to leach into surface and groundwater.

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Chromium Contamination of Groundwater in Vellore, India: Evidence of Chromium Mobility at Contaminated Sites

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Abstract

This study investigated the extent of chromium (Cr) contamination of the groundwaters around selected tanneries in the district of Vellore, sampled in borewells and piezometers. Samples of groundwater were analysed for Cr(III), Cr(VI), pH, electrical conductivity and total salt content. The concentration of total Cr ranged from 50 to 990 µg L^{-1} in borewell waters. A concentration of >500 µg Cr L^{-1} was obtained for the groundwater sampled at 10 m depth inside the Palar River; a concentration of >950 µg Cr L^{-1} was found in a borewell 2 km away from a closed tannery. The normal average background value reported in various parts of India is 4–7 µg L^{-1}. In the majority of water samples the Cr concentration exceeded the maximum permissible limit (50 µg L^{-1}). Of greater concern was the finding that 89–96% of the Cr in most of the borewell waters was toxic Cr(VI). The Cr concentration was below the detectable limit in groundwaters collected from piezo-meters installed at uncontaminated sites. However, during successive sampling sessions at a contaminated site, the Cr, sodium and chlorine concentrations showed an increasing trend. This suggests that with continuous leaching the Cr and salts had moved down the soil profile and contaminated the groundwater. The results demonstrated that Cr is highly mobile in contaminated soils around tanneries. Trivalent Cr(III) is the form of Cr pre-dominantly used in the tanning process and added to soils in the tannery wastes. The presence of Cr(VI) in borewell waters raises questions about the mechanisms that enhance oxidation of Cr(III) to Cr(VI) in groundwaters. The water samples showed microbial activity, so microbial oxidation–reduction may have favoured the transformation.

MAHIMAIRAJAH et al. (these Proceedings) present data to show the extent and severity of contamination in soils around tannery industries in India. The chromium (Cr) and salt-rich tannery effluent and sludge discharged onto land have led to extensive degradation of productive land, due to salinity and sodicity and accumulation of Cr. Chromium in natural waters exists both in trivalent

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(Cr^3) and in hexavalent (Cr^6) states. Generally, the presence of Cr(VI) is indicative of industrial pollution, although naturally occurring Cr(VI) has been found (Robertson 1975). While Cr(III) is considered to be an essential element for humans (Mertz et al. 1974), Cr(VI) can be quite toxic to organisms even at relatively low concentrations (USEPA 1976), because of its biochemical behaviour. Speciation studies (Mahimairajah et al. these Proceedings) provide evidence for the presence of exchangeable and sorbed Cr at concentrations ranging from 5.5 to 128 µg kg^{-1} which are likely to form soluble Cr(VI). Further,

if oxidation of Cr(III) occurs, the resultant Cr(VI) dissolves in water, moves down the soil profile and can contaminate groundwater.

This study was undertaken to assess groundwater contamination by Cr and to examine the transport (mobility) of Cr in soil and its potential to contaminate groundwater.

Materials and Methods

Collection of samples

Replicate samples of groundwater were collected from borewells that were approximately 10 m deep around selected tanneries at Ambur, Walajapet, Vaniyambadi, Vaduganthangal and Vinnamuthi villages in Vellore district. The samples were collected in new 1 L polyethylene containers which previously had been soaked in an acid bath and rinsed several times, first with deionised water and then with groundwater, before filling. The samples were kept in an ice-box and brought to the laboratory.

To examine the mobility of Cr in soil and its potential to contaminate the groundwater, nests of piezometers were installed at depths varying from 50 cm to 200 cm at selected locations around Vaniyambadi, including uncontaminated sites. At each site, boreholes were drilled to depths of approximately 50 cm, 100 cm or 200 cm with a specially designed soil auger, and the piezometers were inserted. Piezometer 1 was located in an uncontaminated area which was situated upstream of the direction of groundwater flow from a chrome tannery. Piezometer 2 was located right in the

centre of a disposal site very close to a chrome tannery, where the distribution of Cr in the soil profile ranged between 8450 mg kg⁻¹ and 73 111 mg kg⁻¹. Piezometer 3 was located approximately 2 km away from the contaminated site, along the direction of the groundwater flow. A total of 22 piezometers were installed, but only nine have escaped human interference. Water samples (piezowaters) were collected from the piezometers at monthly intervals during the rainy season (October 1997 to January 1998) when moisture saturation allowed subsurface flow.

Laboratory analyses

After their pH and electrical conductivity (EC) had been measured, the water samples were acidified with concentrated HNO_3 (2 mL L⁻¹) to a pH of approximately 3.0, to stabilise the original valence state of Cr. The samples were stored at 4°C and analysed within 48 hours (APHA 1980). The water samples were digested using aqua regia at 1:2 ratio, because our earlier studies had shown that undigested but filtered samples of effluent or water recorded a reduced level of total Cr content. Acid digestion recovers Cr both in solution as Cr(VI) and in colloidal particles as Cr(III). After filtration and appropriate dilution, Cr was measured using an atomic absorption spectro-photometer (Varian SpectrAA-200) with air–acetylene flame. The wavelength of 358 nm was used with a spectral slit width of 0.2 nm. The sodium (Na) content was determined using a flame photometer. The concentration of Cr(VI) in the borehole water samples was estimated in samples filtered through

Table 1. Mean pH, EC and total Na, Cl and Cr concentrations of borehole water samples

Site		pH	EC (dS m⁻¹)	Na (mg L⁻¹)	Cl (mg L⁻¹)	Total Cr (µg L⁻¹)	Cr(VI) (µg L⁻¹)
Ambur	Site 1	7.40	6.5	1200	946	178	159
	Site 2	6.78	2.7	4850	395	511	480
Walajapet	Site 1	8.42	1.0	50	105	996	922
	Site 2	8.40	1.1	100	147	923	895
Vaniyambadi	Site 1	7.71	2.5	765	464	720	640
Vaduganthangal	Site 1	7.23	11.2	1600	1628	256	231
Pernampet	Site 1	7.13	6.5	780	947	54	52
	Site 2	8.10	6.9	960	1006	51	48
Vinnamuthi (uncontaminated site)		7.90	1.5	198	221	ND	ND

ND = not detectable
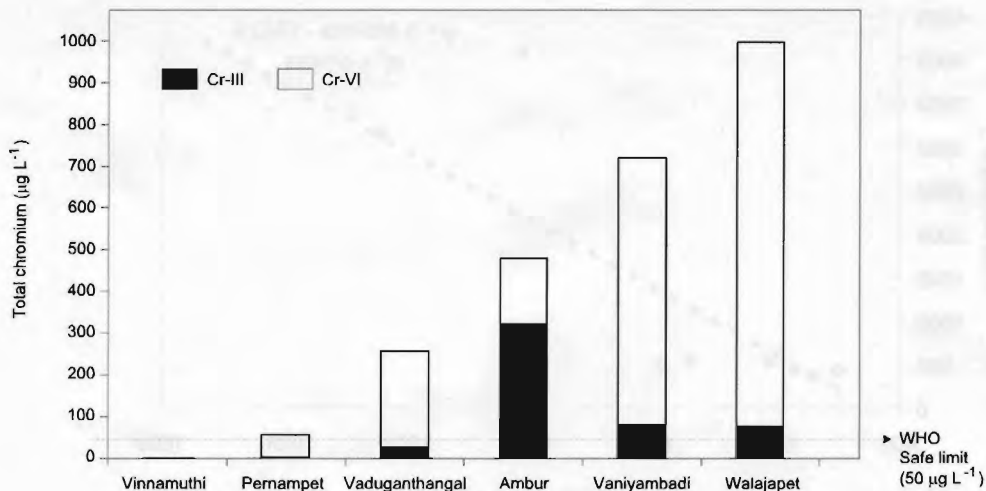
Figure 1. Total Cr and the nature of Cr species in borewell water samples from districts in Coimbatore, India

0.45 µm millipore filters using the colorimetric diphenyl carbazide indicator technique (Clesceri et al. 1989).

Results and Discussion

Chromium in groundwater

The concentration of total Cr in contaminated groundwaters ranged from 51 to 996 µg L^{-1} with a pH variation from 6.78 to 8.42 (Table 1). Wide variation (1.0 to 11.2 dS m^{-1}) was also observed in EC. The concentration of Cr was below the detectable limit in water samples from uncontaminated sites in Vinnamuthi village. A low concentration, only about 50 µg L^{-1}, was recorded for the samples from Pernampet where tanneries have only been established recently and function with a common effluent treatment plant. The well waters at Vaduganthangal, where only one large-scale chrome tannery without a treatment plant has been operating for the past 10 years, contained a relatively high concentration of Cr (256 µg L^{-1}). At Ambur, where many small- and large-scale tanneries are located, Cr concentrations varying from 178 to 511 µg L^{-1} were recorded. The result showed that Walajapet and Vaniyambadi are the worst affected areas, with Cr concentrations of 720–996 µg L^{-1} in the groundwaters, and exceptionally high Cr contents in water samples

from Walajapet. Chromium concentrations of >500 µg Cr L^{-1} in the groundwater sampled at 10 m depth inside the Palar River (Ambur, site 2) and >950 µg Cr L^{-1} in groundwater sampled from a borewell located approximately 2 km away from the effluent outlet of a closed tannery at Walajapet (site 1) clearly indicate the extent of Cr pollution in groundwater. The most worrying feature about this contamination is that these borewell waters are currently in use for potable purposes. Given that many of these villages do not have any other source of potable water, continued consumption of Cr-contaminated water can pose risks to both animals and humans living in these districts.

It was surprising to note that 33–97% of the Cr in groundwaters was in the form of toxic Cr(VI) in concentrations of 48–922 µg L^{-1} (Fig. 1 and Table 1). If site 1 at Ambur is excluded, 89–96% of total Cr occurred as Cr(VI). Chromium(VI) was not detected in the borewell water samples from the uncontaminated site (Vinnamuthi). These results presumably indicate that Cr(III) is being oxidised to Cr(VI) in the soil, and that the soluble Cr(VI) is subsequently moving into groundwater.

The Cr concentration in groundwaters was much higher than the normal average background value of 4–7 µg Cr L^{-1} reported in various parts of India (Handa 1978). A high Cr content in groundwater has been reported by several workers. Davids and

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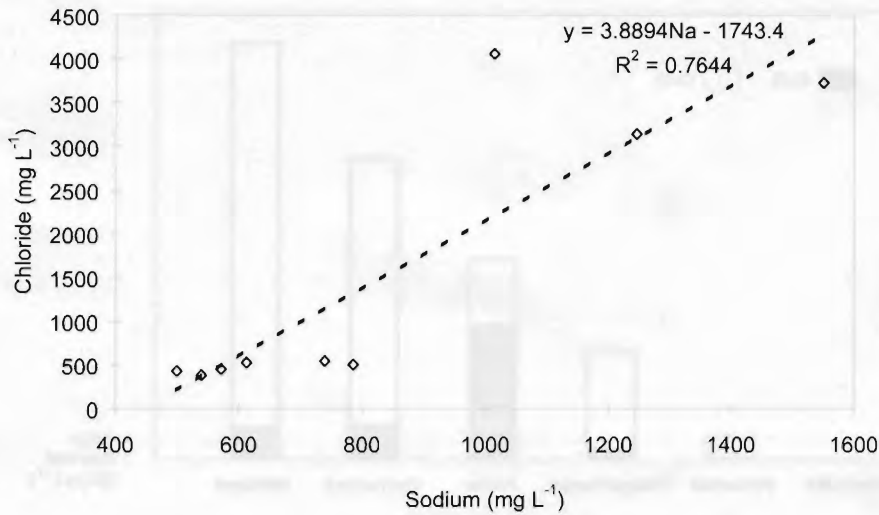
Figure 2. Relationship between Na$^+$ and Cl$^-$ in the piezometer water samples

Lieber (1951) reported an average of 450 μg L^{-1} in groundwater. Förstner and Wittman (1983) reported a mean value of >10 000 μg Cr L^{-1} in groundwater of Tokyo. They suggested that 0.5 μg Cr L^{-1} was the background content of Cr in surface water. Drinking water standards have been set at 50 μg total Cr L^{-1}, because of the toxic effect of Cr(VI) and the possibility that Cr(III) will oxidise to toxic Cr(VI) (USEPA 1976). The Cr content in groundwaters examined in our study also exceeded the maximum permissible limit of the

Australian National Health and Medical Research Council (NHMRC).

Mobility of Cr

At the first sampling of the piezometer nest around Vaniyambadi (after approximately 140 mm of rain) the piezowaters (150–210 cm depth) of the contaminated site had a Cr concentration of only 67 μg L^{-1}, which increased to >100 μg L^{-1} during subsequent sampling (Table 2). Throughout the sampling period, the Cr was below the detectable

Table 2. Salt and Cr content in piezowaters (depth 1.5 m to 2.0 m) around Vaniyambadi

	pH	EC (dS m^{-1})	Na (mg L^{-1})	Cl (mg L^{-1})	Total Cr (μg L^{-1})
			First sampling		
Piezometer 1 (uncontaminated site)	7.89	3.42	786	497	trace
Piezometer 2 (contaminated site)	7.60	21.60	1246	3141	67
Piezometer 3 (2 km away from contaminated site)	7.57	2.58	540	375	trace
			Second sampling		
Piezometer 1 (uncontaminated site)	7.95	3.56	613	518	trace
Piezometer 2 (contaminated site)	8.01	27.9	1014	4057	112
Piezometer 3 (2 km away from contaminated site)	7.68	2.91	500	423	trace
			Third sampling		
Piezometer 1 (uncontaminated site)	8.23	3.70	740	538	trace
Piezometer 2 (contaminated site)	8.18	25.6	1550	3723	106
Piezometer 3 (2 km away from contaminated site)	8.01	3.06	572	445	trace
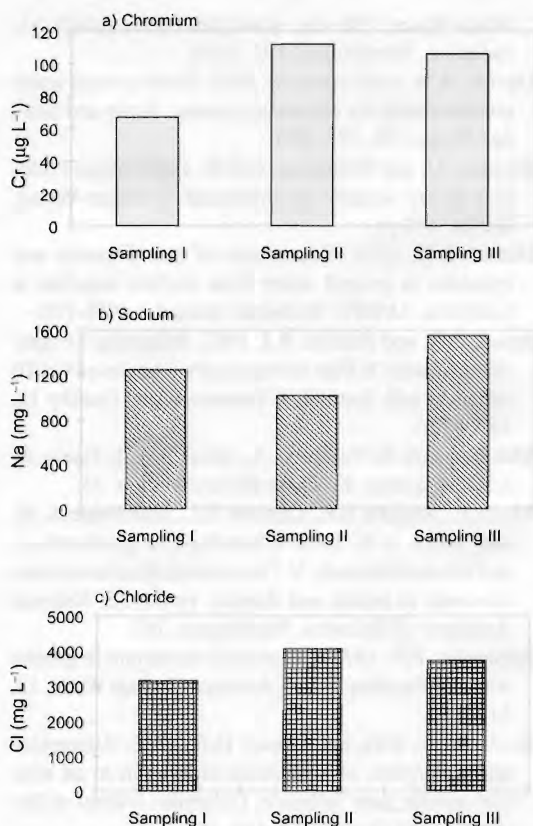
Figure 3. Concentrations of Cr, Na and Cl in piezowater samples (at 1.5 to 2.0 m depth) from contaminated sites

limit in the piezowaters of uncontaminated sites. The Cl concentration followed a trend similar to that of Cr in waters of the contaminated site, but the Na behaved differently. However, when all the results were pooled together, a close relationship ($R^2 = 0.874$) was obtained between Cl and Na in piezowaters (Fig. 2). While the concentration of Na decreased at the second sampling it increased at the third sampling in all the piezowaters. A marked increase in the Cl content (from 3141 to 4057 mg L^{-1}) was observed at the second sampling, but it decreased slightly at third sampling (Fig. 3); this pattern was also reflected in EC values.

The pH varied from 7.57 to 8.23 and increased in all the piezowaters from all the sites (Table 2). The EC, as a measure of total soluble salts, ranged from 2.58 to 27.9 dS m^{-1} and the highest values were observed in piezowaters of contaminated sites at all sampling times (Table 2).

The increase in the concentration of Cr as well as salts (Na and Cl) in piezowaters, with a corresponding increase in EC, suggests that the Cr and salts originated from the disposal of tannery effluent and sludge onto soil. The presence of Cr in piezowaters showed evidence that Cr, which is often regarded as immobile, can leach in these soil environments. The lower Cr concentrations at the first sampling may be attributed to dilution effects resulting from higher rainfall and infiltration of a large volume of water. Another reason could be the transfer of Cr from soil water to soil colloid particles by adsorption processes.

Adsorption was found to be an important mechanism for removing Cr(VI) from solution (Stollenwerk and Grove 1985). However, the increase at second sampling could be attributed to leaching of Cr from contaminated soil.

The soils at different sampling sites are mostly sandy loam to sandy clay loam with saline and alkaline conditions. The presence of Cr in groundwater depends on its solubility and its tendency to be adsorbed by soil or aquifers. The Cr species most frequently found in groundwater studies elsewhere include chromate (CrO_4^{2-}) and cationic hydroxo complexes such as $Cr(OH)^{2+}$, depending upon the pH and Eh (Robertson 1975). In the tanning industry, Cr(III) is the species that is mainly used during the tanning process. In the soil environment, which consists of minerals and organic matter, many previous studies have shown rapid transformation of Cr(VI) to Cr(III) (e.g. James and Bartlett 1983). Therefore the presence of Cr(VI) in borehole waters is surprising and raises questions about potential mechanisms that can enhance transition of the Cr(III) added to soils in the tannery wastes to Cr(VI) in groundwaters. The water sampled in such locations had microbial activity suggesting that microbial oxidation–reduction systems might have favoured the conversion. However, the particular type of organism involved remains to be discovered.

Conclusion

Disposal of tannery effluent and sludge onto land has resulted in severe contamination of soil and deterioration of the quality of groundwater. In Vellore district, the groundwaters examined had high concentrations of Cr and salts (Na and Cl). In the majority of water samples the Cr concentration exceeded the maximum permissible

limit ($50 \mu g L^{-1}$). More than 89% of the Cr in most of the borewell waters was in toxic hexavalent state, Cr(VI), which suggests that transformation of Cr(III) to Cr(VI) has occurred in these soil environments and resulted in the leaching of Cr(VI) which has contaminated the groundwater. The Cr concentration was below the detectable limit in groundwaters collected from piezometers installed at uncontaminated sites. However, substantial levels of Cr were detected in piezo-waters of contaminated sites and they tended to increase during subsequent sampling. Sodium and chloride concentrations also increased. This suggests that with continuous leaching the Cr and salts had moved down the soil profile and contaminated the groundwater. The results also demonstrate that Cr is highly mobile in contaminated soils around tanneries.

Acknowledgment

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Leaching of Chromium from Soils Heavily Contaminated with Tannery Wastes

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Abstract

Monolithic cores, 300 mm diameter and ≤1 m long, from highly contaminated soils at an old tannery waste disposal site, were equipped to study the factors that control chromium (Cr) chemistry and movement in soils. Since Cr can occur as Cr(III) and Cr(VI), mini-electrodes were installed to monitor in situ changes in redox potential. Moisture probes were installed to trace changes in the moisture potential during leaching, and pH was measured as well. At regular intervals, the soil solution was sampled using fibreglass wick samplers installed at several depths in the core. The leachate samples obtained from the wick samplers showed that the pH in the soil monolith decreased from ~8 in the surface soils to ~4 at depths exceeding 40 cm. A similar trend in soluble Cr was recorded in the leachate samples, with values exceeding 1 mg L^{-1} in the surface 10 cm and <0.1 mg L^{-1} at depths exceeding 40 cm. However, Cr was not detected in the solution leaching out of the 1 m long columns. This indicates that Cr that is mobilised in the surface soil layers is rendered immobile towards the deeper end of the profile. In addition to the changes in pH and Cr, fluctuations in Eh and soluble salts were observed in this study, indicating marked changes in soil solution chemistry with increasing depth of the soil profile.

Sources of chromium in the soil environment include wastes from industrial activities such as electroplating, electric power production, the leather and pulp industry, and ore and petroleum refining. These industries generate waste products that contain solid and aqueous forms of chromium (Cr) (Förstner and Wittman 1981). Extensive contamination of soils and groundwater has occurred in many instances due to indiscriminate and unchecked waste disposal on land in a lax regulatory environment prior to the 1970s. After the introduction of legislation in the late 1970s and '80s, landfills became the repositories of such wastes. However, disposal of wastes in landfills can also lead to potential release of Cr(VI) species to surface and subsurface waters. Since Cr(VI) is both toxic and mutagenic (Adriano 1986), it is

imperative that the release behaviour of Cr is properly understood and that techniques are developed for remediating Cr-contaminated water and soils.

In soil, Cr exists in anionic and cationic states, and the nature of the species may vary with changes in the soil environmental conditions, such as fluctuations in soil moisture levels, pH, redox potential, etc. Of the two species, Cr(VI) is of concern because of its high mobility and toxicity. The hexavalent Cr species, being anionic in nature (i.e. $HCrO_4^-$ and CrO_4^{2-}), is generally mobile in neutral to alkaline systems. In acidic conditions, Cr(VI) may be removed from the solution phase either by adsorption involving positively charged sites on oxidic surfaces (Bartlett and James 1988) or by reduction to Cr(III). Trivalent Cr reacts like cationic heavy metals, i.e. it forms complexes with humic matter, is involved in cation exchange on humic acids or clay minerals, and forms hydroxy

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compounds by hydrolysis. Although many studies have been conducted on the behaviour of Cr in the aquatic environment (James and Bartlett 1983a,b,c; Stollenwerk and Grove 1985; Richard and Bourg 1991; Anderson et al. 1994) limited effort has been directed towards studies of the transport behaviour of Cr at heavily contaminated sites.

The objectives of this study were (i) to understand the release and migration behaviour of Cr under flow conditions in intact cores of a soil historically contaminated with leather tannery wastes, (ii) to determine the nature of transformations occurring in the soil profile during the transport of chromium, and (iii) to investigate the transport of other salts from the contaminated soil.

Materials and Methods

Collection and preparation of intact soil monoliths or cores

Eight large intact cores (300 mm internal diameter and up to 1 m long) were collected in November 1996, using a drilling rig mounted at the back of a truck. The time of drilling was chosen so that the soil was neither too wet (because on drying it could shrink inside the column) nor so dry that pushing the barrel into soil would become impossible. The coring rig used here consisted of a barrel fitted with a cutting edge, into which a sleeve could be inserted. The corer cut into the soil in a spiral action and an intact soil monolith moved up into the PVC sleeve. The rig was pushed to the desired depth and lifted out. The two ends of the column were capped and the monolith was taken to the laboratory. Cores ranged from 50 cm to 100 cm in length.

Four intact cores were prepared in the laboratory for transport studies. The empty section of each column was cut to leave PVC edges high enough to accommodate a specially-made solution delivery head (described below). The surfaces at the bottoms of cores were uneven, simply due to shearing and lifting off the core from the profile, and required smoothing. This was done with the utmost care to avoid any smearing of soil and thus any effect on the flow properties of the core. The soil from the bottom of each core was chipped off to obtain a reasonably smooth surface leaving about a 5 cm collar of empty column. This space was filled with a layer of acid-washed sand to facilitate the flow. The sand was held by a nylon

cloth often termed 'shade cloth' glued to the bottom of each column. The column was finally capped and a hole in the middle of the cap was fitted with a funnel leading to the leachate collection bottle (see Fig. 1). One of the main concerns about use of intact cores is that there may be wall effects and the possibility of solution running along the core walls and bypassing the soil matrix. To avoid any preferential flow along the walls of the core, about 1 cm width of soil was dug out to a depth of about 2 cm all round the core at the column wall and filled with vaseline.

Installation of fibreglass wicks as sampling ports

One of the objectives of the transport studies was to assess the movement and transformation of Cr throughout the depth of the soil column. Therefore ports were needed through which samples could be withdrawn at various points in each column. Porous ceramic cups are commonly used as lysimeters to extract solutions from soil profiles. However, the ceramic is known to show high adsorption for several inorganic ions. Significant adsorption of heavy metals including Cr by ceramic cups has been reported. For example in a recent study, Wenzel et al. (1997) observed that ceramic cups almost completely removed Pb, Cr, Cu and As at pH 4, 5 and 6. Therefore in the present study we tried fibreglass wick samplers. The braided wicks were obtained locally, acid washed and tested for Cr retention. A very small amount of Cr(III) retention was noted in the fibreglass wick, as shown later. The wicks were then quenched with phosphate ions and washed again. The wicks were found to have a negligible retention of Cr following this treatment.

The conditioned wicks were cut and inserted into 10 cm long plastic tubes, so that about 1 cm of wick protruded. The tubes were prepared so that about 5 cm of tube could be inserted into the soil column. The tube section to be embedded in soil was split in such a way that the top of the wick was in contact with soil but the lower half had a plastic lip preventing contact with the soil solution below that point. Holes of about the diameter of the tube were drilled 5 cm into each column at 10, 25, 40, 55 and 70 cm depths. The tubes fitted with wicks were then inserted into the holes and sealed with silicone sealant. The ends of the tubes were capped with rubber stoppers.

Probes for measuring redox potential and moisture content

Probes were installed for the measurement of redox potential and moisture contents at several depths in the columns. The redox potential was measured relative to hydrogen electrode potential (Eh) using polished platinum electrodes. The electrodes were calibrated against ZoBell (1946) solution — 0.1M KCl containing 3.33mM $K_4Fe(CN)_6$ and 3.33mM $K_3Fe(CN)_6$ — in the temperature range 25–62°C. The emf readings were recorded on-line with a multimeter fitted to a multi-channel chart recorder. The platinum electrodes were prepared in the laboratory.

The moisture content of the soil column was measured periodically using time domain reflectometry (TDR). Three-pronged probes, each prong 20 cm long, were calibrated against known moisture content and inserted sideways at 12, 27, 42, 57 and 72 cm depths.

Leaching solution delivery system

The leaching solution was fed to the column through a specially-designed delivery head fitted with hundreds of hypodermic syringes and needles to cover the entire cross-sectional area of the column. The flow through the needles was controlled via a peristaltic pump connected to an airtight reservoir on top of the array of needles. Therefore the leaching solution was introduced into the soil in the form of raindrops. To avoid evaporation from the surface of the core, a layer of plastic beads was spread on the soil.

Tracer studies

To characterise the flow properties of the soil monoliths, we carried out tracer studies using bromide (100 mg L^{-1}) solutions. The studies provided valuable insight into the water transmission characteristics of the column, which is essential if any inferences are to be drawn about the transport of reactive solutes from the core.

Treatments imposed during leaching studies

To simulate realistic conditions as closely as practically feasible, we applied the leaching solutions through the aforementioned solution delivery system. In addition, since the rainfall events are often episodic in nature, we provided leaching events intermittently to simulate wetting and drying cycles. This allowed us to assess the
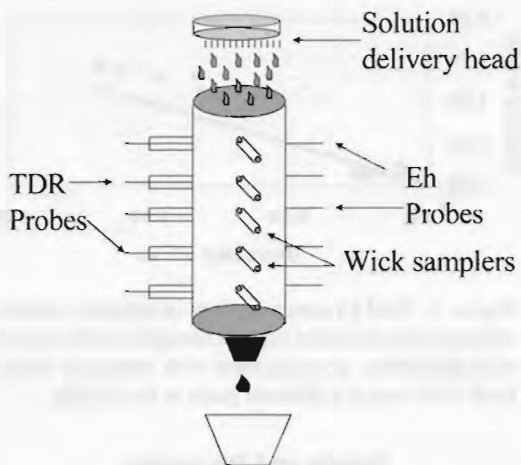
Figure 1. Schematic diagram of a soil monolith and the instrumentation used in the transport study

leaching of Cr and salts available in leaching solutions as well as the potential for Cr(VI) release during the no-flow periods.

Measurements and analysis

Samples of leachates from the cores were obtained through the wick samplers as well as at the bottom of the core. The samples were obtained by applying a small amount of suction with the help of hand-held hypodermic syringes and needles inserted through the bungs. To obtain several samples simultaneously, we also designed a manifold vacuum system for all ports, connected to a suction pump. The vacuum for each line was controlled by a regulator to ensure that the solution from the wick samplers was obtained drop by drop. The total drainage and solution input into the columns were recorded.

The leachate samples obtained were subjected to several analyses. The pH, EC and Cr(VI) were immediately analysed and the solution was then stored at -14°C for multi-element analysis with inductively coupled plasma emission spectrometry. Eh was measured on-line at several points in the column, as discussed above. Moisture was monitored frequently, through TDR probes.

Total Cr in soil solution was measured by flame atomic absorption spectrophotometer and Cr(VI) was analysed using a colorimeteric method based on diphenyl carbazide.
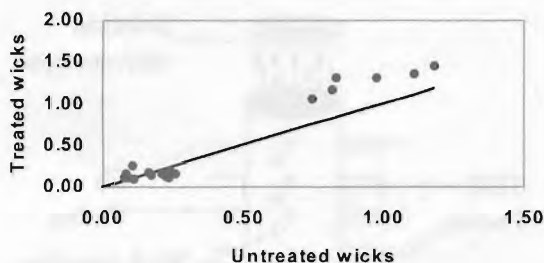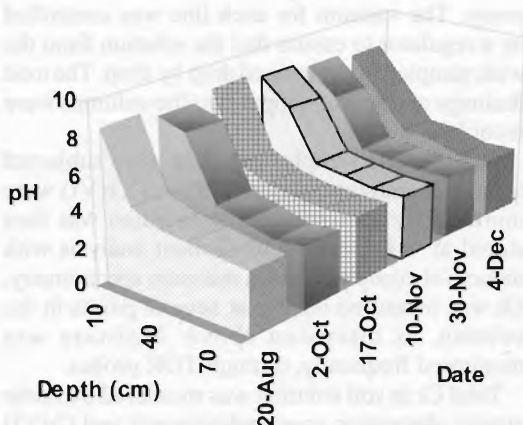
Figure 2. Total Cr concentrations in solution samples obtained from the intact core via fibreglass wicks treated with phosphate, in comparison with untreated wicks. Each wick was at a different point in the column.
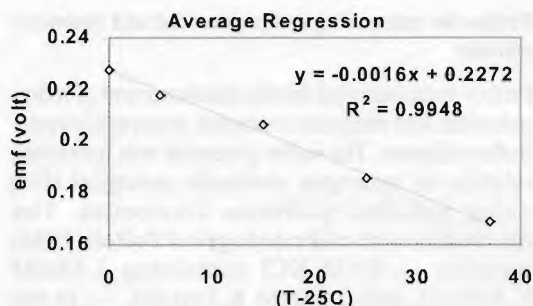
Results and Discussion

Conditioning of fibreglass wick

Before installation of fibreglass wicks as sampling ports the retention capacity of wicks for Cr was measured. It was observed that wicks had a tendency to take up a small amount of Cr(III) but not Cr(VI). It was found that if the fibreglass wicks were soaked overnight in a phosphate solution followed by acid washing, the retention of Cr was negligible. Therefore a study was carried out to assess the differences in total Cr concentrations in solutions obtained through phosphate treated and untreated wick samplers (Fig. 2). In Figure 2, the solid line represents 1:1. Treated samplers gave a slightly higher concentration of Cr than untreated samplers. However, it must be recognised that the wick samplers were obtaining samples from

Figure 4. The regression between temperature and emf (mean of 11 electrodes) measured in ZoBell's solution using Eh electrodes manufactured in laboratory

different points in the column and therefore there was possibly variability between concentrations. The good correlation between the two sets of measurements supports the reliability of the technique. Based on these data, only the treated wicks were used.

pH of soil solution at different depths

The leachate samples taken at the wick samplers showed that pH in the soil monoliths decreased markedly with depth in the profile (Fig. 3). While the pH in the surface layers of the soil (0–40 cm) was high, the profile below 40 cm depth was extremely acidic (pH < 4). The acidity in the subsurface layers of the soil had a major effect on the movement of Cr and other elements through the soil profile, as discussed later.

Figure 3. The measured pH values of the solution samples obtained at various depths during the leaching study
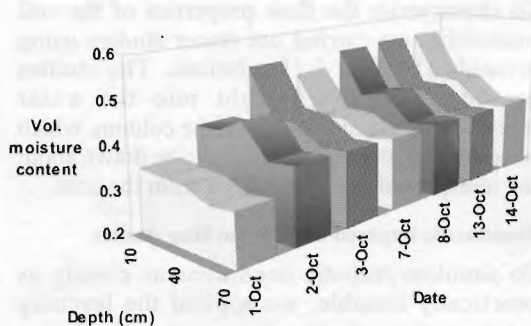
Figure 5. An example of moisture profiles in the column, as measured by the TDR probes shown in Fig. 1, from the start of leaching on 1 October in a relatively dry column
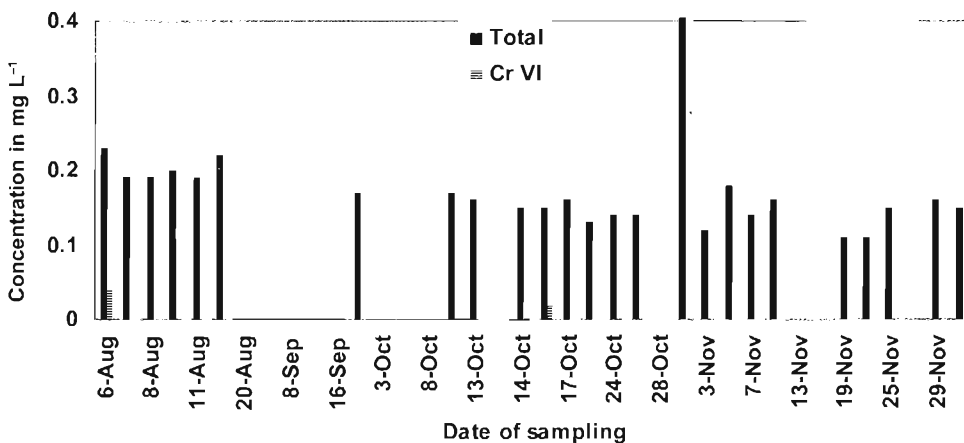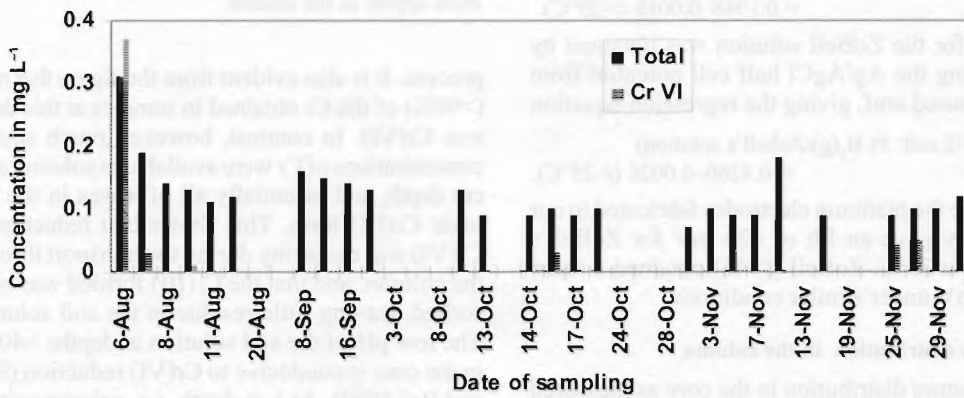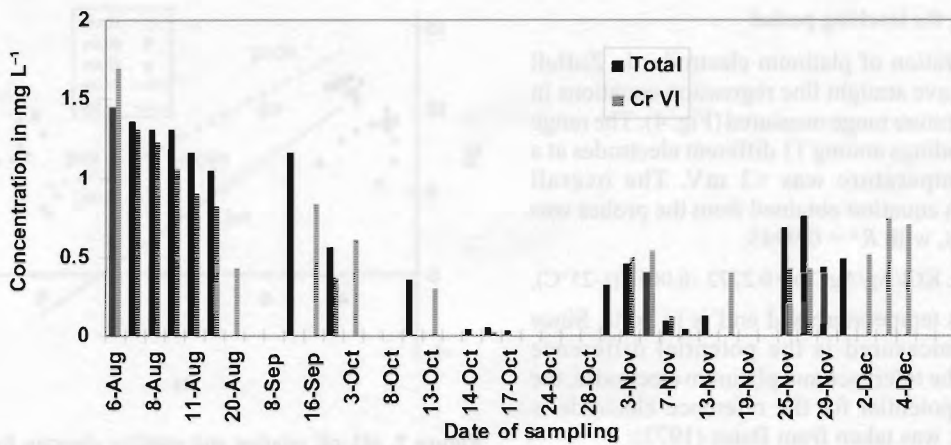
Figure 6. A time series of total Cr and Cr(VI) concentrations (mg L⁻¹) in the intact core at 10 cm depth (top graph), 40 cm depth (middle graph) and at column exit 100 cm (bottom graph)

Eh during the leaching period

The calibration of platinum electrodes in ZoBell solution gave straight line regression equations in the temperature range measured (Fig. 4). The range of emf readings among 11 different electrodes at a given temperature was <3 mV. The overall regression equation obtained from the probes was as follows, with $R^2 = 0.9948$:

$$emf(Pt/sat. KCl/Ag/AgCl) = 0.2272 - 0.0016 (t-25°C),$$

where t is temperature and emf is in volts. Since the emf measured is the potential difference between the reference and platinum electrodes, the half-cell potential for the reference electrode is needed. It was taken from Bates (1973):

$$emf (Pt, H_2(g)/sat.KCl/Ag/AgCl) = 0.1988 - 0.0010 (t-25°C).$$

The Eh for the ZoBell solution was obtained by subtracting the Ag/AgCl half cell potential from the measured emf, giving the regression equation

$$emf (1/2 cell: Pt H_2(g)/Zobell's solution) = 0.4260 - 0.0026 (t-25°C).$$

Therefore the platinum electrodes fabricated in our laboratory gave an Eh of 426 mV for ZoBell's solution at 25°C. ZoBell (1946) obtained a value of 430 mV under similar conditions.

Moisture distribution in the column

The moisture distribution in the core as measured with TDR probes (Fig. 5) shows that the flow through the deeper layers (>40 cm depth) was relatively slower than through the profile layers above, and hence there was accumulation of water at a depth of about 40 cm. This is consistent with the field observations that the surface materials, at 0–30 cm or so appeared to be aggregated— possibly deposited during the former effluent disposal period. This layer supported rapid transport of water. The layers below about 30 cm consisted of sticky clay.

Movement of chromium through the soil column

Total Cr versus Cr(VI)

The concentrations of Cr obtained at 10 cm, 40 cm and 1 m depth (at the exit) of the column are shown in Fig. 6 for total Cr and Cr(VI). The figure shows that fairly high concentrations of Cr (>1 mg L^{-1}) were available in the solution phase at 10 cm depth, especially in the initial parts of the leaching
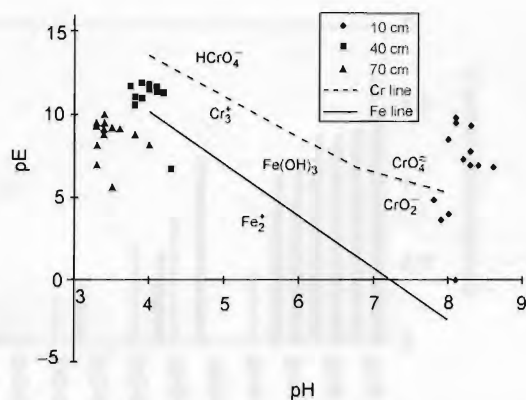
Figure 7. pH–pE relation and stability diagram for Cr and Fe; data points are observed values of pE and pH at three depths in the column

process. It is also evident from the figure that most (>90%) of the Cr obtained in samples at this depth was Cr(VI). In contrast, however, much smaller concentrations of Cr were available in solution at 40 cm depth, and essentially all of it was in the less toxic Cr(III) form. This shows that reduction of Cr(VI) was occurring during the transport through the column, and that the Cr(III) formed was more sorbed, leaving little residue in the soil solution. The low pH of the soil solution at depths >40 cm in the core is conducive to Cr(VI) reduction (Eary and Rai 1989). At 1 m depth, i.e. column exit, Cr was still being leached out of the system, but the total Cr concentrations were about the same as at 40 cm depth and consisted of Cr(III) species, because Cr(VI) was not detected in the solution leaching out of the column exit.

pH–pE conditions in the intact core profile

Figure 7 shows the redox potential plotted against pH at various depths in the column. For reference, the stability lines between oxidised and reduced species for Cr and Fe redox couples are provided in the figure. It is evident that in the surface layer of the profile, the conditions were favourable for the stability of the oxidised form of Cr, whereas in the subsurface layers the converse was true. Soil pH distribution in the soil profile had the main influence on the nature of Cr speciation. This explains why the Cr(VI) mobilised from the surface layers of the profile did not appear in solutions obtained from depths greater than 40 cm. It is

Table 1. The average concentrations in mg L^{-1} of elements present in soil water at different depths in the columns during leaching from August to November 1997

Depth (cm)	Cu	Fe	Mn	P	Zn
10	0.01±0.04	BDL	BDL	0.4±0.70	0.08±0.06
25	BDL	BDL	BDL	1.05±1.8	0.23±0.12
40	0.08±0.07	BDL	BDL	0.66±0.81	0.36±0.19
55	0.19±0.08	BDL	BDL	0.69±0.9	0.28±0.21
70	0.23±0.10	0.30±0.35	BDL	1.28±1.41	0.48±0.21
100	0.34±0.04	BDL	0.14±0.14	0.99±0.67	0.33±0.12

BDL = below detection limit

highly likely that Cr(VI) anions were reduced either by organic matter or by ferrous iron to the Cr(III) cation at lower pH in the subsurface. This has been observed by several other workers (Eary and Rai 1991; Weng et al. 1996). At low pH Cr(III) sorption is likely to be small, so Cr(III) leached out of the column.

Effect of wetting and drying cycles on Cr(VI) movement

It was observed that, with continuous leaching , Cr(VI) concentration progressively decreased with time (Fig. 6a). For example, after the start of leaching, in the first week of August, the Cr concentration progressively decreased. However when the column was allowed to dry for a period, the subsequent leaching produced greater

concentrations of Cr in the soil solution. This is evident for leaching periods in early September and early November which coincided with the leaching event following a dry period. This suggests that either the sorbed chromium is being released during the drying phase or that oxidation of chromium is occurring in the drying phase.

Movement of other elements

Due to the very high salinity of the effluent which had been disposed of at the site in the past, the soil was heavily contaminated with salts. The leachate samples from different depths were analysed for Al, B, Ca, Cu, Fe, K, Mg, Mn, Na, P, S and Zn. Some of the elements were present at very low concentrations in solution (Table 1). Others, such as Na, S and Al, were present at very high
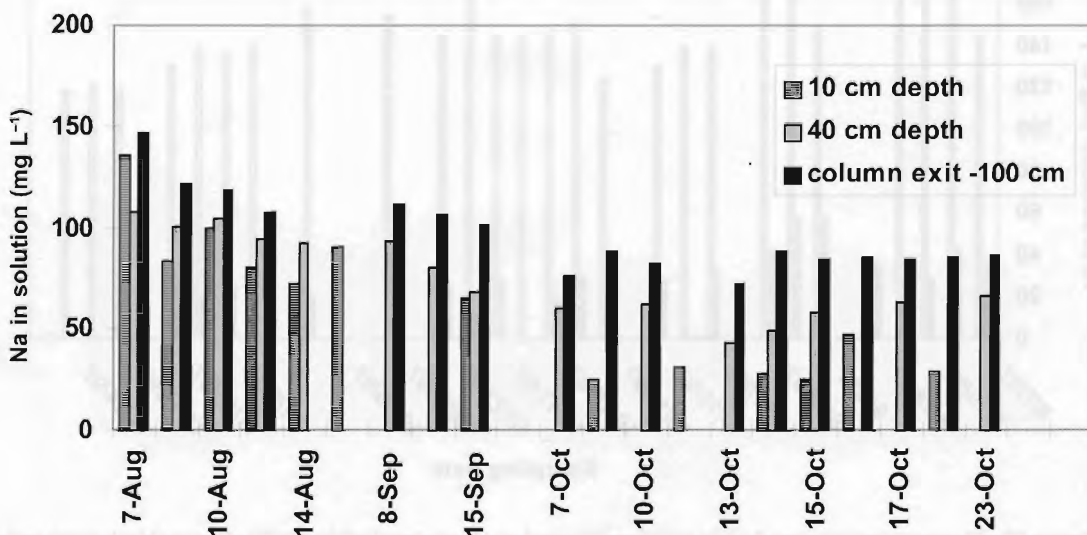
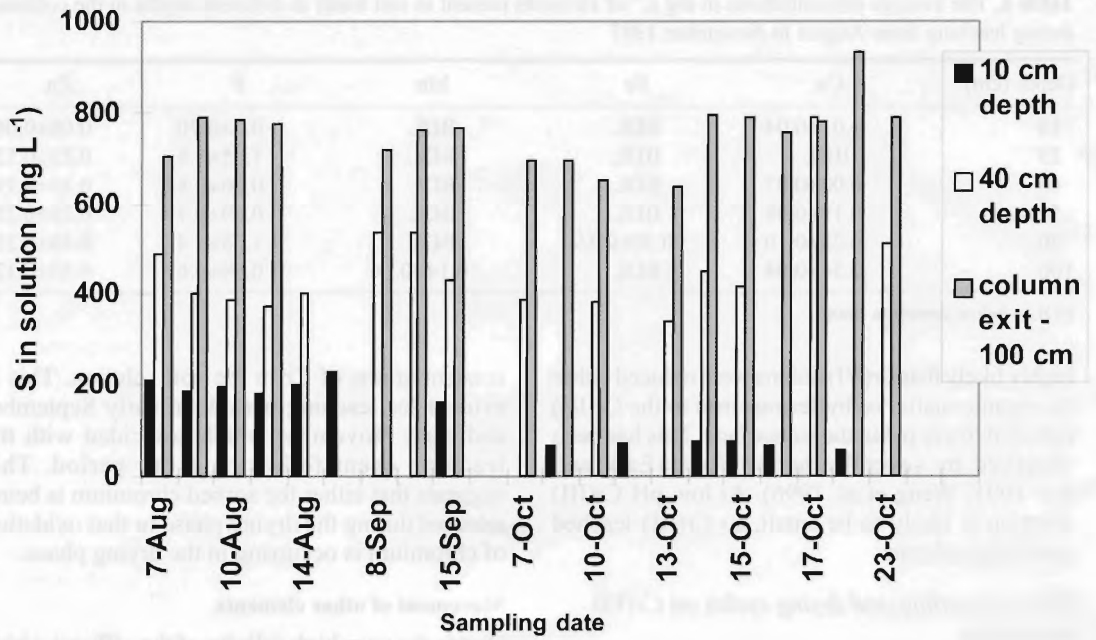**Figure 8.** Na concentrations (mg L^{-1}) in solution obtained at three depths in the core during leaching

Figure 9. S concentrations (mg L^{-1}) in solution obtained at three depths in the core during leaching

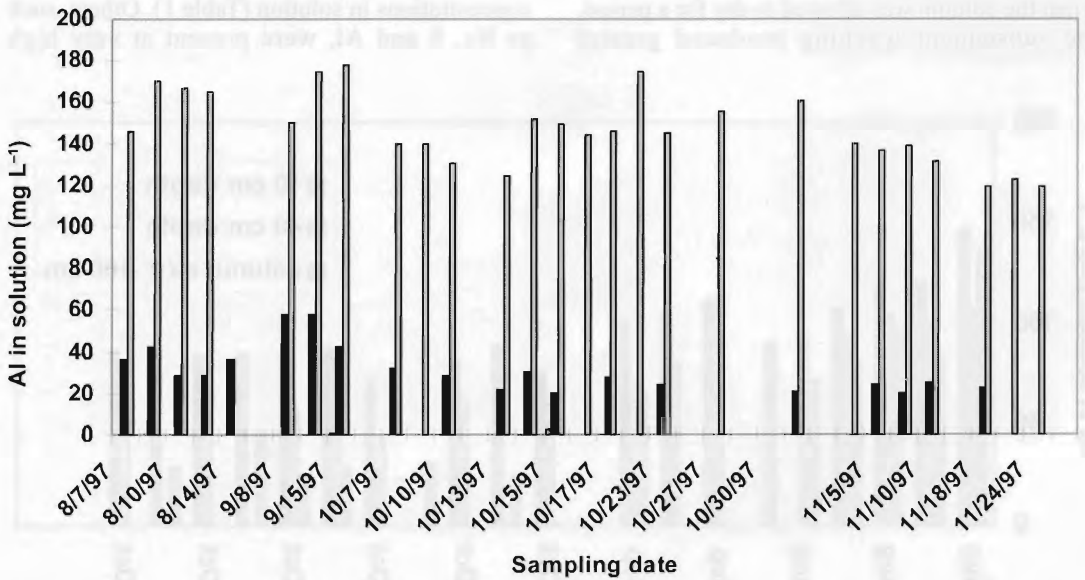**Figure 10.** Al concentrations (mg L^{-1}) in solution obtained at 10 cm (negligibly small), 40 cm (black bars) and 100 cm (grey bars) in the core during leaching

concentrations (Figs 8, 9, 10). Concentrations of Na, S and Al were higher deeper in the column, and this was because of leaching during the last 35 years in the case of mobile elements such as Na and S; but the very low pH (< 4) in the column at depth was responsible for mobilising Al. In soil solutions at 10 cm depth the concentrations of Al were negligible but they were very high at the column exit (Fig. 10). Very high Na, Ca and S concentrations moving through the system (Figs 8 and 9) would be very detrimental to the quality of surface and groundwater at the site studied.

Conclusions

Several conclusions can be drawn from the study.

- High concentrations of Cr(VI), up to 2 mg L^{-1}, are present in the surface 30 cm layer of soil.
- Cr(VI) moving from the surface layers of the profile was reduced to Cr(III) in the subsurface (> 40 cm depth) under highly acidic conditions (pH < 4.5) in the soil profile.
- Cr was mobile through the entire length of core and it was detected in solution at column exit i.e. at 1 m depth. However Cr(III) instead of Cr(VI) dominated in solutions at deeper levels.
- Both the mobile Cr and high concentrations of salts leaching beyond 1 m depth in the profile can seriously affect water quality at the site.

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Biodynamics at Sites Contaminated with Tannery Waste

Impacts of Tannery Wastes on Soil Ecosystems: Preliminary Observations

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Abstract

India is rich in cattle, but the waste from manufacture of leather is a hazard to environmental safety. The skins and hides of the animals are processed for leather through vegetable and chemical tanning. India is a leading leather exporter and also supports several small-scale processing industries. Chrome (Cr) tanning is preferred, but the use of hexavalent chromium, Cr(VI), during processing poses the problem of its release in waste water. Because of this fact, attempts are being made to use trivalent chromium, Cr(III), or to recycle the Cr in tanneries. Long-term use of several chemicals including Cr in tanneries has spoiled the land and water ecosystem. More detailed studies in the Palar River basin provide clues that may circumvent the present difficulties. Attempts are being made to treat the effluent through common effluent treatment plants, using the treated effluent for irrigation, and recycling the sludge for productive purposes. Selective sorption of Cr by a few microbes, plants and animals is known, but a technology to exploit these systems is wanting. The reduction of Cr(VI) to Cr(III) by microbes and their products provides additional possibilities. Attempts to reduce the toxicity of Cr(VI) in land and water are summarised. India has the resources (skin and hides) and the process chemicals (chromium and tannins). It is time to make safer use of these systems, for the sustainable progress of humanity and ecosystem.

TANNERIES have attractive foreign exchange earning potential, but also cause pollution of the agroecosystem. Tanning is a process by which animal hides are converted to leather. The hides and skin, after dehairing and removal of flesh and fat, are treated with chemicals to form stable durable leather material. Once India was a net exporter of raw hides and skin. After the Second World War, necessity compelled the government to set up tanneries to satisfy the local need for leather. In the beginning, vegetable tanning was practised as a cottage industry. As the demand increased, industrialisation and associated improvements in tanning were introduced. At present, in Tamil Nadu alone, there are 1008 small-scale tanneries and 75 large-scale tanneries with

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an employment potential of one million persons; they account for 6% of the world's leather production. Chrome tanning, a widely practised method, uses 276 chemicals including 14 heavy metals. It is estimated that approximately 32 000 t of basic chromium sulfate salts are used annually in Indian tanneries.

Resources for Tanneries

In the conversion of raw hides into finished leather, the industry uses approximately 30 kL water t[-1] raw hide. Water consumption in the tannery starts from the initial removal of the sodium chloride used for temporary preservation. Table 1 shows the projected supply of skins and hides in India for the year 2000, and the expected discharge of effluent from tanneries for that year. Chrome (Cr) tanning will be continued, either as Cr(III) or as Cr(VI) with a recovery system, in association with

Table 1. The numbers of hides and skins expected to be available in India in the year 2000, and anticipated discharge of tannery effluent (from Kotasek 1997)

	Hides or skins supply	Wet salted wt	
		kg piece^{-1}	kg x 10^6
Cattle	27 x 10^6	9.8	288
Buffalo	23 x 10^6	12.0	279
Goat	126 x 10^6	2.3	290
Sheep	42 x 10^6	3.8	161
Total	218 x 10^6	10	17

Average discharge of effluent: 40 L kg^{-1} wet salted weight
Annual discharge: 40 x 10^6 kL approximately

Table 2. Characteristics of the raw and treated tannery effluent

	Before treatment	After treatment
pH	7.0–9.0	6.5–8.5
Total suspended solids (mg L^{-1})	2000–4000	10–10
Total dissolved solids (mg L^{-1})	11000–16000	5000–10000
Chlorides as Cl$^-$ (mg L^{-1})	6000–9500	1600–5000
Sulfates as SO$_4^{2-}$ (mg L^{-1})	2400–4000	800–2000
BOD (mg L^{-1})	2500–8000	150–400
Oils & greases (mg L^{-1})	1.5–4.0	0.2–2.5

traditional vegetable tanning. The concentration of Cr in the discharge effluent ranges from 2000 to 5000 mg L^{-1}. This accounts for an annual loss of nearly 2000 to 3200 t of Cr, which could be recycled instead, to reduce the cost of production. These monetary considerations rather than pollution considerations have forced the industry to accept Cr recovery. Besides the hides and skin available in India, some imported hides are also processed.

Tannery Effluent Characteristics

Tannery waste water is a serious pollutant to the receiving land and water ecosytem. In North India, tanneries located at Agra and Kanpur are the major contributors of the suspended solids and chromium in the Ganga river. Likewise in Tamil Nadu the entire Palar River basin is affected by the tannery discharges from the Vaniyambadi, Walajapet, Pernampet and Ranipet areas. The changeover to chrome tanning from vegetable tanning has resulted in the accumulation of solids and sludges in most of the tanneries, because the presence of Cr and salt has made the sludge unacceptable for land application. The environmental damage to the ecosystem is so visible in the Palar River basin that a systematic scientific study is in progress to quantify the extent of damage to land by tannery effluent. At the same time, action is being taken to install Cr recovery and reuse in the tanneries. In selected locations, vegetable tanning is being brought back. Within the next six months, it is expected that the Cr release to the environment will be to the accepted standard of 2 mg L^{-1} of total Cr or 0.5 mg L^{-1} of Cr(VI), as a result of

combined effluent treatment plants that are being erected in the tannery complexes.

Based on the success of the Ganga Action Plan, treatment facilities are being built and maintained by the joint efforts of tanneries, Central Leather Research Institutes, Pollution Control Boards and the Ministry of Environment. Currently we have achieved a considerable reduction in pollution. However, even though the biological oxygen demand (BOD) and Cr levels are reaching the prescribed standards, the total dissolved solids (TDS) are still very high (Table 2). The effluent still requires additional treatment before being suitable for land disposal or for agricultural use.

Distribution of Chromium in Air, Water and Food

Chromium is widely used in the metallurgical, refractory and chemical industries, for chrome alloys, chrome plating, pigment production, tanning, oxidising agents and corrosion inhibitors and in the textile, ceramic, glass and photographic industries. Orissa is the State that is by far the most important producer of chromite (the principal ore of Cr), accounting for 96% of the country's total production. Karnataka is the second largest producer of chromite. Bihar, Tamil Nadu and Andhra Pradesh together account for less than 1% of India's total output of chromite.

Chromium in air originates from wind erosion of shales, clay and other kinds of soil, mining,

Table 3. Number and percentage of water samples exceeding quality guidelines in Indian states (Krishna Murti and Viswanathan 1991)

	Cd		Cr		Cu		Mn		Pb		Zn	
	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%
Tamil Nadu	5	2.0	5	2.0	0	0	34	13.5	68	27	3	1.2
Kerala	1	19	0	0	0	0	2	3.8	6	7.5	1	1.9
West Bengal	0	0	12	12.5	0	0	28	29.2	61	63.5	0	0
Orissa	0	0	0	0	0	0	2	12.5	14	87	5	0
Uttar Pradesh	4	2.7	7	4.7	1	0.7	14	9.3	98	65.3	1	0.7
Bihar	9	9.0	3	3	0	0	41	41	56	56	0	0
Gujarat	11	7.3	6	4.0	0	0	17	11.3	33	21.8	0	0
Rajasthan	8	7.1	7	6.2	0	0	10	88	7	6.2	0	0
Chandigarh	15	22.7	2	3.0	0	0	7	10.6	3	4.5	0	0
Him. Pradesh	20	37.7	7	13.2	0	0	2	3.8	10	18.9	0	0
Haryana	43	2.4	10	12.2	0	0	4	4.9	5	6.1	1	1.2
Punjab	49	63.6	4	5.2	0	0	~4	5.2	17	22.1	1	1.3
Andhra Pradesh	1	1.2	3	3.5	0	0	9	10.5	6	7.0	2	3
Karnataka	0	0	0	0	1	1.7	6	10.5	3	5.3	1	1.7

forest fires and volcanic eruptions. Human-induced sources include all types of combustions and emissions by the Cr industry. Mean concentrations in towns are typically about 0.02 µg m^{-3}. In heavily industrialised areas, readings 20 times this value have been recorded, particularly near coal-fired power plants, cement plants, iron and steel industries and municipal incinerators. Ferrochromium plants have the highest emission rates. In Punjab, all samples analysed contained measurable Cr, above the detectable limits. In 10–20% of the samples from Uttar Pradesh (UP), Rajasthan, Chandigarh, Himachal Pradesh (HP) and Karnataka, and in less than 10% of the samples collected from the rest of the states, Cr could be detected but not measured. In drinking water samples collected from Orissa, Cr was not detected by the sensitive method of DC plasma spectrometer. In Chandigarh, HP and Haryana, in one or two samples Cr concentrations were below the detectable limit. In Tamil Nadu, Kerala, and West Bengal, Cr concentrations were below the detectable limit in 40–80% of the samples. In the other states, Cr concentrations were below the detectable limit in 10–30% of the samples.

The highest concentrations observed were in samples collected in Gujarat urban area in summer (5 µg mL^{-1}). In Kerala and Karnataka, the maximum concentrations were around 0.02 µg mL^{-1}.

In West Bengal and Punjab, 1.2 and 1.6 µg mL^{-1}, respectively, were the highest concentrations observed. In other states, concentrations between 0.1 and 0.5 µg mL^{-1} were the maximum observed. The actual numbers and percentages of water samples exceeding the guidelines are given in Table 3. In West Bengal, HP and Haryana 12–13% of the samples exceeded the guideline values, while in other states less than 6% exceeded the guideline values. The Cr content of all the water samples collected in Kerala and Karnataka was within the World Health Organization guideline value.

Chromium was detected in food in almost all the samples analysed. In Haryana, Punjab and Chandigarh the maximum concentration observed was between 105 and 140 µg g^{-1} dry weight. In Tamil Nadu, West Bengal, UP, Bihar and HP the maximum individual concentration was between 10 and 22 µg g^{-1} while in the rest of the states it was less than 10 µg g^{-1}. The Cr contents of vegetarian and non-vegetarian types of food in West Bengal and Orissa did not show any significant difference (Table 4). The mean levels of Cr in food constituents in several states are given in Table 5 (Krishna Murti and Viswanathan 1991).

Pollution and Toxicity Due to Chromium

Chromium is a potential contaminant of soil, surface water, groundwater, sediment and air. High

Table 4. Mean Cr concentrations in air, water and food constituents ($\mu g\ g^{-1}$ dry weight) (Krishna Murti and Viswanathan 1991)

		Range
Tamil Nadu	Air	0.002–0.09
	Water	0.22 –0.98
	Food	0.14 –11.86
Kerala	Air	0.003–0.07
	Water	0.007–0.02
	Food	0.058–9.7
West Bengal	Air	0.002–0.83
	Water	0.010–1.12
	Vegetable	0.030–14.98
	Non-vegetable	0.080–17.50
Orissa	Air	0.007–0.67
	Water	0.018–1.64
	Vegetable	2.130–8.83
	Non-vegetable	5.550–8.75
Uttar Pradesh	Air	0.002–0.99
	Water	0.002–0.24
	Food	0.020–22.34
Bihar	Air	0.005–0.68
	Water	0.002–0.09
	Food	0.190–13.8

Table 5. Mean Cr concentrations in food types ($\mu g\ g^{-1}$ dry weight) (Krishna Murthi and Viswanathan 1991)

States	Cereals	Pulses	Leafy vegetables	Non-leafy vegetables
Tamil Nadu	0.23	–	14.84	2.73
Kerala	2.00	–	17.69	5.47
West Bengal	5.83	3.34	9.57	4.95
Orissa	<DL	<DL	0.36	0.55
Uttar Pradesh	0.14	0.33	0.41	0.17
Bihar	0.21	0.30	0.33	0.24
Gujarat	0.50	0.79	5.65	0.67
Rajasthan	0.26	0.46	12.97	2.07
Chandigarh	0.52	0.77	4.48	1.75
Him. Pradesh	1.68	1.58	10.14	3.53
Haryana	1.07	1.34	5.38	2.85
Punjab	0.59	0.90	9.28	2.62
And. Pradesh	0.16	0.40	4.27	4.03
Karnataka	0.18	0.22	14.43	5.13

<DL = less than detectable level; – not determined

soil Cr is usually associated with human-induced contamination, mainly from industrial operations such as tanning (Thangavel et al. 1997) and direct disposal of sludge and waste water for land application. Chromium's toxicity and mobility depend on its oxidation state. The trivalent form, Cr(III), is relatively immobile, more stable and lower in toxicity than the hexavalent form, Cr(VI). It forms a large number of relatively kinetically inert complexes, mostly amines. Chromium is not a significant contaminant of plant tissues, except at site-specific discharge points. Oxidation of Cr(III) to Cr(VI) by abiotic means, mainly by Mn oxides and dissolved oxygen, is known. Biological reduction of Cr(VI) to Cr(III) is common in soils but biological oxidation of Cr(III) to Cr(VI) is unknown. High concentrations of Cr(VI) are the result of man-made pollution. Hexavalent Cr is a highly soluble, toxic carcinogen. On the other hand, a more positive feature is that the mid-point potential of the Cr(VI)–Cr(III) couple (approximately 1.3 V) indicates that the known physiological electron donors for microbial metabolism also can potentially serve as electron donors for the reduction of Cr(VI) to stable Cr(III).

Athalya et al. (1995) reported that chelation can reduce toxic Cr to Cr(III) and can increase the uptake of Cr by plants. Addition of amendments also influences the transformation of Cr in soil (Das et al. 1991).

Because Cr(VI) is toxic, on-site remediation is aimed at reducing it to Cr(III). Positive reduction and complexing (Ramasamy 1997) are carried out by *Bacteroides* and *Methanosarcina* (by its proteinaceous cell wall and reductase system). As a means of detoxification, *Bacteriodes ovates* is able to convert tannin to an easily settleable brownish black pigmented polymer, with flavenol and indole in the early stages and gallic acid and catechol during later stages as intermediary compounds (Vetriselvan et al. 1990).

Sediment chromium concentrations from fresh-water industrial zone sources generally range up to 50 mg kg^{-1}. Unlike some metals, Cr neither concentrates in specific tissues nor accumulates in fish. As a result, the burden is low in marine and freshwater species. Concentrations in fish tissues are below 0.25 mg kg^{-1}. Under most conditions, mercury, cadmium, copper, lead, nickel, and zinc are more toxic than Cr. Growth inhibition in aquatic plants generally occurs at 0.5–5 mg Cr(VI) while potassium dichromate may

Table 6. Chromium concentration in groundwaters of North Indian locations

Location	Cr ($\mu g\ L^{-1}$)
Varanasi	133
Bhadohi	418
Sunderpur	800
Kanpur	1200
Anwarkanj, UP	27000
Lucknow	550
Barabanki	43
Aligarh	56
Ludhiana	210
Faridabad	31000

stimulate the growth of some species. Abbasi and Soni (1984a,b) have reported that the larvae of amphibian *Rana tignina* and freshwater teleost *Nuria denricus* are affected by Cr in the water. The freshwater prawn *Macrobrachium lamarrei* is also known to be affected by Cr toxicity (Murti et al. 1983). However, little is known about the factors influencing the uptake of Cr by aquatic plants, though Rai et al. (1995) have reported the accumulation of Cr in *Hydrilla verticillata*.

Toxicity to plants depends on the pH of the media and hence on the availability of the free and chelated ions. Other factors such as the presence of organic chelators, cations, nutrients, and other heavy metals in solution influence the toxicity to plants.

Effluent discharges have damaged the biodiversity of the region through stress-induced initial enhancement of reproduction (Abbasi and Soni 1983) in earthworm *Octochaetus pattoni*. Recent studies indicate that the presence of organic matter and Cr-tolerant grasses support the earthworms in the rainy season. However, the earthworm population declines in the dry season, during which period the toxicity is acute because of reduced dilution or wash-off by the rain. Such variations lead to changes in biodiversity and the cropping system. Studies on the nematode population, another dominant faunal component of soil, find an increased population in polluted soils (150–220 per 100 cm^3 soil) compared to normal soils, the dominant species being the plant parasitic *Xiphenema* sp. (Ramasamy 1997).

Chromium is not acutely toxic to humans. This is because of the high stability of natural Cr complexes in abiotic matrices; the acidic nature of Cr imparts strong affinity for oxygen donors rather than sulfur donors present in biomolecules. However, Cr(VI) is more toxic because of its high rate of absorption through intestinal tracts. In contrast to the biomagnification of methyl-mercury and cadmium, Cr is not shown to accumulate and biomagnify, but accumulation of Cr far above the average levels is known, both in the plant kingdom (Prasad and VIjayasarathi 1986; Azeez and Banerjee 1988; Prasad and Raghu 1994; Ramana and Sastry 1994; Misra et al. 1995) and in the animal kingdom (Murthi et al. 1983; Sastri and Sunitha 1984; Balasubramanian et al. 1995). In normal soils with total Cr of 20–100 mg kg^{-1}, the plants grown have less than 1 μg Cr g^{-1} dry weight and seldom exceed 5 μg Cr g^{-1}. Like plants, most invertebrates die before accumulating amounts of Cr that might prove toxic to predators. Among the animals, gastropods are known accumulators of Cr, to concentrations of 140–440 mg Cr kg^{-1} dry weight including shells. For the Indian subcontinent, with 178 million ha of annual renewable water resources, the average Cr content of natural waters is 6 μg Cr L^{-1}. Thermodynamic considerations show that at pH 8 and at slightly lower Eh, the Cr content should be less than 0.5 μg L^{-1}. However, Cr(VI) can occur at much higher concentrations depending on the pH and Eh of the water (Handa 1988).

Chromium in Groundwater

Studies on groundwater occurrence of Cr have been confined to Uttar Pradesh, Rajasthan, Jammu and Kashmir, Punjab, Haryana, Delhi, coastal areas of Saurashtra and Gujarat, and a few samples from Maharashtra and Kerala. Nearly 50% of the dug wells analysed·had <2 μg Cr L^{-1}. Table 6 gives the Cr concentrations in the groundwater of some of the major cities of North India.

Examination of the data clearly indicate that in some areas the groundwater has exceptionally high Cr content compared to the normal average background levels found in different parts of India. The Cr content in such areas does not remain constant but shows considerable variations, apparently depending on the Cr content in the polluting plume and the local hydrogeologic features. Anwarkanj (UP), Kanpur, Sunderpur (Varanasi), Bhadohi (Varanasi), Faridabad — Delhi area, Ludhiana (Punjab) and Lucknow are the areas with high Cr content in groundwater. In

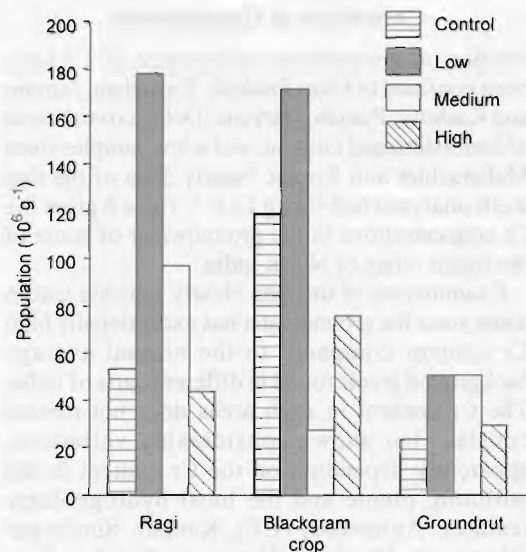**Table 7.** Cr concentration in surface waters

Location	Cr (µg L^{-1})
Ganga, Kanpur	21–23
Gomathi, Gaughat, Lucknow	50–120
Assi drain, Lanka, Varanasi	1300
Lower Ganga canal, Muradnagar	41

Table 8. Distribution of Cr in soil, surface water and groundwater (from Mahimairajah et al. 1997)

Sample	pH	EC (dS m^{-1})	Na (mg L^{-1})	Cr (µg L^{-1})
Raw effluent	6.17	11.4	2280	26200
Treated effluent	8.17	13.4	2040	8800
Soil				
Ambur	7.81	15.5	40698	5728
Vaniyambadi	8.16	5.5	10125	1314
Pernampet	7.70	20.8	29239	16158
Water	7.80	6.0	780	59
Borehole water	8.20	6.9	1600	511
Groundwater				
Ambur	7.40	6.5	1200	178
Walajapet	8.42	1.0	50	996
Vaduganthangal	17.23	11.2	1600	256
Pernampet	7.13	6.5	780	54

general, surface waters contain Cr at concentrations lower than 50 µg L^{-1}. The River Ganga is highly polluted by the nearby industries; the concentration varies from place to place according to the density of the industries (Table 7).

Our attempts to characterise the effluents of tanneries in and around the Palar River basin show that the rate of pollution is higher in underground waters beside surface waters that contain toxic levels of Cr, mostly Cr(VI) (Table 8).

Distribution and Activity of Soil Biota in Polluted Areas

The tannery waste discharged onto the land has its own deleterious effect. The pH and EC and the distributions of Na and Cr in surface and subsurface soils around selected tanneries showed an increase in concentration (Table 8) compared to uncontaminated sites (Mahimairajah et al. 1997).

In all the locations, the Cr content did not show a definite pattern with soil depth but accumulated in soil. In some locations, Cr exceeded 70 000 mg kg^{-1} at depths greater than 70 cm. Salinisation of soil has been shown to have a major impact on the soil macro- and microfauna.

The distribution of aerobic and anaerobic microflora varied depending on the concentration of the prevalent form of Cr. At low concentrations, Cr had a stimulatory effect: here, there were larger populations of bacteria (Fig. 1) and fungi than in soils devoid of Cr. Some of the important bacterial genera include *Pseudomonas, Beijerinckia, Azotobacter* and *Bacillus*. The fungi were *Penicillium* and *Aspergillus*. It was observed that anaerobes were stimulated, like aerobes. As the concentration increased, a decline was observed in the distribution. The predominant bacterium was *Pseudomonas* sp. (Parwin Banu and K. Ramasamy, unpublished observation, 1997).

Microbial reduction of Cr(VI) is attractive for several reasons. Microbes reduce Cr under either aerobic (Gopalan and Veeramani 1994) or anaerobic conditions (Ramasamy 1997). The reason that some microbes have developed a capacity for Cr(VI) reduction has not yet been adequately explained. It has been suggested that
- the reduction may be a mechanism for chromate resistance;
- Cr(VI) reduction may provide energy for some microbes;

Figure 1. Effect of various concentrations of chromate on total soil aerobic bacteria

Table 9. Chromate sorption by anaerobic bacteria	
	Sorption (%)
Methanogens	
Methanosarcina sp.	88.7
Methanothrix sp.	74.7
Cellulolysers	
Acetivibrio sp.	16.8
Clostridium sp.	40.8

Table 9. Chromate sorption by anaerobic bacteria

Table 10. Viable colony count at various Cr concentrations (Nair and Krishnamoorthy 1991)

Total Cr (mg L^{-1})	[Cr(VI)] (No. x 10^1)	[Cr(III)] (No. x 10^8)
0	5.51	7.69
10	5.30	6.93
20	5.10	6.47
40	4.84	5.17
60	4.54	3.93
80	3.21	0.57
100	1.17	0.46

- Cr(VI) reduction may just be a fortuitous reaction carried out by enzymes that have other physiological substrates.

Chromium reductase is widespread in microbes, but it is primarily present in the soluble fractions of the microbial cell. Our laboratory experiments with Cr-tolerant *Pseudomonas* and *Beijerinckia* revealed that 35–68% Cr reduction could be achieved during the exponential growth phase; the Cr(VI) was completely transformed after 72 h incubation (Figs 2, 3).

Methanogens and anaerobic cellulolytic clostridia can perform this reduction through their enzyme complexes. Our results on the sorption of hexavalent Cr by methanogens and cellulolysers (Table 9) reveal that *Methanosarcina* and *Methanothrix* cells sorb over 80% and over 70%, respectively, within 6 h. The membrane protein and the cell wall components appear to be important for Cr(VI) reduction by bacteria. Direct and indirect microbially-mediated bioreduction of Cr(VI) have been observed. Anaerobic bacterial strains with accelerated Cr(VI) reducing capabilities have been isolated from chromate-contaminated water and sludge. It is evident that anaerobic bacteria can effect preferential bioreduction of chromates under reducing conditions.

Toxic and mutagenic effects of Cr on microbes are known. Soil bacteria have been inhibited with 10–12 mg L^{-1} Cr(VI). Chrome-electroplating waste is toxic to saprophytic and nitrifying bacteria.

The presence of both trivalent and hexavalent forms of Cr at higher concentrations decreased the viable cell count of *Pseudomonas* (Table 10). The effect was marked at higher concentrations of the metal ion (Nair and Krishnamoorthy 1991). There was a direct effect on the cellular contents, as shown

Table 11. Effect of Cr(VI) and Cr(III) on cellular contents of *Pseudomonas aeruginosa* (Nair and Krishnamoorthy 1991)

[Cr]	Form of Cr	Protein	Carbohydrate (mg dry weight)	Lipid	DNA	RNA	Increase in amino acids (%)	Cr sorbed (mg kg^{-1})
10	Cr(III)	4.3	1.2	5.0	1.5	2.0	8.0	0.6
	Cr(VI)	–	1.2	–	–	0	4	
20	Cr(III)	16.6	3.4	16.0	8.0	7.0	14.0	0.9
	Cr(VI)	4.8	7.0	5.0	10.0	12.0	10.0	0.5
40	Cr(III)	24.0	12.0	25.0	16.0	19.0	22.0	1.5
	Cr(VI)	15.6	10.0	15.0	18.0	21.0	14.0	0.6
60	Cr(III)	33.0	24.0	32.0	22.0	32.0	36.0	1.9
	Cr(VI)	23.7	20.4	21.0	28.6	45.0	23.0	0.8
80	Cr(III)	62.0	36.0	56.0	36.0	47.0	53.0	2.4
	Cr(VI)	36.3	28.4	32.0	40.0	50.0	37.0	0.9
100	Cr(III)	*	*	*	*	*	*	*
	Cr(VI)	59	34.3	38.0	46.0	46	46	1.2

– no inhibition; * no growth at 100 mg L^{-1} concentration
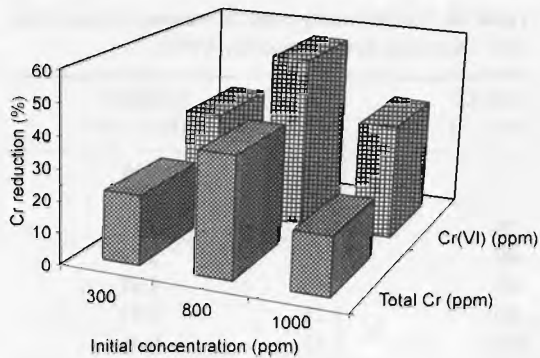
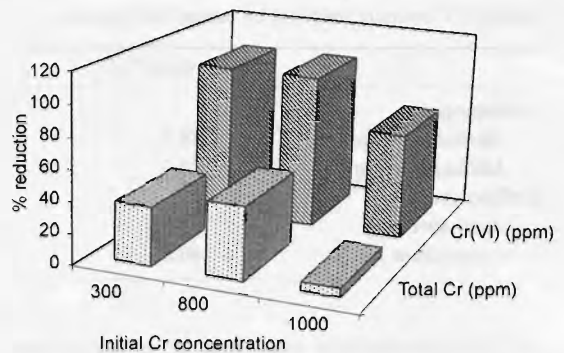**Figure 2.** Cr reduction by *Pseudomonas*

Figure 3. Cr reduction by *Beijerinckia*

by Table 11; they decreased, and only free pool amino acids increased. The decrease in the oxygen uptake was more pronounced in the trivalent than the hexavalent form of Cr.

Bacteria can live in varied environments where heavy metals occur naturally at high concentrations, because they evolve with resistance mechanisms, including the ability to transform toxic species through the processes of methylation, demethylation, oxidation, reduction, hydrogenation, hydroxylation, or dehydroxylation changes in uptake or transport of metals. Anaerobic growth with acetate, ethanol, malate, or succinate favours reduction of Cr.

Mitigation of Chromium Pollution

There is a need to search for innovative methods for minimising the pollution. What is needed is a practical method that can be implemented soon, to curtail the much feared toxicity of Cr, the foul smelling sulfides and the quantities of common salt in tannery effluents. Many of our tanneries are small-scale industries and hence it is not economic for them either to construct waste water treatment plants or to treat the waste waters chemically. It is necessary at this stage to work out an economical treatment process which will effectively alleviate the problem. One approach could be to use biological waste water treatment processes. It is known that all biological processes work faster in tropical conditions. It is possible that microorganisms could be used to degrade the pollutants, and then their fate in the natural

environment could be worked out. Tannin, which is the biggest pollutant in the effluents of vegetable tanning, is an organic and a phenolic compound. Hence microbial degradation of this compound is possible. Microbial accumulation of Cr is a possibility in biological waste water treatment processes which can be broadly classified into anaerobic and aerobic treatment.

Anaerobic digestion of vegetable tan liquor can reduce BOD by 95%, but this is reported at a low loading of 0.8 kg m^{-3} of volatile solids and a high retention period. Our group has isolated and characterised an anaerobic bacterium, *Bacteroides* sp., capable of degrading tannin from the combined effluent (Vetriselvan et al. 1990). We have also characterised the intermediary compounds formed by these bacteria and developed a treatment strategy for removing residual tannin from a composite effluent from tanneries.

Russian researchers first proposed the use of Cr(VI)-reducing bacterial isolates for the removal of chromates from industrial effluents. Since then, various reduction parameters have been evaluated for a diverse group of microorganisms. The parameters accelerate the microorganisms' Cr(VI)-reducing capabilities. There is the prospect of developing commercially viable bioremediation techniques exploiting these organisms (Rai and Dubey 1988, 1989; Rai and Raizada 1989; Gopalan and Veeramani 1994). Bioreactors are used which basically consist of a reduction phase with Cr(VI)-reducing bacteria immobilised on inert matrices within the reactor, followed by a settling or filtration phase to remove Cr(III) precipitates.

Chromate-contaminated effluent is pumped into the reactor and supplemented with various carbon sources and nutrient additives; the Cr(VI) is then reduced, precipitated and removed. A disadvantage here is that the lowest achievable effluent Cr concentrations are probably around 1 mg L^{-1}, considerably higher than the national Environmental Protection Agency drinking water standard of 0.05 mg L^{-1}. Also the reaction rate is slow. However, combining aerobic polishing with aquatic floating weeds would solve the problem of Cr concentration in water, because plants in constructed wetlands selectively sorb Cr from water containing low levels of Cr.

The majority of the bioreactors employ sulfate reducers as efficient consortia for chromate reduction, and they also have an added advantage of reducing the sulfate from the effluents. In our studies we observed that the photosynthetic purple and green sulfur bacteria were predominant and capable of reducing 20–25% sulfur at lower concentrations from the effluent. Maximum reduction occurred during the first two weeks and declined gradually afterwards. Cultures that had acclimatised to higher concentrations (500–600 mg SO_4^{2-} L^{-1}) showed a lag phase initially, but were able to reduce 10–12% of sulfate in the effluent (Ramasamy, unpublished observation).

Studies have indicated that at a mixed liquor suspended solid (MLSS) concentration of 3000–4000 mg L^{-1} the BOD of the pretreated effluent can come down to 34 mg L^{-1} from 988 mg L^{-1} within 24 hours of aeration. Generally a BOD removal of 85 to 95% can be expected from this system. We have isolated and characterised several floc-forming bacteria associated with sewage sludge digestion. Similar cultures adapted to agro-industrial wastes have performed well in association with other heterotrophic bacteria, reducing the protein concentration and metals. Most of the metal removal is by sorption and sedimentation. The BOD of pretreated vegetable tannery effluent can fall from 900 mg L^{-1} to 158 mg L^{-1}. Settling of the filtered effluent reduces the BOD to 56 mg L^{-1}. In the case of chrome tanning waste, the BOD can be reduced to 88 mg L^{-1} from 129 mg L^{-1} and further reduction in BOD can be obtained at a value of 56 mg L^{-1}, after settling the effluent from trickling filtration. A BOD removal of 70–90% can be achieved with this system. Solar evaporation ponds and combined aerated lagoons support algal blooms. Concerted study is needed to assess the algal growth and salt reduction.

The use of constructed wetlands with native water plants and floating macrophytes (Garg and Chandra 1990; Gupta et al. 1994; Srivastav et al. 1994) will also be a good alternative. Some macrophytes accumulate heavy metals faster than terrestrial plants can, and are suitable candidates for use in tertiary treatment. An artificial wetland provides an environment that is aerobic and micro-aerophilic; it is a positive system to translate so as to reduce the heavy metal contamination and organic loading in waste water.

Conclusion

In India, with its increasing population, scarcity of land and water are major issues limiting increased and sustainable land use. Any detrimental change to these ecosystems will definitely hamper progress. By pooling and testing our fragments of knowledge, we have been able to formulate a combined treatment system, with initial anaerobic processing of effluent and secondary aerobic polishing. Tertiary treatment with macrophytes should follow these treatment systems. Demonstration of this combined system is in progress with cooperation from tanners, planners and researchers.

As well as efforts to treat the waste water from the tanneries, sincere attempts are being made to reduce the release of Cr into the environment. These attempts should at least reduce or perhaps control the future damage to the ecosystem. What about the damaged ecosystems in which Cr and salt concentrations are above the permissible limits? Remedial measures may be chemical, physical or biological. Plant and microbial remediation is being investigated intensively. Selective sorption and removal of contaminants from the contaminated sites through microbial products and macrophytes, being tested by the scientific community, will pave the way for sustained growth of tanneries in India. What is more encouraging is the reduction of toxic Cr to a non-toxic form by anaerobes in the groundwater. The resulting precipitation will protect the village population from the drastic toxicity of Cr(VI).

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Transformations of Chromium by Soil Microorganisms, and Toxicity of Chromium to Earthworms

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Abstract

Chromium (Cr) contamination of soils from tannery waste disposals, effluents and sludges is a serious environmental pollution problem worldwide. Chemical oxidation mediated by manganese oxides is the only proved mechanism for the oxidation of Cr(III) to Cr(VI). This study evaluated the ability of bacteria isolated from a dried sludge to oxidise Cr(III) and found that one of the bacterial isolates was capable of oxidising Cr(III) to Cr(VI) in liquid culture, but at a slow rate. Standard direct toxicity experiments were used to test the toxicity of Cr(VI) to earthworms and determine the LD_{50} values for Cr(VI) on *E. fetida* over three time periods. The LD_{50} is an arbitrary value that measures the relative toxicity of metals but rarely predicts the impact of toxins on organisms in the soil, firstly because not all toxins cause death in a short period of time and secondly because a number of physical and chemical properties of soil control the bioavailability of heavy metals. Therefore, the ability of earthworms to exclude Cr was also tested. Finally, measures of earthworm performance other than survival or death were considered, to determine whether there were any biomarkers which could be used to predict, more accurately, the impact of metals on earthworms in soil. The Cr accumulation by earthworms in soils contaminated with low levels of Cr was measured in 14 d laboratory experiments. There was a strong negative relationship ($r^2 = 0.791$, $P < 0.05$) between the level of Cr accumulated in earthworms and the Cr adsorption partition coefficient (*kd*).

THE chromium (Cr) contamination of soils by tannery effluents and sludges is one of the most serious environmental pollution problems facing the world, including Asia and Australia (ACIAR 1996). Although Cr may exist in a number of oxidation states, the two most common forms found under natural conditions are the trivalent Cr(III) and the hexavalent Cr(VI) species. The transformations between the two forms (oxidation–reduction reactions) may be mediated

by chemical and biological reactions (Bartlett and James 1994; Naidu and Kookana, these Proceedings). Thermodynamically, Cr(III) is less susceptible to oxidation (kinetic inertness) and is less toxic to biota. In contrast, Cr(VI) is highly unstable, is toxic to animals and plants, and readily changes to Cr(III) (Bartlett and James 1988). Therefore, even in soils with high levels of total Cr, the concentration of Cr(VI) is often relatively low. Money (1991) reported that there is little likelihood of oxidation of Cr(III) to Cr(VI) in soils because conditions favour Cr reduction (i.e. low Eh and the presence of organic matter). However this contrasts with results reported by Bartlett and James (1979) who demonstrated that the potential for Cr(III) oxidation is significant in fresh moist soils. The extent of Cr oxidation was found to be dependent on the form of Cr(III) (e.g. its solubility

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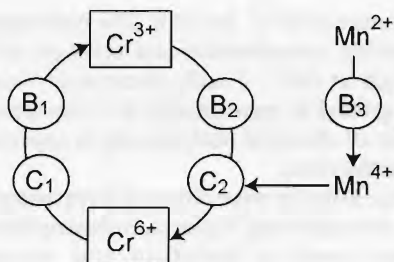
Figure 1. Conceptual diagram indicating the various factors regulating the oxidation–reduction reactions of chromium in soils (based on information in Bartlett and James 1988; Ishibashi et al. 1990; Arillo and Melodia 1991; Skinner and Fitzpatrick 1992; Naidu and Kookana, these Proceedings). B1 — biological reduction of chromium is mediated by bacteria, fungi, algae and earthworms whereas chemical reduction (C1) is mediated by Fe and organic compounds. C2 — Mn oxides are the principal regulators of Cr oxidation whereas evidence is lacking for either the direct microbial oxidation of Cr (B2) or for indirect influence via the oxidation of Mn (B3).

and complexation with organic materials) but independent of dissolved oxygen (James and Bartlett 1983; Eary and Rai 1987).

A number of reports show that as well as chemical agents there are soil biota (bacteria, fungi and earthworms) capable of reducing Cr(VI) to Cr(III) (Komori et al. 1989; Ishibashi et al. 1990; Arillo and Melodia 1991). However, oxidation of Cr(III) to Cr(VI) has only been demonstrated in the presence of manganese oxides, Mn(IV) (Bartlett and James 1979; Johnson and Xyla 1991). Presence of oxidised forms of Mn and conditions that favour oxidation of Mn are considered to be limiting factors for Cr oxidation. No published reports documenting direct oxidation of Cr by microorganisms exist in the literature. Oxidation of Cr(III) may also be mediated by indirect oxidation processes that involve microbial coupling of chemical agents such as Mn oxides that have a lower chemical potential than Cr(VI) (Naidu and Kookana, these Proceedings). A diverse array of soil biota (bacteria, fungi, algae) are capable of catalysing Mn(II) oxidation (Ghiorse and Ehrlich 1992; Tebo et al. 1997) which in turn could cause oxidation of Cr. Figure 1 illustrates how oxidation of Cr(III) could occur either by direct transformation of Cr or through microbially-mediated Mn oxidation. Experimental evidence to support either hypothesis is lacking.

The ecotoxicological effects of Cr(VI) on soil biota depend on the soil solution concentration of Cr(VI). The soil solution is the medium for plant growth and determines the availability both of nutrients and of other ionic species to microbes. The concentration of a contaminant that is supposedly available for uptake by animals and plants is often called its 'bioavailability'. Most of the current measurement techniques for bioavailability are based on chemical extraction procedures (Luoma 1995). However, such chemical extraction techniques often overestimate the bioavailability indices, given their high ionic strength and the markedly different mode of action of the extractants compared to the ionic composition of the soil solution. The toxicity of a heavy metal (e.g. Cr) to biological organisms in soil will not only depend on the concentration of the toxic form of the metal but will also be influenced by a number of physical and chemical properties of soil. These properties may affect the processes governing the transformation of the toxic species, and also the response of biota to changing environmental conditions (van Gestel 1997; van Straalen and Lokke 1997). For these reasons the responses of biological organisms to contaminants are better measures of bioavailability.

A number of laboratory tests using microflora, microfauna, meso- and macro-fauna have been evaluated and some have been recommended for determining the toxicity of environmental contaminants including heavy metals (Moss and Adak 1986; Maltby and Calow 1990; Lebrun et al. 1995; Luoma 1995; Crommentuijn et al. 1997; Gupta and Naidu 1997; Paton et al. 1997; Rundgren and Nilsson 1997). A suitable bioassay should be simple, inexpensive, amenable to standardisation and reproducible by different operators or analysts. The interpretive and predictive depth of the data determines the test's wider use.

Bioassays using earthworms as test organisms have tested for various types of contaminants, including heavy metals. Based on this, standard procedures have been developed (EEC 1982, 1983) in which LD_{50} values are calculated for earthworms using standard techniques over a set period of time. Currently the LD_{50} values are arbitrary measures of the relative toxicity of chemicals or metals to earthworms. They do not

accurately predict the impact of toxins on organisms in the soil, firstly because not all toxins cause death in a short period of time, and secondly because the properties of soil affect the bioavailability of the toxin to earthworms.

Standard procedures are set at a fixed time: two days for contact filter paper and two weeks for artificial soil. However, some toxins do not cause death on contact. Toxins that are highly carcinogenic, such as Cr, affect DNA replication and lead to cytotoxicity and mutagenicity (Ono 1988). It may take some time before their effects are expressed as earthworm death. For these toxins, tests for toxicity may have to run for a longer period of time to allow expression of the toxicity. Alternatively, some other measure of earthworm performance may be found that will predict whether earthworms will die as a result of exposure.

Soil properties such as clay content, organic matter and pH affect the availability of toxins to organisms. Measurement of total levels of toxins is not very useful because they do not accurately reflect the concentrations of toxins that the biota are exposed to in soil. Static measurements of extractable concentrations of toxins in soil are not useful because they do not consider temporal changes in solution concentrations. Therefore, a method is required that can accurately predict the behaviour of toxins in the soil.

The objectives of this study were two-fold: first, to determine the role of bacteria, isolated from sludges, in the oxidation of Cr(III); and second, to evaluate the toxic effects of Cr(VI) on earthworms and their influence on the earthworm bioassay as a method for measuring the bioavailability of Cr in soils

Materials and Methods

Transformations of chromium

Soils and sludges

The soil used in earthworm experiments was an Oxisol with an organic carbon level of 1.4% and 46% clay. It was air-dried, then crushed to pass through a 2 mm sieve, before all laboratory studies. Lime (analytical grade Ca(OH)$_2$) was thoroughly mixed into replicate samples of the soil. The lime rates were chosen to obtain a pH span of about 5.1–7.15. After thorough mixing, the soils were moistened with distilled deionised water to field moisture capacity and allowed to react at a temperature of 60°C for 24 h. The moist samples were dried, remoistened and allowed to react overnight at 60°C. Finally these soils were air-dried, ground to pass through a 2 mm sieve and used for all chemical analyses and in experiments with earthworms.

Sludge samples were obtained from tanneries in South Australia and Victoria. Subsamples of the sludges used in isolation and oxidation experiments were stored samples of the air-dried sludges, ground to pass through a 1 mm sieve. More details of sludges are given by Naidu et al. (these Proceedings).

Chromium adsorption partition coefficient (kd)

The partition coefficient of Cr was estimated by using a single point isotherm. To 30 mL of solution, 120 μg of Cr(VI) and 1 g of soil were added (1:30 soil:solution ratio) and the mixture was allowed to equilibrate end-over-end for 16 h. Then the samples were centrifuged at 15 000 rpm and passed through a 0.45 μm millipore filter. The Cr(VI) in the extract was analysed. The Cr sorbed was calculated by difference and the partition coefficient was obtained by taking the ratio of Cr sorbed and Cr in solution.

Isolation and identification of bacteria

Bacteria were isolated from the dried sludge material SL21-3 and its enriched liquid leachate. The enriched liquid leachate was obtained by incubating the dried sludge in inorganic nutrient solution for two weeks at 20°C on a rotating shaker at 100 rpm. The supernatant, after a 2 min settling of the enrichment culture, was directly used for plating for isolating bacteria. Serial dilutions of the sludge material (SL21-3) were made using saline phosphate buffer; 0.1 mL of the appropriate dilution was plated onto 1/10 TSA plates (3 g of Difco tryptic soy broth with dextrose, 15 g Oxoid agar no. 3 L^{-1}, pH 6.8). All the inoculated plates were incubated at 25°C, and after 48 h individual colonies were marked for differences in colony morphology and transferred onto TSA plates with cyclohexamide (400 μg mL^{-1}) for purification. After three transfers, microscopic observations and gram stain reaction tests were made on the purified isolates and 12 different isolates were prepared for identification using a MIDI-FAME (fatty acid methyl ester) identification system.

Individual colonies of purified isolates were inoculated onto trypticase soy broth agar (TSBA) plates and incubated at 27°C, in the dark. After 24 h, or longer for slow growing bacteria, cells were harvested by scraping colonies with a sterile spatula. They were suspended in 3.75M NaOH. Saponification, methylation and extraction were done using the Sherlock Microbial Identification System (MIS) method (MIDI 1993) developed by the Microbial ID (MIDI, Inc., Newark, DE, USA). The fatty acid methyl ester mixtures were separated using a Hewlett-Packard 5890 series II gas chromatograph fitted with an HP Ultra 2 capillary column (cross-linked 5% phenyl methyl silicone fused silica capillary column, 25 m x 0.2 mm x 0.33 μm film thickness) and a flame ionisation detector. A MIDI calibration standard (a mixture of the straight chain saturated fatty acids 9:0 to 20:0 in length) was included after every tenth sample.

The MIDI program automatically identified the peaks as specific bacterial fatty acids on the basis of their equivalent chain length. The MIS system reads the fatty acid profiles of the unknown isolates and compares them to stored data bases (TSBA Rev. 3.90, CLIN Rev. 3.90) using a covariance matrix, principal components analysis and pattern recognition software. To assign a name to an unknown isolate the pattern recognition software uses ratios between fatty acid amounts of the unknown isolate, in addition to the principal component base. Finally the system gives a similarity index for the suggested bacterial identification.

Cr(III) oxidation by pure cultures of bacteria

Pure cultures of bacterial isolates from agar plates were inoculated into 10 mL of sterile inorganic salt (INS) medium in McCartney bottles and incubated at 25°C. The INS medium is made as follows: dissolve K_2HPO_4 1.21 g, KH_2PO_4 0.34 g, NaCl 4 g, $(NH_4)_2SO_4$ 1 g, $MgSO_4.7H_2O$ 0.03 g, $CaCl_2$ 0.1 g, glucose 2 g, and yeast extract 0.1 g in 1 L of distilled water, adjust pH to 6.8 and autoclave sterilise (20 min at 121°C). Bacterial cultures in their logarithmic growth phase, after 48 h, were used as inoculum for the oxidation experiments which were carried out in the INS medium supplemented with filter-sterilised Cr(III) at 50 ppm. Inoculated Cr-media bottles were incubated at 25°C on a rotary shaker (at 150 rpm) and subsamples were analysed for Cr(VI) by the modified method of Templeton (C. Templeton

pers. comm. 1997). Briefly, 5 mL of liquid sample was centrifuged at 10 000 rpm for 2 min. To a 4 mL subsample of the supernatant, 10 mL of 1N H_2SO_4 and 4 mL of diphenyl carbazide reagent were added and mixed. The optical density of the developed colour was measured at 540 nm and the concentrations of Cr(VI) in solution were calculated from a calibration curve prepared using a $K_2Cr_2O_7$ standard. All samples were analysed in duplicate.

Cr(III) oxidation by sludge materials

Subsamples of SL21-3 sludge materials were sterilised by autoclaving at 121°C for 20 min on two consecutive days. Sterile INS medium (15 mL) in test tubes was supplemented with filter-sterilised Cr(III) at 50 ppm and inoculated with 0.2 g of sterile or non-sterile sludge material. Inoculated medium was incubated at 25°C on a rotary shaker (150 rpm), and after 7 or 14 days subsamples were analysed for Cr(VI) by the method of Templeton (pers. comm. 1997).

Toxicity of chromium to earthworms

Earthworms of species *Eisenia fetida* (Savigny) were obtained from commercial suppliers (Worms R Us, Adelaide, South Australia). Species *Aporrectodea caliginosa* (Savigny) was collected from a pasture near Smithton, northern Tasmania, and kept in soil and sheep dung in the laboratory at 20°C for up to one year. Both species of worms were washed (three times) with Cr-free distilled water. To remove soil from earthworm intestines and standardise the water content of their tissues before use, all earthworms were placed overnight in 50 mL plastic vials (two worms per vial) containing Whatman #42 (5 cm diameter) filter paper wetted with distilled water (Dalby et al. 1996). This procedure was used for all earthworms in the study.

Solution experiments with E. fetida: (1) LD_{50}

Individual earthworms, their intestines cleared and weights recorded, were placed into 9 cm diameter petri dishes containing one 7 cm Whatman #41 filter paper and 5 mL of either distilled water or Cr(VI) solution of known concentration. One earthworm was used per petri dish and each treatment had ten replicates. The concentrations of Cr(VI) tested were 0, 6, 12, 24, and 48 μg mL^{-1}; $K_2Cr_2O_7$ was the source of Cr(VI). Individual plates

were closed using non-toxic adhesive tape to prevent earthworm escape and the plates were incubated in the dark at 18°C (±1°C) for 14 days. Observations were made at regular intervals to note the behaviour and death of earthworms.

(2) Cr accumulation and enzyme activities

Details of earthworm preparation and filter paper assays were similar to those for LD_{50} experiments. In experiment 2, the concentrations of Cr(VI) tested were 0, 12, 24, 30, 36, 42, 48, 54, 108 and 162 µg mL^{-1}; $K_2Cr_2O_7$ was the source of Cr(VI). Individual plates were closed using non-toxic adhesive tape to prevent earthworm escape and the plates were incubated in the dark at 18°C (±1°C). Observations were made daily to note the behaviour and death of earthworms.

In both experiments, after 48 h, earthworms were removed from treatment petri dishes, washed (twice) with distilled water and freeze dried (using a Thermovac model FD-3-V7 freeze drier for 2 d) after snap freezing using liquid nitrogen. Freeze-dried earthworms were stored at –20°C until analysed for enzyme activity.

Phosphatase assay

Freeze-dried earthworms from experiment 2 were macerated in liquid nitrogen and a known quantity of powdered earthworm was added to 2.5 mL of modified universal buffer (pH 10) and mixed by vortexing for 30 s. After incubation for 1 h at room temperature (20°C), the activity of phosphatase enzyme was determined using 50 mM p-nitrophenyl phosphate-disodium salt as substrate (Tabatabai 1982).

ATP assay

The activity of adenosine 5'-triphosphate (ATP) in earthworms was measured using the ATP assay diagnostic kit (Procedure No. 366-UV) of Sigma Aldrich Pty Ltd. The principle of the method is that ATP is catalysed by the enzyme phosphoglycerate phosphokinase (PGK) in the presence of added NADH and the decrease in absorbance at 340 nm is determined as a measure of the amount of ATP originally present (Sigma Diagnostics 1997). Freeze-dried earthworms from experiment 2 were ground into fine powder and 2 mL of 12% trichloroacetic acid was added and mixed by vortexing for 15 s. The mixture was allowed to stand for 5 min in an ice bath. Samples

were centrifuged at 3000 rpm for 5 min and the supernatant was used for the ATP assay (Sigma Diagnostics 1997). Final reaction mixtures were centrifuged at 6000 rpm for 2 min prior to the measurement of optical density of sample, to avoid interference from turbidity. A solution of known concentration of ATP was assayed to verify the accuracy of the procedure.

Soil experiments

The effects of soil pH and added Cr(VI) on the behaviour of earthworms were investigated using *E. fetida* (experiment 3) and *A. caliginosa* (experiment 4). Subsamples of the soil were limed to soil pH values 5.56, 6.20, 6.55 and 7.15. For each sample, 30 g of air-dried soil was weighed into a 9 cm diameter plastic petri dish and moisture adjusted with either distilled water or Cr(VI) solution to give a water potential of 10 kPa. Each treatment had six replicate petri dishes and one earthworm was added to each dish. Initial weights of earthworms were recorded (after clearing soil from their intestines; Dalby et al. 1996) before the worms were placed in appropriate petri dishes, and the petri dishes were incubated at 18°C (±1°C), in the dark. Observations were made at regular intervals to note if any deaths occurred. After 14 d, earthworms were removed from the soil and washed (twice) with distilled water to remove surface adhered soil. Earthworms were again placed in containers with moist filter paper to void gut contents and standardise tissue moisture. All the worms were snap frozen using liquid nitrogen and freeze dried for 2 d using a Thermovac model FD-3-V7 freeze drier.

Analysis of total Cr in earthworms and soils

The concentrations of total Cr in freeze-dried earthworms were analysed using the method of Cartwright and Spouncer (1987) and Cr concentrations per unit dry weight were calculated. Total Cr in soil samples was measured as described by Merry and Zarcinas (1980).

Statistical analyses

Data were analysed using one-way analysis of variance (ANOVA), and differences between means were determined using Tukey's test ($P = 0.05$). Proportions (proportional change in weight, survival) were transformed by the square root of $(x + 0.5)$, and counts were transformed by

Table 1. A list of bacterial species isolated from the sludge SL21 and soil, and their ability to oxidise Cr(III) in solution culture*

Bacterial species** (with colony identity numbers)	Source	Colony type	Cr(III) oxidation (μg Cr(VI) L^{-1})
Pseudomonas fluorescens (3,4)	dried sludge	type 1	<0.01
P. fluorescens (1,2)	dried sludge	type 2	<0.01
Bacillus thuringiensis (5)	dried sludge	type 3	<0.01
B. mycoides (6)	dried sludge	type 3	0.135 ± 0.008
P. fluorescens (7)	enriched leachate	type 1	
P. chlororaphis (8)	enriched leachate	type 1	<0.01
P. fluorescens (9)	enriched leachate	type 1	0.053 ± 0.001
P. fluorescens (10, 11)	enriched leachate	type 2	<0.01
P. fluorescens (12)	enriched leachate	type 2	0.081 ± 0.075
B. thuringiensis	soil	–	<0.01

* Bacterial cultures from their logarithmic growth phase were inoculated into Cr-oxidation media and incubated at 20°C
** MIDI-FAME analysis gave a similarity index, based on TSBA library, for the pseudomonads ranging from 0.713 to 0.859, whereas for *Bacillus* species it was only 0.307–0.639

log(x + 1). If the variances differed significantly (as determined by Bartlett's test), a Kruskal–Wallis analysis was used instead of ANOVA.

Results

Chromium transformations by bacteria and sludge

Six different bacterial types were isolated from the sludge material SL21-3. They were identified as *Pseudomonas fluorescens* (two colony types), *Bacillus mycoides* and *B. thuringiensis* (Table 1). Two species of bacteria (*P. fluorescens* and *P. chlororaphis*) were isolated from the enrichment culture. *Pseudomonas fluorescens* (two colony types) was common to both the sludge and the enrichment culture. The similarity index values for the *Pseudomonas* species ranged from 0.713 to 0.859 and 0.307 to 0.639 for *Bacillus* species. With the MIS system the values observed for our isolates are considered normal. Microscopic observations provided supporting evidence for the isolates identified as *Bacillus* species.

The ability of isolated bacteria to oxidise Cr(III) in the absence of Mn was determined in liquid culture experiments. Ten out of 12 bacteria isolated from the dried sludge SL21-3 and its enriched leachate failed to oxidise measurable amounts of Cr(III) after one week of growth in the presence of 50 μg mL^{-1} of Cr(III) in the aerated inorganic liquid medium at pH 6.8 (Table 1). One bacterial isolate from the dried sludge (i.e. *Bacillus mycoides*) showed measurable levels of Cr(III) oxidation after one week of growth.

Measurable Cr(III) oxidation was observed in the presence of the dried sludge sample SL21-3 and its liquid leachate after 10 days of incubation at 25°C (Table 2).

Toxicity of chromium to earthworms

Experiment 1

The LD$_{50}$ of Cr(VI) to *E. fetida* was ~50 μg mL^{-1} after 3 days and 5.6 μg mL^{-1} after 6 d (Fig. 2). The concentration of Cr in *E. fetida* after 6 d increased as the Cr(VI) treatments increased (Figs 3a,b). The

Table 2. Cr(III) oxidation in the presence of tannery sludges in aerated liquid culture

Treatment	Source	Presence of Mn	Cr (III) oxidation (μg Cr(VI) L^{-1})
Enriched leachate of SL21-3	Mt Barker-old	not added	1.83 ± 0.6
Dried SL21-3	Mt Barker-old	not added	2.42 ± 0.3
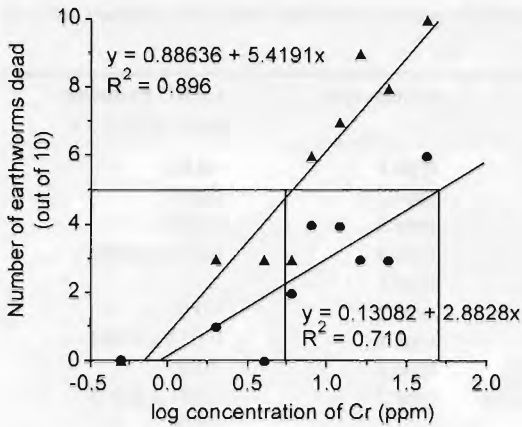
Figure 2. LD_{50} values for *E. fetida* on exposure to Cr(VI) after 3 days (●) and 6 days (▲) in a filter paper assay

level of Cr was significantly lower in the control compared to the treatments with added Cr(VI) (one-way ANOVA, df = 4,15, F = 8.99, $P < 0.001$). There was a trend for Cr concentration to remain constant at the 6, 12 and 24 μg mL^{-1} treatments (944–1015 μg mL^{-1}) and then increase dramatically between the 24 and 48 μg mL^{-1} treatments (1015–15 410 μg mL^{-1}), but this increase was not significant. The concentrations of Cr(VI) in solution in the 0–24 μg mL^{-1} treatments were associated with a linear increase

($r^2 = 0.76$, $P < 0.05$) in the tissue concentrations of Cr(VI) in *E. fetida*.

Experiment 2

The survival of *E. fetida* earthworms ranged between 65% and 100% in the 0–48 μg mL^{-1} treatments and then fell from 70% to 20% between the 54 and 108 μg mL^{-1} treatments (Table 3). The two-day exposure of earthworms to Cr(VI) gave a considerably higher value for LD_{50}, 79 μg mL^{-1}, than the three-day and six-day exposures observed in Experiment 1. Over 48 h, the average weight dropped in every treatment, by 3.06% in the control to 21% at 42 μg Cr(VI) mL^{-1} (Table 3). Calculations of weight change were not made beyond 54 μg mL^{-1} because of the high mortality rate. Earthworms in all treatments with Cr(VI) added lost significantly more weight than in the control treatment, and weight loss was significantly greater at the 42 ppm treatment than at the 12 and 30 ppm treatments (one-way ANOVA, df = 6,124, $F = 14.58$, $P < 0.001$).

The concentration of Cr in the surviving earthworms ranged from 0.99 μg g^{-1} dry weight in the control to 118 μg g^{-1} dry weight in the 108 μg mL^{-1} treatment (Fig. 3b). Chromium concentrations were significantly higher in all treatments with added Cr(VI) than in the control. There was no significant difference in the concentration of Cr between treatments with 12
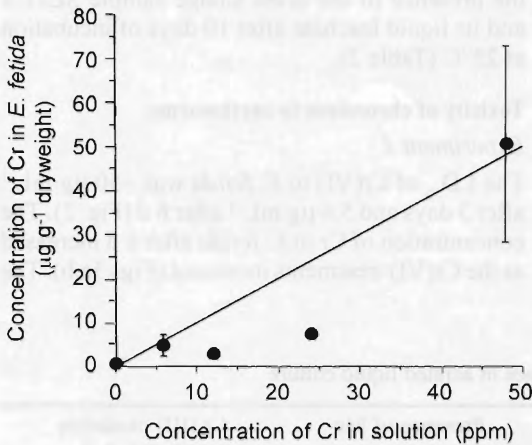
Figure 3a. Cr concentrations in *E. fetida* in a filter paper assay (Experiment 1)
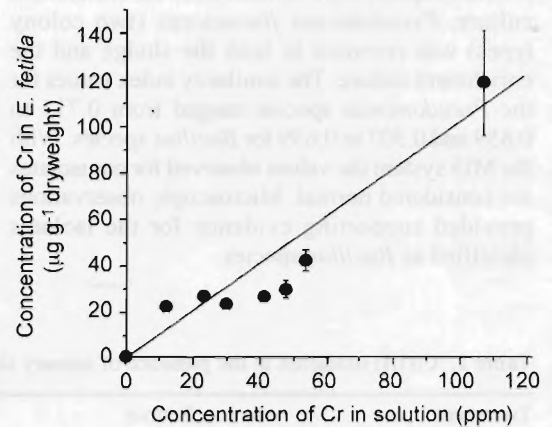
Figure 3b. Cr concentrations in *E. fetida* in a filter paper assay (Experiment 2)

Table 3. Weight change and survival of *E. fetida* on exposure to various levels of Cr(VI) in a filter paper assay after 2 days (Experiment 2)

Cr(VI) (ppm) in solution	Weight change (%)	Survival (%)
0	−3.1 (1.7)	100
12	−15.2 (1.5)	100
24	−16.9 (1.4)	100
30	−14.5 (1.0)	95
42	−21.1 (1.4)	100
48	−17.1 (1.1)	100
54	−16.0 (1.7)	65
108	na	20
162	na	10

Table 4. Enzyme activity in *E. fetida* on exposure to various levels of Cr(VI) after 2 days (Experiment 2); numbers in brackets are standard errors of the mean.

Cr(VI) (ppm) in solution	ATP activity ($\mu g\ g^{-1}$ dry wt)	Phosphatase activity (μg PNP released h^{-1})
0	2.847 (0.298)	468.2 (61.4)
12		473.0 (35.6)
24	2.194 (0.493)	400.4 (42.0)
30		368.1 (45.3)
42		615.1 (72.7)
48	1.728 (0.578)	485.9 (67.9)
54		531.1 (88.8)

and 48 $\mu g\ mL^{-1}$, but a significant increase in Cr concentration in earthworms was observed at the 54 and 108 $\mu g\ mL^{-1}$ treatments.

The activity of ATPase dropped between the 24 and 48 $\mu g\ mL^{-1}$ treatments and then rose again. However these trends were not significant (one-way ANOVA, df = 4,9, $F = 1.14$, $P = 0.3968$) (Table 4). Phosphatase activity dropped between the 0 and 30 $\mu g\ mL^{-1}$ treatments and then rose again at the 42 $\mu g\ mL^{-1}$ treatment and above, although the means were not significantly different (one-way ANOVA, df = 6,27, $F = 2.18$, $P = 0.0761$) (Table 4).

Experiment 3

The mean weight of the earthworms (*E. fetida*) decreased in each treatment over the course of the experiment, with weight loss ranging from 10.6% to 14.0%. There was no significant effect of pH (two-way ANOVA, df = 2,31, $F = 0.20$, $P = 0.820$) nor of concentration of Cr (two-way ANOVA, df = 2,31, $F = 0.09$, $P = 0.912$) on weight loss. Although all earthworms survived the treatments,

by the end of the two weeks they were either aestivating or inactive.

There was no significant difference between the final concentrations of Cr in earthworms from soil with different amounts of Cr added because of the high variability within the treatments (data not included). There was a tendency for higher concentrations of Cr in earthworms at higher pH, but this was not significant (one-way ANOVA, df = 3,16, $F = 3.9$, $P = 0.763$).

Experiment 4 — Aporrectodea caliginosa

Only one *Aporrectodea caliginosa* died during the two week incubation period. Between 20% and 80% of living earthworms were aestivating after one week and all were aestivating after two weeks. There was a trend for earthworm aestivation to increase in soil with a higher pH (lower *kd*). All earthworms lost weight (13–23%) during the experiment. Earthworms lost significantly more weight in soil at pH 5.5 than in soil at pH 6.2 and 6.55 (one-way ANOVA, df = 3,15, $F = 4.59$, $P < 0.018$) (Table 5).

Table 5. Weight change and aestivation of *A. caliginosa* in Cr-contaminated soils of differing pH after 2 weeks (Experiment 4); values in brackets are standard errors of the mean; means followed by different letters are significantly different

Soil pH	Weight change (%)	Aestivation (%) after 1 week	Aestivation (%) after 2 weeks
5.56	−23.0 (1.8) a	20 a	100 a
6.2	−13.6 (1.6) b	40 a	100 a
6.55	−12.9 (2.8) b	80 a	100 a
7.1	−17.0 (2.1) ab	60 a	100 a
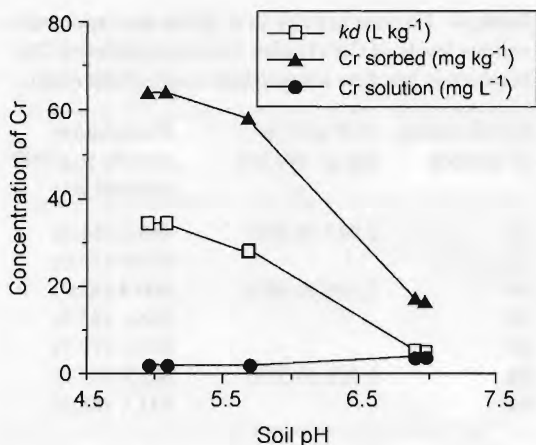
Figure 4. Effect of pH on Cr sorption and partition coefficient (kd) in an oxisol

The more acid the soil treatment, between pH 7.2 and 5.5, the lower the concentration of Cr(VI) in solution ('bioavailable'). The concentration of Cr in earthworms was significantly higher at pH 7 than at pH 5 or 6 (Kruskal–Wallis, $U = 11.34$, $P \leq 0.0034$). Data in Fig. 4 (average values only, error bars not shown) indicate the adsorption partition coefficient values (kd) in soils at various pH values; kd values reduced from 30 mL g^{-1} at pH 5.5 to 0.8 mL g^{-1} at pH 7.2. A strong negative relationship ($r^2 = 0.791$, $P < 0.05$) was observed
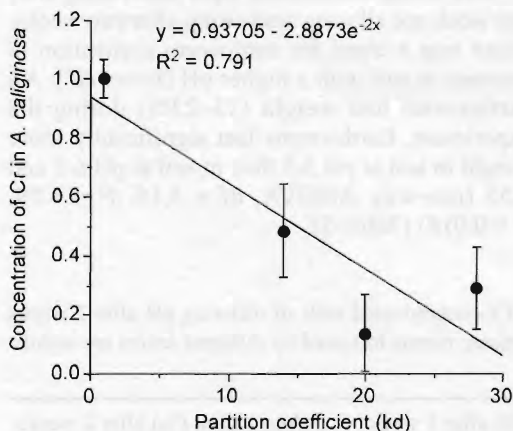
Figure 5. Levels of Cr in *A. caliginosa* from soils with different partition coefficients (kd) after two weeks of exposure

between the level of Cr accumulated in earthworms incubated in soils with different pH and the Cr-adsorption partition coefficient (kd) (Fig. 5).

Discussion

Biohazards from the toxicity of Cr in land-disposed industrial wastes such as tannery sludges depend mainly on the concentration of Cr(VI) in soil solution. Oxidation of the less toxic Cr(III) into the acutely toxic Cr(VI) is one of the critical transformation processes that regulate the toxicity arising from Cr contamination. Direct biological oxidation of Cr(III) is one possible mechanism of Cr(VI) formation. We evaluated the ability of bacteria isolated from tannery sludge from South Australia to oxidise Cr(III) in solution culture. During a two week incubation assay, only one of the isolates (*Bacillus mycoides*) was able to oxidise Cr(III) into Cr(VI). Bartlett and James (1979) reported the oxidation of Cr(III) mediated by Mn oxides. Since no Mn oxides were added in either the original growth medium or the oxidation medium, the appearance of Cr(VI) in the liquid culture could only be from a direct oxidation mediated by the test bacteria. No measurable Cr(VI) was found in the sterile liquid medium. However, the concentration of Cr(VI) measured was very low. This suggests that the kinetics of the process are extremely slow. Bacterial reduction of Cr(VI) into Cr(III), mediated by various enzymatic reactions associated with soluble protein, has been previously reported (Ishibashi et al. 1990). Organic material such as mucus, and saliva compounds such as thiols, can also react with hexavalent Cr and cause reduction (Wiegand et al. 1984; Arillo and Melodia 1991). We did not test the reductive capacity of Cr by the test bacteria.

The direct microbial oxidation of Cr observed in the present study is only preliminary and its potential role in the oxidation of Cr in sludges and soil–sludge mixtures needs to be further assessed. Another microbe-mediated pathway for Cr(III) oxidation may be through step reactions involving indirect chemical oxidation of Cr(III) following biological oxidation of Mn(II) to Mn(IV). A number of studies have been reported showing the abilities of various types of soil biota (bacteria, fungi, algae) capable of oxidising Mn (Ghiorse and Ehrlich 1992). Thus the Mn^{2+} formed during the oxidation of Cr is further oxidised by biota, keeping

the Cr oxidation cycle active, but experimental evidence for these processes is lacking.

Values for LD_{50} were dependent on the length
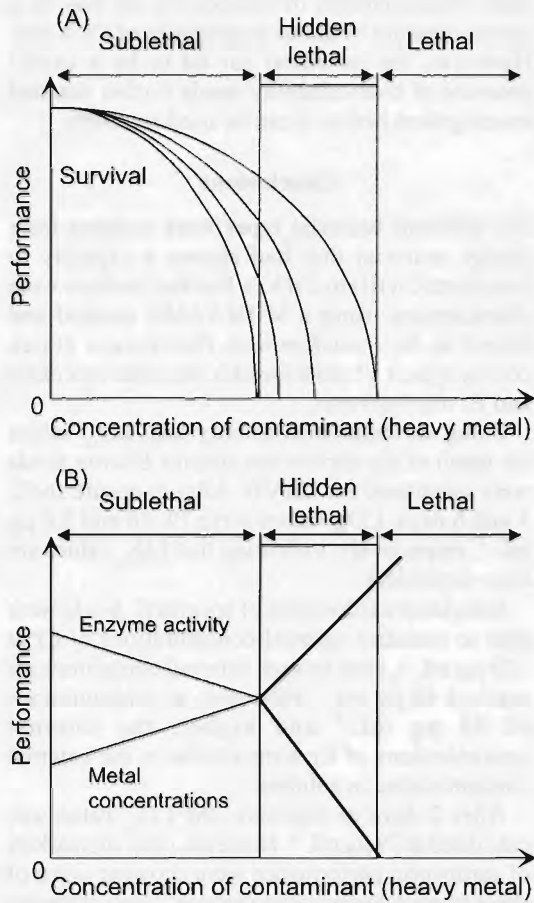
Figure 6. A conceptual diagram indicating the relationship between concentration of heavy metal and various performance indicators of earthworms. Note: Lethal concentrations are levels of Cr that cause more than 50% death in earthworms; sublethal concentrations may cause metabolic stress but not result in death; 'hidden' lethal concentrations do not cause greater than 50% death over the time period of an assay, but will cause death in the longer term. (A) Survival of earthworms is affected by the concentration and time of exposure; increased time of exposure will result in reduced survival; (B) Metabolic performance indicators such as enzyme activities and accumulated metal concentrations are affected by concentration of metal.

of exposure of earthworms to Cr. This means that an LD_{50} of 79 ppm calculated after two days exposure is not a true reflection of how earthworms respond to similar concentrations of Cr in soil solution. There is a 'hidden mortality' which is not expressed in just two days, and earthworms in field soil are likely to die on exposure to a solution concentration of 5.6 $\mu g\ mL^{-1}$ and perhaps lower. Therefore the LD_{50} value does not seem to be the most appropriate measure of toxicity, because it is unable to predict an environmental outcome.

However, there are other performance indicators which can indicate fatal concentrations after only a short period of time (Fig. 6). For example, even though the LD_{50} was calculated as 79 $\mu g\ mL^{-1}$, earthworms were unable to exclude Cr when solution concentrations were ~50 $\mu g\ mL^{-1}$ (see below). Phosphatase activity dropped steadily in response to increasing external concentrations at 0–30 μg Cr mL^{-1} and then increased, indicating a decoupling of metabolic pathways. The earthworms' change in weight was significantly smaller at concentrations of 12 $\mu g\ mL^{-1}$ compared to the control, which indicates that there had already been a metabolic cost at this concentration. Further investigation is required to find a
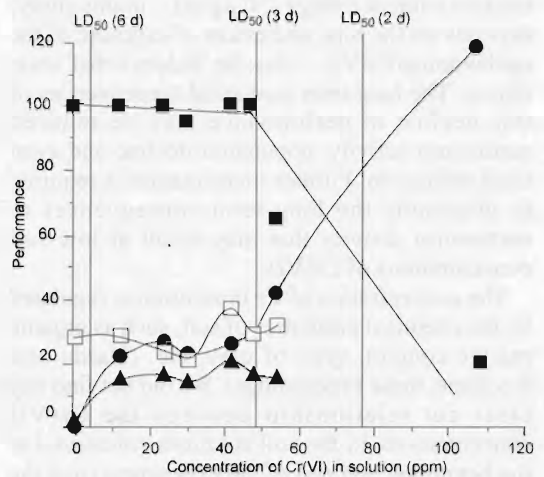
Figure 7. Changes in survival at 2, 3 and 6 days of Cr exposure in solution assays and the effect of Cr concentration on various metabolic properties of earthworms at 2 days; ■ = % survival; ● = Cr concentration; ▢ = phosphatase activity; ▲ = weight loss

biomarker that is sensitive to Cr at low concentrations, that will indicate Cr concentrations which eventually are toxic to earthworms, that can be rapidly tested for, and that is easy to interpret (Weeks 1995).

Earthworms are able to metabolically exclude Cr from their tissues up to a concentration in solution of ~50 μg mL^{-1}. Beyond this concentration, Cr levels in earthworms rise according to the concentration of Cr in solution. There is a metabolic cost involved in excluding Cr which eventually becomes too great to maintain (Fig. 7). The metabolic cost may be the energy required to actively excrete Cr from cells (van Straalen 1996) or to reduce Cr(VI) to Cr(III) (Arillo and Melodia 1991).

Earthworms are able to maintain internal concentrations of Cr at ~20 μg mL^{-1} even when external concentrations reach up to 48 μg mL^{-1}. However there is a decline in earthworm performance, as measured by phosphatase activity and change in weight even at these lower concentrations. At levels of Cr concentrations exceeding 50 μg mL^{-1}, earthworms are unable to exclude Cr and the concentration of Cr in earthworm tissues mirrors that in solution. It is not clear whether this is due to cytotoxicity of Cr to the cells or the metabolic cost of Cr exclusion. The level of Cr in solution that an earthworm cannot tolerate without dying (~50 μg mL^{-1} in this study) depends on the time and extent of exposure of the earthworm to Cr(VI) — thus the 'hidden lethal' toxic effects. The long-term ecological consequences of this decline in performance may be reduced earthworm activity, population decline and even local extinction. Further investigation is required to determine the long-term consequences to earthworm activity that may result at low soil concentrations of Cr(VI).

The concentration of Cr in solution is regulated by the chemical properties of soil, such as organic matter content, type of clay, etc. (Naidu and Kookana, these Proceedings). We did not find any clear cut relationship between the Cr(VI) concentrations in the soil solutions (measured at the beginning and end of the experiment) and the Cr accumulated in the earthworm *A. caliginosa*. The level of heavy metal accumulated in the earthworms will have depended on the solution Cr concentrations that the earthworms were exposed to during the two week incubation assay. We found a significant negative relationship between the adsorption partition coefficient (*kd*) and the concentrations of Cr accumulated in the earthworms (*kd* describes the Cr transfer between soil solution and other soil constituents). This suggests that, unlike the total Cr level in soil and static measurements of solution Cr, *kd* may be a useful measure of the bioavailability of Cr in soil. However, the potential for *kd* to be a useful measure of bioavailability needs further detailed investigation before it can be used routinely.

Conclusions

Six different bacterial types were isolated from sludge material that had shown a capacity to transform Cr(III) to Cr(VI). Purified isolates were characterised using a MIDI-FAME method and found to be *Pseudomonas fluorescens* (three colony types), *P. chlororaphis*, *Bacillus mycoides* and *B. thuringiensis*.

Using an earthworm toxicity test, LD$_{50}$ values for death of the earthworm species *Eisenia fetida* were calculated for Cr(VI). After exposure for 2, 3 and 6 days, LD$_{50}$ values were 79, 50 and 5.6 μg mL^{-1}, respectively, indicating that LD$_{50}$ values are time-dependent.

Individual earthworms of species *E. fetida* were able to maintain internal concentrations of Cr at ~20 μg mL^{-1}, even though external concentrations reached 48 μg mL^{-1}. However, at concentrations of 54 μg mL^{-1} and higher, the internal concentrations of Cr were similar to the external concentrations in solution.

After 2 days of exposure, the LD$_{50}$ value was calculated at 79 μg mL^{-1}. However, other biomarkers of earthworm performance were showing signs of stress at much lower concentrations. These measures of earthworm performance may be better than LD$_{50}$ values as indicators of the long-term impact of toxins on earthworm activity and survival in soil.

A change of soil pH from 7.2 to 5.5 reduced the concentration of Cr(VI) in solution ('bioavailable') which resulted in a declining trend in the concentration of Cr(VI) accumulated in the earthworms. The heavy metal adsorption partition coefficient (*kd*) may be a useful measure of the bioavailable level of that toxin in soil and needs further investigation.

Future research should investigate whether there are other biomarkers which could be used to predict earthworm response to toxins in soil. These could

include physiological, behavioural or ecological measures of earthworm performance.

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Management of Tannery Wastes and Effluents: Laboratory and Field Studies

Is it Safe to Use Tannery Chrome Sludge for Growing Vegetables? Results from a Glasshouse Study

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Abstract

The effect of tannery chrome sludge on the growth of three vegetable crops, namely bhendi (*Abelmosches esculentus*), brinjal (*Solanum melongena*) and chillies (*Capsicum annum*), was studied. Incubation of soils with sludge led to marked changes in the soil pH (6.8–7.9), electrical conductivity (0.11–0.83 dS m^{-1}), organic carbon and the major nutrients including N, P and K. Sludge applications also had a marked effect on plant and produce yield. In general, there was an appreciable increase in both shoot and produce yield up to a total soil chromium (Cr) concentration of 750 mg kg^{-1}; above this there was a sharp decline in yield in all the crops except chillies, but the decrease was not statistically significant compared to the control. However, the Cr uptake by the plants was significant in all the test crops. Of the total plant Cr uptake, 30–40% accumulated in shoots and 10–15% in fruits. The critical plant concentration was 30–40 mg Cr kg^{-1} dry matter. Above this level, toxicity symptoms were recorded that persisted throughout the growth period.

THERE is increasing interest in the agricultural application of sludge obtained from waste water treatment plants, because of the possibility of recycling valuable components such as organic matter, N, P, K and other nutrients (Sommers 1977). An increase in crop yield often exceeding that of well managed fertilized controls has also been reported by many researchers (e.g. Moreno et al. 1996).

The tannery industries discharge about 50 000–60 000 t of sludge as biological wastes in India each year (Rajamani and Buljan 1997). The sludge retains 40% of the chromium (Cr) used during the manufacturing processes. The discharge of this sludge has already degraded over 50 000 ha of agricultural land in Tamil Nadu, India (Naidu and McLaughlin 1993). The major problems associated with soils contaminated with tannery waste include high salt and Cr contents. These are of concern because of phytotoxicity and heavy metal accumulation in the plant tissues (Chaney 1990). Also there is a possibility that Cr will be translocated and accumulate in the produce. The present study aimed to analyse the influence of tannery sludge applications on soil, vegetable yields and the uptake of Cr by the plants.

Materials and Methods

Soil

Surface soils (0–15 cm) were sampled from Vaduganthangal, air dried and crushed to pass through a 2 mm sieve. The sieved soils were homogenised and randomised before being used in the growth studies. Pertinent properties of the study soils are listed in Table 1.

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Table 1. Soil and sludge characteristics

Parameters	Soil	Sludge
pH	6.85	7.86
EC (dS m^{-1})	0.11	3.50
Organic carbon (%)	0.16	9.56
Nitrogen (%)	0.08	0.43
Phosphorus (%)	0.33	0.51
Potassium (%)	0.19	0.004
Calcium (mg kg^{-1})	5332	8000
Chromium (mg kg^{-1})	38.4	812
Chlorides (mg kg^{-1})	8.29	287
Sulfate (mg kg^{-1})	6500	40000

Table 2. Treatment details

Treatments	Wt of sludge added (kg pot^{-1})	Amount of Cr added (mg kg^{-1})
T1	0	0
T2	0.92	750
T3	1.85	1500
T4	3.7	3000

Sludge

Chrome sludge accumulating after the waste water treatment process was collected from RSL tannery, Virinjipuram, Tamil Nadu, India. It was air dried, passed through a stainless steel 2 mm sieve and analysed for its nutrient status and other characteristics (Table 1). The amount of sludge added to soils ranged from 0 to 3.7 kg pot^{-1}. This corresponded to Cr concentrations ranging from 0 to 3000 mg kg^{-1} soil (Table 2). The soil–sludge mixture was transferred to pots at 5 kg pot^{-1} and incubated for a week at field moisture capacity. The control treatment (three replicates) had no addition of chrome sludge. After completion of the experimental study, the results were analysed statistically in a randomised block design.

The experimental crops chosen were brinjal (*Solanum melongena*), bhendi (*Abelmosches esculentus*) and chillies (*Capsicum annum*) because these are the major crops grown in the region polluted by tannery effluent.

Growth studies

The crops were grown from seed in controlled glasshouse conditions. Three weeks after germination the seedlings were thinned to two plants per pot. Following the establishment of the seedlings, soil was kept at field moisture capacity using double-distilled water. The study period lasted five months. The fruits were collected at the reproductive stage and weighed. At the end of the study period the crops were harvested, thoroughly washed and dried.

Soil and sludge analysis

The soil and sludge was dried and sieved (2 mm) before analysis. The pH, electrical conductivity (EC), chlorides, sulfates and water extractable Cr were measured in subsamples in 1:5 soil:water suspension following end-over-end shaking for 12 h. The total organic carbon was measured by chromic acid wet digestion (Walkley and Black 1934), available N was measured by the alkaline permanganate method, available P by the Olsen et al. (1954) method, and available K by the ammonium acetate extraction method (Piper et al. 1966).

Subsamples of the soil and sludge were ground, passed through a 2 mm sieve and subjected to nitric–hydrochloric digestion for the analysis of macronutrients and total Cr content.

Plant analysis

The oven dried plant samples were digested in aqua regia (HCl:HNO$_3$ 3:1) for 1.5 h, and analysed both for total Cr content and for macronutrients. The roots, shoots and fruits were separately dried, ground in a pestle and mortar, and digested in aqua regia, after which the total Cr concentration was estimated by atomic absorption spectrophotometer using air acetylene flame.

Data analyses

The data were analysed statistically using a randomised block design and GENSTAT.

Results and Discussion

Composition of the sludge

The tannery sludge was alkaline (pH 7.89) with an EC of 3.5 dS m^{-1}. Its organic carbon, nitrogen, phosphorus and calcium contents were high (Table 1). The sludge contained high levels of Cr, chlorides and sulfates. These results are not

Table 3. Effect of sludge on soil characteristics

Treatments	pH	EC (dS m^{-1})	Organic carbon (%)	Ca (mg L^{-1})	Water extractable Cr (mg kg^{-1})
Control	7.1	0.28	1.2	80.1	0.188
S1	7.2	0.35	1.3	100.1	0.4
S2	7.6	0.46	2.2	120.1	2.23
S3	7.9	0.61	3.9	160.1	3.38

surprising given the large number of chemicals added during the skin preservation and leather tanning processes. However, the high nutrient content may be beneficial to plant growth. The sludge Cr content is of concern especially if the Cr is bioavailable.

Effect of sludge on soil properties

The addition of sludge to the soil at several rates changed the characteristics of the soil (Table 3). There was an increase in soil pH from 7.2 to 7.9, EC from 0.35 to 0.61 dS m^{-1}, organic carbon from 1.3 to 3.9% and Ca from 100.1 to 160.1 mg L^{-1}. The water extractable Cr also increased from 0.19 mg kg^{-1} in the control to 3.38 mg kg^{-1} at the highest sludge application rate.

Effect of sludge on plant characteristics

With regard to fruit yield, the lowest Cr treatment resulted in an apparent but non-significant increase in the yields of brinjal and bhendi (Fig. 1). Treatments with sludge Cr at levels exceeding 1500 mg kg^{-1} resulted in 40–50% decrease in yield compared to control treatments. However, the sludge treatments did not significantly affect the yields of the vegetable crops tested (Fig. 1). Examination of the water extractable nutrients suggested that the treated soils were sufficient in nutrients. Therefore, the major factor responsible for yield reduction may have been the accumulation of Cr in plants. Deleterious effects due to the accumulation of Cr in soils have been reported for various crops including radish, *Raphanus sativus* (Yiyong et al. 1989), ryegrass, and clover (Nishimura and Takayashi 1982).

Plant Cr uptake

The amounts of Cr taken up by plants varied considerably both between plant species and between rates of sludge application. The Cr uptake was least in chillies, intermediate in brinjal, and greatest in bhendi. Accumulation by bhendi was 2–3 times higher than the other crops. These results suggests that bhendi is a more effective absorbent of Cr than the other crops and may not be appropriate for cultivation in Cr-contaminated soil.

Increase in sludge application rate led to an appreciable increase in Cr uptake by plants (Fig. 2).
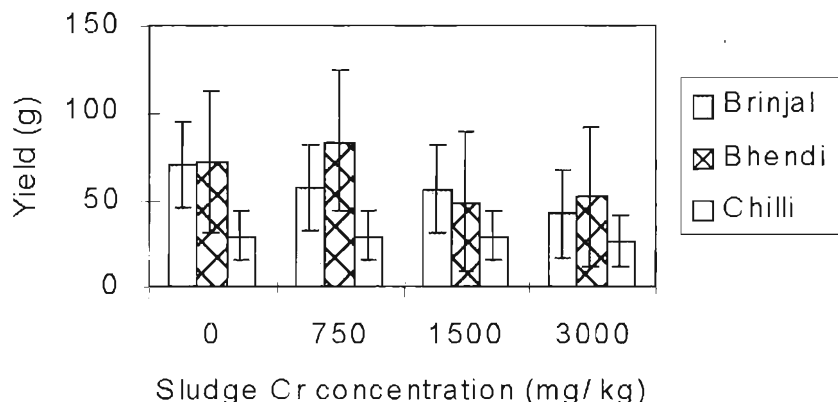
Figure 1. Effect of sludge Cr on the growth of selected commonly used vegetables
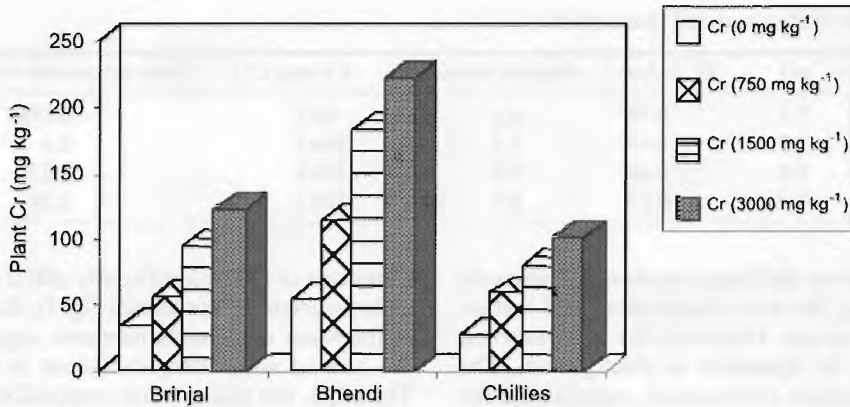
Figure 2. Effect of sludge Cr on Cr uptake by selected commonly used vegetables

The increased uptake may be attributed both to increased Cr in the soil solution and to the alkaline pH of the soil at the higher applications of sludge. The data showed elevated levels of Cr in soil water extracts from treated soils. Since a large proportion of soluble Cr is present as Cr(VI) it is likely that this factor enhances Cr uptake by plants. Numerous investigations have demonstrated the importance of soil pH in plant absorption of heavy metals (e.g. Moraghan and Mascagni 1991). In alkaline soils, Cr can exist as Cr(VI) and is more readily available to the plants than in acidic soils in which precipitation of Cr may decrease Cr availability (Losi et al. 1994). Apart from pH, the redox potential, cation exchange capacity, organic matter, ligand ions and dissolved organic carbon of the soil have also been reported to play major roles in

Cr uptake by plants (Sumner and Naidu 1997). Analyses of soil water extracts of treated soils show that most of these parameters increased with increasing sludge application rate.

The amount of total Cr in soil was directly and significantly correlated with plant Cr uptake in all the vegetable crops (LSD = 6.27, 4.9, 1.37 for root, shoot, fruit, respectively). This was surprising because the bioavailable fraction is the most labile component that is directly available for plant uptake. However, total Cr content of the soils may also control the concentration of Cr in the soil solution through the quantity–intensity relationship and the partition coefficient. Thus, in soils with the same partition coefficient, increasing total Cr content would lead to increased soil solution concentration. Of the total Cr added to the soil,
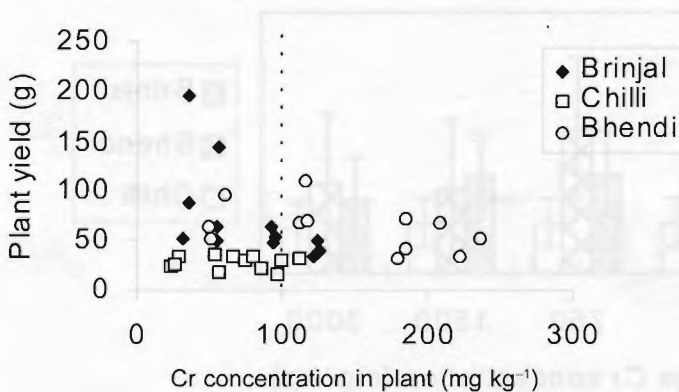
**Figure 3.** Relationship between plant tissue Cr concentration and plant yield
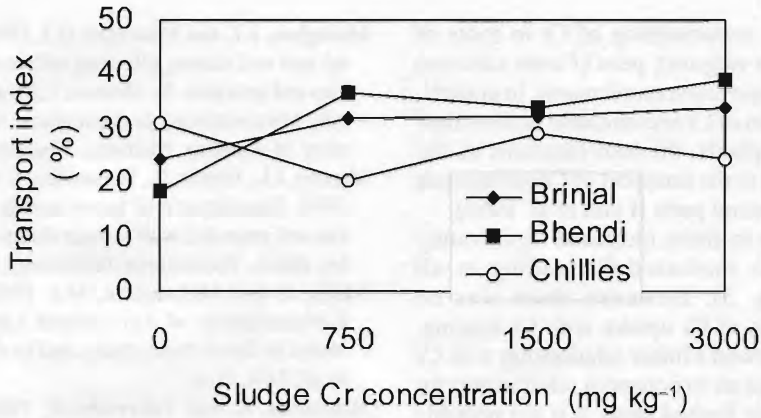
Figure 4. Effect of increasing sludge Cr concentration on the Cr transport index

4–7% was taken up by the plants, with least uptake by chillies. Keefer et al. (1986) made similar findings using field lysimeters. They demonstrated that the uptake of Cr by alfalfa (*Medicago sativa*) in loamy soils was directly correlated with the Cr content of the soils. These investigators, however, reported that less than 1% of the total Cr was taken up by plants due to increased application of sewage sludge to the sandy loam soils.

In the present study, comparison of the plant Cr uptake and yield data showed that the critical plant Cr concentrations were 100 mg kg^{-1} for bhendi and 55 mg kg^{-1} (Fig. 3) for brinjal. Beyond these levels, marked decreases in yield were observed.

Root–shoot relationship

The transport indices of the Cr for brinjal, bhendi and chillies (Fig. 4) ranged from 21% to 39%, which confirmed the higher accumulation of Cr in the roots. The roots of bhendi accumulated more Cr than those of the other plant species. Further, the transport index remained constant even with increased application of sludge. This implies that the root–shoot Cr ratio remained the same for all the crops and was independent of the amount of total Cr added to the soil. The roots retained 40–50 mg Cr kg^{-1}. There existed direct and significant correlations among Cr uptakes by roots, shoots and fruit of all crops. Ramachandran et al. (1980) also
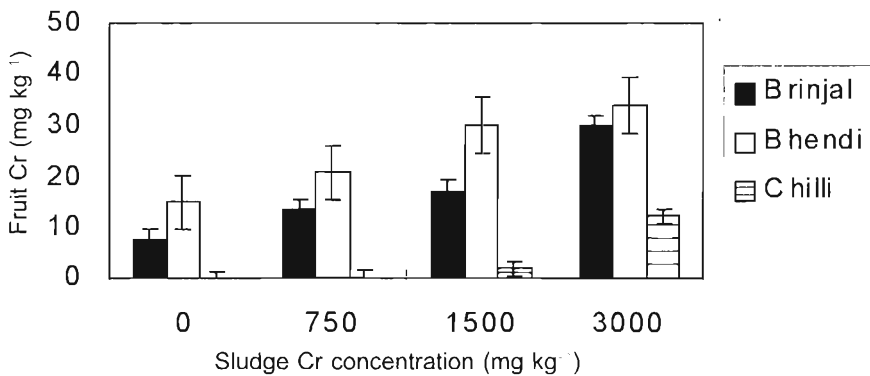
Figure 5. Effect of increasing sludge Cr concentration on the Cr content of vegetable produce

observed higher accumulation of Cr in roots of barley (*Hordeum vulgare*), peas (*Pisum sativum*) and tomato (*Lycopersicon esculentum*). In general, a larger proportion of Cr accumulated in roots than shoots. In most plants, the root functions as the important barrier to the transport of Cr compounds into the aboveground parts (Lyon et al. 1969).

The Cr uptake in fruits increased significantly ($P < 0.05$) with increased Cr loading in all vegetables (Fig. 5). However, there was no consistent pattern of Cr uptake with Cr loading. While brinjal showed a linear relationship with Cr loading, there was an exponential relationship for chillies. From this limited study it is not possible to explain the exponential uptake by chillies. The total uptake accounted for only 1% of the total available concentration. Among the crops tested, chillies recorded the lowest accumulation (0.4%) of the total Cr in soil. Apart from total Cr available in soil, the water extractable Cr also plays a major role in Cr uptake by plants.

Summary and Conclusion

The results of this study confirmed that there is uptake of Cr by plants when tannery chrome sludge is applied to the soil. Transport indices also confirmed this trend. However, further studies are warranted to confirm the complementary effects of other nutrients such as calcium and phosphorus on Cr uptake by plants. It is mainly the nonconsumable parts, especially the roots, that accumulate the Cr. However, because the edible parts contain some of the Cr uptake, it is necessary to understand the consumer use efficiency so that the risks involved can be understood.

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Soil–plant Transfer of Chromium from Tannery Waste Sludge: Results from a Glasshouse Study

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Abstract

The effect of tannery waste sludge on the growth of clover (*Trifolium fragiferum*) and on soil solution chemistry of three acidic soils from South Australia was investigated in a replicated glasshouse study. The composition of the sludge material varied considerably. Chromium (Cr) concentrations ranged from 1% to 3% with similar variation in the concentrations of lime and major and minor nutrients. Incubation of soils with varying amounts of sludge led to significant ($P < 0.001$) changes in pH (from 5 to >7), and soil solution concentrations of Cr (12–222 µg mL^{-1}) and all the major and minor nutrients. Scatter plot diagrams together with correlation studies revealed a strongly significant ($P < 0.001$) relationship between soil solution Cr and pH and Cr and manganese (Mn) ions. The strong relationship between Cr and Mn may indicate Mn(IV)-induced oxidation of Cr(III) in these soils. Pots of the study soils were seeded with clover and germination was recorded in all treatments. However, seedling emergence and plant shoots in 'high' treatment pots showed symptoms similar to those induced by metals such as aluminium. These symptoms persisted throughout the growth period. Markedly smaller yields were recorded at sludge applications exceeding 4 g kg^{-1} in two sludge treatments and 2 g kg^{-1} in the other sludge treatment. Examination of the plant composition data and the soil solution Cr concentrations showed severe toxic effects of Cr on plant growth in soil solutions exceeding 40 µg Cr L^{-1}. These results confirm the toxic effect of Cr on plant growth. The Cr concentrations of plant tissues also increased initially with sludge application and then decreased at high sludge additions. The decrease was mainly related to the Cr toxicity to plant roots.

THE tanning industry generates approximately 50 000 t of solid waste per year from chromium-mediated leather tanning in India and the surrounding countries (Ramasamy, these Proceedings). Approximately 60% is waste water from hair removal and tanning operations. While tannery wastes in many industrialised countries are disposed of in landfills, trenches or lagoons, in developing countries these wastes have been released onto land and into freshwater bodies.

The sludge and effluent wastes consist of heavy metals such as cadmium, chromium (Cr), copper,

nickel, lead and zinc, so the disposal sites must be carefully managed to ensure minimal percolation of water and to control trace element mobility that may be hazardous both to plants and to human health. Of the heavy metals present in the tannery waste, Cr is of particular concern because of its high concentrations in the waste material. However, the Cr added during the tanning process is in the non-toxic trivalent form. Numerous investigators (Bartlett and Kimble 1976a,b; Bartlett and James 1979; Ciavatta and Sequi 1989) have shown that the environmental pollution risks induced by the presence of Cr(III) in soils are very low. Given that the major factors controlling Cr reduction in soils include low Eh and the presence of organic matter, the likelihood of Cr(III)

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Table 1. Mean pH, EC and chemical composition of three sludge samples (M1, M2, M3); all concentrations are in mg kg^{-1} sludge except where indicated

	EC dS m^{-1}	pH	CaCO$_3$ %	Ca %	Cr %	Cu	Fe	K	Mg	Mn	Na	P	S %	Zn
M1	4.84	8.81	32.3	12.8	1.44	11	1473	510	2.82%	1152	2890	1990	0.97	102.5
M2	35	7.71	11.7	4.7	3.04	66.5	1.09%	3549	1852	1.32%	4.67%	4032	1.89	467
M3	3.33	9.44	50.3	17.9	1.15	8.5	2829	269	1.88%	1.00%	6719	1438	0.91	142

oxidation to Cr(VI) has been claimed to be low (Money 1991). This was also evident from Chaney et al. (1991) who found no Cr build up in soils below the zone of tillage and no increase in Cr in plants beyond the first crop year following land application of sewage and tannery sludges as fertilizers. These findings indicate that Cr(III) binds strongly to soil colloid particles, and they contrast with the observations of Bartlett and James (1988) who have demonstrated that Cr(III) in tannery wastes can oxidise to Cr(VI) in soils.

Although Cr(III) is not itself a hazard, the potential for oxidation to Cr(VI) can make it a significant threat to the environment. In natural systems, manganese (Mn) oxides have proved to be the only compounds capable of oxidizing Cr(III) to Cr(VI) (Bartlett and James 1979; Nakayama et al. 1981; Saleh et al. 1989; Johnson and Xyla 1991). Therefore, any conclusions regarding the disposal of tannery wastes must consider the presence of manganese oxides in the natural system. Although Money (1991) argues against the potential for Cr(III) oxidation in the sludge and soil system, she ignores the presence of MnSO$_4$ that is added to control odour during the waste treatment process. Preliminary studies in our laboratory reveal the presence of high concentrations of Mn and Cr(VI) in leachates from a number of tannery industries in Australia. The Cr(VI) detected in surface and groundwaters at tannery waste disposal sites in Australia (Naidu et al., these Proceedings) and in India (Handa 1988; Mahimairajah et al., these Proceedings) is of concern, especially where people depend solely on groundwater for their drinking supplies.

The phytoavailability of Cr added to soils is generally low (Huffman and Allaway 1973; Cary et al. 1977a,b; Bartlett and James 1988), with little Cr translocated to plant tops and edible plant parts.

Huffman and Allaway (1973) studied Cr uptake using Cr-51 labelled Cr(III) and Cr(VI) in bean and wheat plants grown in nutrient solution. At maturity bean plants could remove as much as 55% and wheat plants as much as 81% of the added Cr-51. More than 90% of the Cr taken up by the crops remained in the roots. Similarly, the Cr concentration in corn leaves was not affected by application to soil of up to 5860 mol Cr ha^{-1} in sewage sludge (Mortvedt and Giordano 1977). Although these studies indicate minimum translocation of Cr from root to shoot, recent studies on Cr uptake by onions (Srivastava et al. 1994) and maize (Mishra et al. 1995) found significantly higher uptake of both forms of Cr when supplied through irrigation water. This suggests greater bioavail-ability of Cr in the presence of irrigation water.

The conflicting data on Cr uptake from sludge material necessitate further investigation of the potential phytoavailability of Cr in tannery waste sludges. This is also important if guidelines are to be set up for the disposal of tannery wastes. Guide-lines for the re-use of sludge in agriculture in USA, developed by the US EPA (503 regulations; USEPA 1993) have identified that plant phytotoxicity is the major limiting pathway for regulation of Cr applications to soil, and that risk to human or animal health is minimal. A cumulative threshold rate of 3000 kg ha^{-1} has been suggested. However, regulations have been based mostly on studies of municipal sewage sludges, with only a few reported studies of crop uptake of Cr from tannery wastes or smelter emission contamination (Wickliff et al. 1982; Stomberg et al. 1984) being used to develop the guidelines. In this study we investigate the effect of sludge incorporation on the growth of clover (*Trifolium fragiferum*) in three agricultural soils from South Australia.

Table 2. Rates of sludge and Cr added to Bordertown soil for the growth study

Treatment	Amount added (g kg⁻¹)	Cr in sludge (mg kg⁻¹)	CaCO₃ in sludge (mmol kg⁻¹)
Sludge M1	3.1	52	20
	7.74	130	50
	31	521	200
Sludge M2	2.14	72	5
	6.41	215	15
	17.1	573	40
Sludge M3	1.5	19	15
	4	50	40
	20	248	200
K₂Cr₂O₇	0.141	50	na
	0.354	125	na
Control	0	0	0

Rates of Cr added to other soils were identical but the amount of sludge added varied slightly among the soils depending on the total Cr content of the sludge

Materials and Methods

Sludge

Bulk samples of sludge were obtained on three occasions from a tannery in South Australia. The samples were air dried and ground to pass through a 2 mm mesh stainless steel sieve, and then stored in polyethylene bottles for subsequent chemical analyses and plant growth studies. Some chemical properties of the three sludge materials M1, M2 and M3 are given in Table 1. The sludges contained 1.7%, 3.3% and 1.2% Cr, respectively.

Table 3. Lime added per treatment for the incubation study

Treatment	Amount added (mmol(+) kg⁻¹ soil)	Amount added (g kg⁻¹ soil)
Control (L0)	0	0
Lime (L1)	10	0.05
L2	25	1.25
L3	40	2
L4	60	3
L5	100	5
L6	150	7.5
L7	200	10

Soils

This investigation was conducted using soils with different chemical and physical properties from three sites in South Australia: Bordertown, Kapinnie, and Cooke Plains. Soil samples (collected at 0–10 cm depth) were air dried, passed through a 2 mm stainless steel sieve and stored in polythene bottles for laboratory incubation and glasshouse studies. The pH of the soils ranged from 4.5 to 5.1 (1:5 suspension of soil in 0.01 M CaCl₂) and all soils were classed as Duplex (Australian soil classification) or Xeralf (US soil taxonomy).

Preparation of soils

Incubation with sludge samples

The prepared sludge samples (M1, M2, M3) were added to separate 1 kg samples of the three soils at rates based on the USEPA regulations and depending on the Cr content of the sludge material. The concentrations of Cr added in the sludge ranged from 19 to 573 mg kg⁻¹. After thorough mixing, the soils were moistened to field capacity and incubated in pots, with provision for aeration at a temperature of $20 \pm 2°C$, for four weeks. All treatments were replicated four times. The sludge treatments are listed in Table 2.

Incubation with lime

All tanning involves application of lime during the waste treatment and leather tanning process, so incubation of soils with sludge resulted in significant ($P < 0.001$) increases in soil pH and lime levels. Each of the three soils was initially assessed for this expected increase in soil pH by adding varying amounts of CaCO₃ (Table 3) to 50 g soil samples, at field moisture capacity, and then incubating them at 60°C (Barrow and Cox 1990). The pH was measured in 1:5 suspensions of soil : 0.01 M CaCl₂ in subsamples taken at 0, 5, 30, 54 and 96 hours. Buffer curves were drawn from which the amounts of CaCO₃ needed to effect prescribed pH shifts could be calculated for sludge incubation studies.

To examine the effect of lime on plant growth and uptake of Cr, subsamples of the Kapinnie soil were also incubated with lime (AR grade CaCO₃). The lime additions were based on the amounts of CaCO₃ added through sludge applications, and ranged from 15 to 200 mmol (+) CaCO₃. Two levels

of Cr (20 and 50 mg kg⁻¹ soil) were added to the lime-treated Kapinnie soil. All treatments were replicated four times.

Glasshouse study

Because the sludge samples contained several major and minor nutrients that are essential for plant growth (see Table 1), major and minor nutrients were added to an additional four replicates of each soil to monitor plant growth without sludge. Also Cr(VI) was added as potassium dichromate (at 50, 125, 500 or 3000 mg kg⁻¹ soil) to the Bordertown soil pots.

Seeds of clover (*T. fragiferum*) were sown in these pots and in the pots containing the soils incubated with sludge or lime. Two weeks after germination, the plants were thinned to six plants per pot. Plants were watered daily, to keep the soil moisture at about field capacity. Plastic beads were arranged on the soil surface to prevent plants being contaminated with soil from splashes during watering. Twelve weeks after germination the plants were harvested, washed thoroughly to remove any adhering soil, and dried for 2–3 days at 65°C. They were ground and stored in sealed plastic bags ready for chemical analyses. Sub-samples of the soils were air dried, passed through a 2 mm sieve and stored in polypropylene bottles.

The growth and Cr uptake of the clover plants were compared between soil treatments.

Chemical analyses

Soils

Before use and after harvest, the pH and electrical conductivity (EC) of the incubated soils were measured in water, at a soil:solution ratio of 1:5, using a combination glass electrode. Total Cr concentrations in all soil samples were estimated following a 2 hour digestion in aqua regia. The digested samples were filtered and then analysed. Chromium was determined by graphite furnace atomic absorption spectroscopy; Mn was determined by flame atomic absorption spectroscopy; remaining elements were determined by inductively coupled plasma emission spectroscopy.

Plants

The total Cr content of the ground plant samples was estimated following digestion in nitric acid. The samples were analysed using graphite furnace atomic absorption spectroscopy.
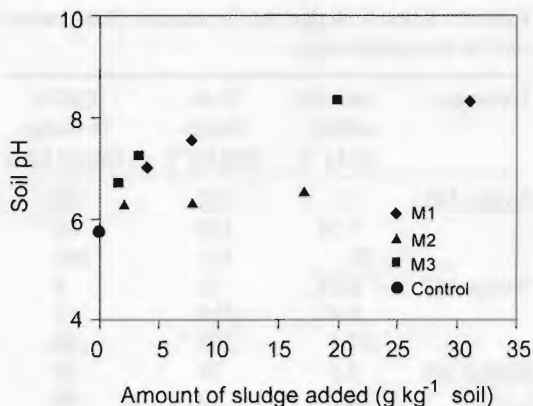
Figure 1. Effect of sludge on the pH of study soils

Statistical analyses

The data were analysed statistically using a randomized block design and GENSTAT.

Results and Discussion

Chemical characteristics of sludge

The data in Table 1 show that the sludge materials were alkaline in reaction (pH 7.7–9.4 in water) and contained a wide range of elements which are essential for plant growth. The concentrations of phosphorus (P) and sulfur (S) ranged from 1400 to 4000 mg kg⁻¹ and 0.9% to 1.90%, respectively. A large proportion of P was available in water extracts. The concentrations of calcium (Ca; 5–18%), magnesium (Mg; 0.2–2.8%), sodium (Na; 0.3–4.7%) and Mn (0.1–1.3%) were extremely high. This is not surprising given that lime, Na and Mn salts are added during the waste treatment process. As with P and S, large proportions of these metals were extractable in water. A wide range of trace metal ions were detected in the sludge samples. The concentration of Cr was also very high, ranging from 1.2% (M3) to 3.3% (M2).

Apart from high Na and Cr concentrations most of the ionic species present in the sludge have beneficial effects on soil physical properties and plant growth. Thorstensen and Shah (1979) analysed wastes from four tanneries and reported a similar composition in sludges: concentrations ranged from 3 to 5% for total N, 5 to 143 mg kg⁻¹ for Zn, 5 to 323 mg kg⁻¹ for Pb and <0.01 to 2% for Cr. Conrad et al. (1976), however, reported

Table 4a. Effect of sludge added at various rates (g kg⁻¹ soil) on soil solution composition of the Bordertown soils (EC in dS m⁻¹, Cr in μg L⁻¹ and all other ions in mg L⁻¹)

Sludge	Rate	pH	EC	Cr	Ca	Mg	K	Mn	P	S	Na	Zn
Control	0	5.59	0.04	4.2	9.6	2.5	4.5	0.15	0.54	1.7	39.3	0.12
M1	3.1	6.61	0.05	28	37.8	13.8	2.7	0.12	0.9	5.6	39.9	0.09
	7.74	7.59	0.12	60	127	61	1.9	0.14	0.9	16.6	58.8	0.12
	31	8.19	0.42	127	157	226	9.9	0.22	6.1	79.6	151	0.57
M2	2.14	6.00	0.13	20	50.4	12.3	16.8	1.8	0.33	36	206	0.90
	6.41	5.89	0.45	38	245	39.6	51	25.8	0.42	116	756	0.39
	17.1	6.76	0.72	71	526	58.8	82	59.3	0.57	247	1960	0.36
M3	1.5	6.64	0.03	12	17.4	3.5	3.7	0.10	0.60	13.8	57.6	0.06
	4.0	7.23	0.08	15	87.8	21.8	5.4	0.27	0.52	69.6	82.6	0.06
	20	8.25	0.31	70	200	77.4	10.8	1.4	0.72	167	207	0.18

15.5–75.0 mg Cr, 0.05–5.8 mg Cu and <10–800 mg Pb per kilogram of dry matter. These results suggest that while the concentrations of metals are usually high, they vary considerably between tanneries and that therefore caution must be exercised during the disposal of such wastes.

Effect of treatments on soil chemical properties

Sludge

Incubation of soils with sludge had a marked effect on soil chemical properties. In general, soil pH increased from 5.6 in the control samples to >7 at the highest rate of sludge application (Fig. 1). Thus application of sludge material to acid soils could reduce potential toxicity of native or applied metals such as Al, Mn, Zn or Cu (Jackson et al. 1967).

Repeated application of sludge with high CaCO₃ content might produce strongly alkaline conditions and limit availability of such nutrients as P and Zn (Naidu et al. 1990).

The effect of sludge on other soil properties was more pronounced than the effect of lime at the rates used. Incubation of soils with sludge caused an almost two-fold increase in the cation exchange capacity (CEC) of the soils relative to the control samples whereas with the addition of lime the effect was less marked (data not shown). This increase in CEC may be attributed to the greater organic matter content of the sludge samples and the subsequent increase in soil organic matter following incubation. Wickliff et al. (1982) reported marked increases in the amounts of humic substances and total N in soils treated with tannery sludge.

Table 4b. Effect of sludge, added at various rates (g kg⁻¹ soil), on the soil solution composition of the Kapinnie soils (EC in dS m⁻¹, Cr in μg L⁻¹ and all other ions in mg L⁻¹)

| Sludge	Rate	pH	EC	Cr	Ca	Mg	K	Mn	P	S	Na	Zn
Control	0	5.86	0.04	4	13.6	3.4	14.8	0.15	1.1	5.9	35.6	0.11
M1	3.86	7.09	0.06	37	50.7	18.3	21.6	0.36	0.75	44.1	61.8	0.04
	7.74	7.61	0.13	40	134	59.7	37.5	0.15	0.87	118	98.7	0.06
	31	8.32	0.36	132	262	272	58.6	0.26	1.1	286	185	0.11
M2	2.14	6.26	0.13	18	42.2	10.2	33.4	1.1	0.5	26.8	180	0.08
	7.7	6.33	0.36	40	186	35.4	78	6.4	0.48	126	603	0.24
	17.1	6.57	0.76	70	421	58.8	125	32.5	0.6	235	1120	0.18
M3	1.5	6.72	0.05	23	18.4	4.6	18.7	0.21	1.1	12.4	49.0	0.54
	3.5	7.21	0.06	30	50.9	12.4	18.5	0.45	1.64	36	69.6	0.30
	20	8.34	0.42	51	453	138	75.6	0.91	0.85	181	230	0.35

Table 4c. Effect of sludge added at various rates (g kg^{-1} soil) on soil solution composition of the Cooke Plains soils (EC in dS m^{-1}, Cr in µg L^{-1} and all other ions in mg L^{-1})

Sludge	Rate	pH	EC	Cr	Ca	Mg	K	Mn	P	S	Na	Zn
Control	0	6.24	0.03	11	12.7	2.5	5.1	0.18	0.33	3.1	23.9	0.11
M1	3.86	6.91	0.04	87	36	10.2	3.6	0.12	0.36	15.6	19.2	0.24
	5.42	7.03	0.06	122	92.2	33.9	4.3	0.51	1.3	26.2	27.2	0.19
	31	8.52	0.28	222	162	260	4.3	0.43	1.4	279	71	0.75
M2	2.14	6.81	0.09	27	45	6.6	5.4	0.58	0.72	23.1	144	0.12
	6.4	6.98	0.17	55	70	8.1	10.8	1.3	0.78	51	301	0.06
	12.8	7.49	0.24	82	103	1	30.0	4.1	1.7	82.2	506	0.12
M3	1	6.57	0.04	35	27.6	4.1	5.3	0.49	1.1	3.8	26.2	0.06
	2.5	7.36	0.05	18	45.3	8.7	13.8	0.15	1	9.9	36	0.12
	20	8.41	0.13	218	88.4	36.8	6.8	0.4	0.6	48	81.2	0.32

As expected there was also a pronounced increase in the soil solution concentration of Ca, Mg, Na, K, Cr and S (Tables 4a,b,c). The increased concentrations of the major nutrients reflect an increase in the intensity and the quantity of these species in the soil following sludge additions. Because plant roots are dependent on the nutrient intensity (i.e. nutrient concentration in the soil solution), the marked increase in this parameter following sludge additions suggests that sludge could have a larger impact on crop growth than lime. However, as well as increased concentrations of the essential elements, sludge additions also led to pronounced increases in the concentrations of Cr and Cl.

Effect of lime on soil properties

Lime applications led to a significant ($P < 0.001$) increase in the pH of all soils. Depending on the rate of application, the soil pH increased from <5 in the control samples to >7 at the highest lime rate (Fig. 2). In keeping with the increased pH, the CEC (data not reported here) of all soil samples also increased although the changes were not as marked as with sludge applications. Unlike sludge-treated soils, the soil solution concentrations of all major cations (except Ca) and minor cations decreased with increasing lime rate, while the nutrient anions increased with increasing rates of
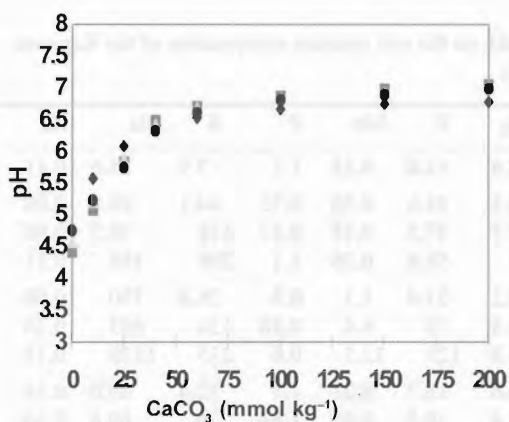
Figure 2. Effect of lime on the pH of soils in this study

$$y = 0.099e^{0.8498x}$$
$$R^2 = 0.553^{***}$$
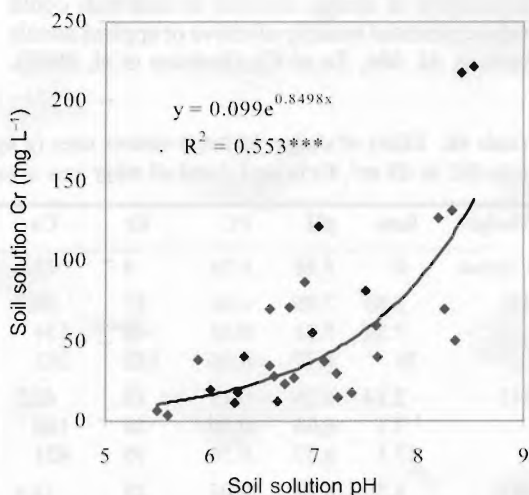
Figure 3. Relationship between soil solution pH and Cr(VI) in sludge-treated soils
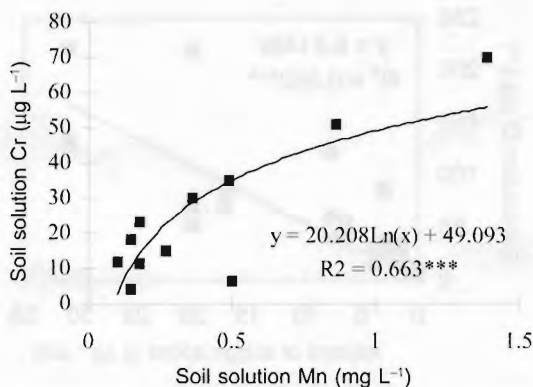
Figure 4. Relationship between Mn and Cr(VI) in soil solution in Bordertown soil treated with sludge M3

application. These trends confirm many previous observations on the effects of lime on the surface chemical properties of soils (e.g. Naidu et al. 1990).

Relationship between soil solution pH, Cr and Mn

There was a significant ($P < 0.001$) relationship between soil solution pH and the total concentration of Cr in the soil solution (Fig. 3). Increasing soil solution pH led to a marked increase in the concentration of Cr, and greater than 95% of Cr was present as Cr(VI). Given that Cr(VI) is the toxic form of Cr, the increase in solubility with pH indicates increased bioavailability with sludge applications and with liming. Examination of the soil solution Mn data reveals a significant relationship with soil solution Cr (Fig. 4). These results indicate that soil solution Mn concentration is related to increased availability of Cr(VI) suggesting Mn-mediated oxidation of Cr(III) in the sludge-amended soils.

Effect of sludge on plant growth

There was a significant ($P < 0.001$) effect of sludge on plant growth in all soils (Fig. 5; only typical trends presented). In general, increasing amounts of added sludge led to an increase in the dry matter yield to a maximum value and then a decline.

The sludge level at which maximum yield occurred varied both between the soils and between sludges. For the Bordertown soil, maximum yield occurred at the lowest level of sludge addition whereas for the Cooke Plains soil, highest yield
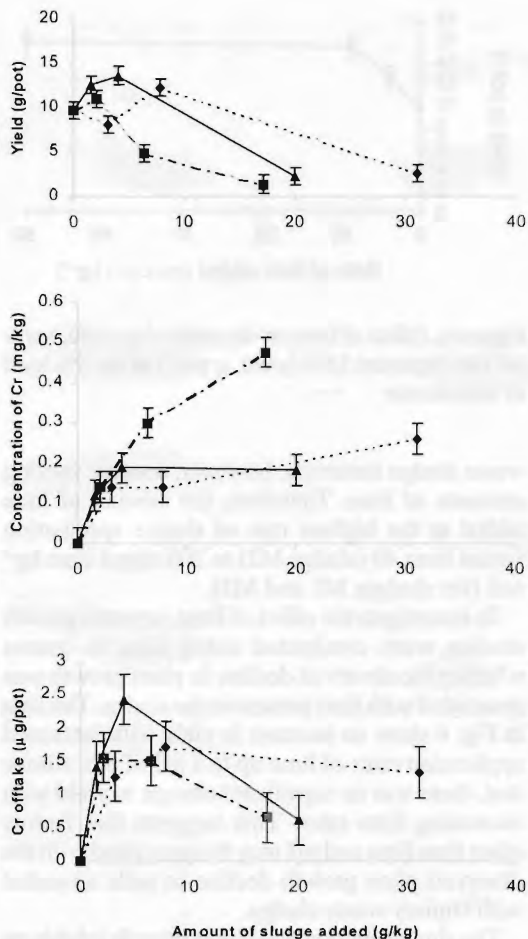
Figure 5. Plant yield (g pot [-1]), Cr concentration in plant tissue (mg kg [-1]) and Cr uptake (µg pot [-1]) by clover plants grown in soil from Kapinnie (◆ = sludge M1; ■ = sludge M2; ▲ = sludge M3)

occurred at the medium level sludge additions. These sludge levels corresponded to pH values of 5.9–6.6 for Bordertown soil, 6.3–7.2 for the Kapinnie soil and 6.9–7.4 for the Cooke Plains soil. The pH at which yield decline occurred generally varied between 5.9 and 6.5. These pH values also correspond to lime-induced crop decline in strongly weathered soils, which has been reported by numerous investigators (e.g. Naidu et al. 1990). These investigators found that plant growth was adversely affected at low and high pH values even in the presence of added P. Tannery
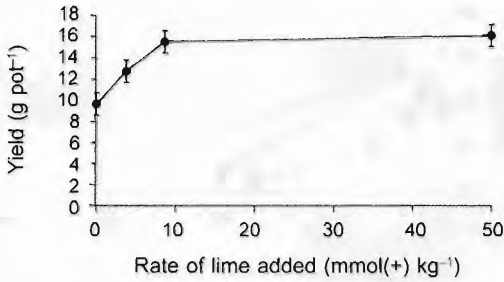
Figure 6. Effect of lime on dry matter top yield; vertical bars represent LSD (yield, g pot⁻¹) at the 5% level of significance

waste sludge materials, however, contain varying amounts of lime. Therefore, the amount of lime added at the highest rate of sludge application varied from 40 (sludge M2) to 200 mmol lime kg⁻¹ soil (for sludges M1 and M3).

To investigate the effect of lime, separate growth studies were conducted using lime to assess whether the observed decline in plant growth was associated with lime present in the sludge. The data in Fig. 6 show an increase in yield with increased application rates of lime up to a pH of 6.6. Above that, there was no significant change in yield with increasing lime rates. This suggests that factors other than lime and pH may be associated with the observed plant growth decline in soils amended with tannery waste sludge.

The sludge material itself is extremely inhibitory to plant growth and concentrations exceeding 2–8 g sludge per kg soil reduced shoot growth by 40–50% and caused stunting at the highest rate of application, i.e. 2–3% (w/w). This contrasts with many previous studies on plants grown in soils amended with either Cr(III) as soluble Cr(OH)₃, or tannery wastes, or sewage sludge. Also, in the previous studies, there was no effect of sludge on plant tissue Cr concentrations. The concentrations of Cr in plant tissue in treated soils were often similar to the Cr concentrations in control plants (Bolton 1975; Cunningham et al. 1975; Cary et al. 1977a,b, 1983; Kelling et al. 1977; Lahouti and Peterson 1979; Sykes and Earl 1981; Stomberg et al. 1984). Contrary to the present investigation, the previous results indicate a low soil–plant transfer coefficent for Cr.

The stunting observed at the highest application rate is similar to that recorded for plants growing
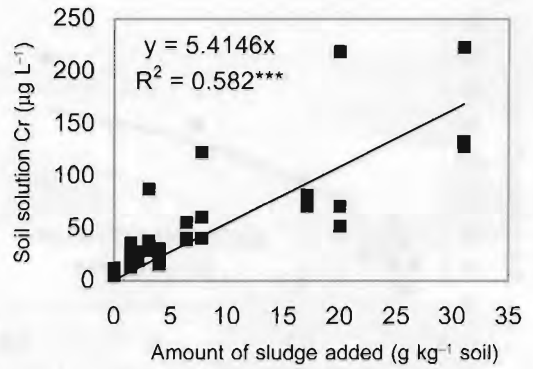
Figure 7. Relationship between the amount of sludge added and the concentration of Cr in soil solution

in metal-contaminated soils, resembling Al toxicity (Naidu et al. 1990), and Cr toxicity reported by Bartlett and James (1979). Examination of the soil solution composition of sludge-treated soils showed a pronounced increase in the concentration of Cr with increasing sludge applications (Fig. 7). Speciation of soluble Cr indicates that over 90% of Cr was present as Cr(VI). The increased concentration of soil solution Cr may be one reason for the observed stunting of the plants. However, there was no significant relationship between soil solution Cr and yield when all the data were pooled together. This may be due to the widely different
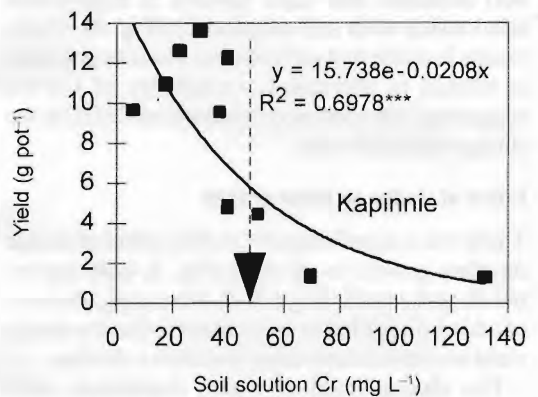
Figure 8. Effect of concentration of Cr in soil solution on dry matter top yield in the Kapinnie soil
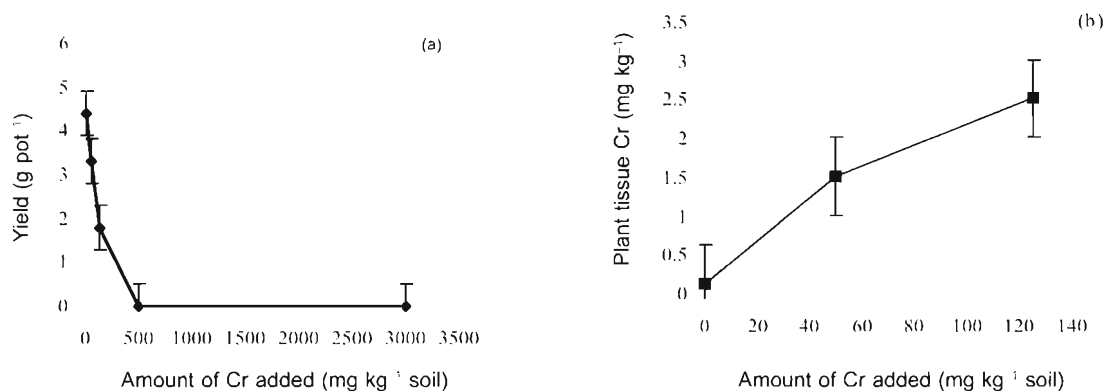
Figure 9. Effect of Cr (added as K$_2$Cr$_2$O$_7$) on dry matter top yield (a) and plant tissue Cr concentration (b) in clover grown in the Bordertown soil

properties of the soils and the varying native Cr and other ionic species pertinent to plant growth present in the soil solution. When the data for the different soils were considered separately, a strongly significant ($P < 0.001$) relationship was evident between soil solution Cr and yield. The data in Fig. 8 indicate that Cr concentrations exceeding 40 µg L^{-1} severely retard plant growth. While the data for Bordertown soil did not yield a significant relationship there was a trend consistent with that of the Kapinnie soil, indicating a marked decrease in yield at soil solution Cr concentrations exceeding 40 µg L^{-1} (data not presented).

To investigate further the effect of Cr(VI) on plant growth we incubated one soil with pure potassium dichromate (K$_2$Cr$_2$O$_7$) and studied the growth of clover. The results in Fig. 9 show a marked toxic effect of Cr(VI) on the clover. There was no germination in pots containing soils with Cr contamination exceeding 125 mg kg^{-1}. However, even in soils with 125 mg Cr(VI) kg^{-1} soil, plants were stunted and there was damage to shoots and stems. Thus as Cr concentration increased the plant yield declined markedly, such that at concentrations exceeding 125 mg Cr kg^{-1} soil there was no germination while at 125 mg kg^{-1} there was 60% reduction in growth compared to the control soil. The adverse effect of Cr(VI) on plant growth has been reported previously. James and Bartlett (1984) found that levels of Cr in *Phaseolus vulgaris* L. roots after 46 days of growth were highly correlated ($R^2 = 0.99$) with soluble Cr(VI) concentrations in unplanted field moist soil

amended with the same levels of Cr(III) but in the form of Cr(OH)$_3$ or tannery wastes. Despite the linear relationship between Cr(VI) and Cr(OH)$_3$, levels of Cr in bean tops were only increased above those of the control at the highest Cr treatment (10 mmol Cr(OH)$_3$ kg^{-1} soil). Based on these observations, James and Bartlett concluded that oxidation of Cr(III) enabled anionic Cr(VI) formed in the soil to diffuse to the roots and be absorbed by them.

Bartlett and James (1979) studied the effect of air-drying on Cr uptake by mustard (*Brassica rapa* L.), barley (*Hordeum vulgare* L.), and alfalfa (i.e. lucerne; *Medicago sativa* L.) using a pot study. They found that all the plants were severely stunted, misshapen and chlorotic after growing for 2 weeks in fresh field-moist Eldridge Loamy fine sand (Aquic Udorthent) treated with 30 mmol CrCl$_3$ kg^{-1} soil. However, there was little plant injury when the soils were air dried prior to the addition of CrCl$_3$ and the yield was at least three times greater than in the continuously moist soils. They found that 40 hours after the addition of CrCl$_3$, there was a mean value of 260 µmol exchangeable Cr kg^{-1} in the continuously moist soil compared to 20 µmol Cr kg^{-1} in the rewet air-dried soil.

Effect of sludge on Cr offtake

The data for Cr in plant tissue show trends identical to those in the yield response curves. When the data were compared to the yield and the total Cr offtake, there was a marked increase in Cr concentration with decreasing yield (Fig. 5). This

indicates a concentrating effect of Cr with reduced plant growth. Similarly, in the data on plant growth studies using the soils treated with potassium dichromate, the plant growth declined with increasing Cr concentration and this corresponded with an increase in Cr in the plant material (Fig. 9). These results suggest that Cr toxicity may be one reason for the decline in plant growth at high sludge levels. The plants at the highest sludge application rate and in Cr-treated soils all showed visibly stunted growth similar to that reported for metal toxicity.

Conclusions

Both laboratory and glasshouse studies revealed that incubation of soils with tannery waste results in an increase in the bioavailability of Cr. Incubation of soils with varying amounts of sludge led to significant ($P < 0.001$) change in pH, soil solution Cr concentration (12–222 µg L^{-1}) and all the major and minor nutrients. Correlation studies revealed strongly significant ($P < 0.001$) relationships between soil solution Cr and pH and Cr and Mn. When the pots were seeded with clover, germination was recorded in all treatments although seedling emergence and plant shoots in 'high' treatment pots showed symptoms similar to those induced by metals such as Al. A marked decline in yield was recorded at sludge levels exceeding 3 g kg^{-1} in two sludge treatments (M1 and M3, containing Cr concentrations of 1.7% and 1.2%, respectively) and 2 g kg^{-1} in the other sludge treatment (M2, Cr concentration 3.3%). The decline in yield was attributed to the toxic effect of Cr on plant growth.

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Tannery Effluent Irrigation for Tree Plantations: Preliminary Observations from Field Experiments

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Abstract

Tannery industries produce millions of litres of secondary treated effluents that are currently discharged into water bodies and have led to extensive degradation of land and water resources in many parts of India This study investigated the potential for using secondary effluent in commercial tree plantations of three multipurpose tree species, namely *Acacia leucophloea*, *Casuarina equisetifolia* and *Eucalyptus tereticornis*. Secondary effluent was applied at three concentrations (100% effluent, or 50% effluent + 50% water, or 100% water) and its effects on tree production and on soil chemical properties and the quality of surface and groundwater at the study site were measured. The treated effluent has high concentrations of total dissolved solids (13 245 mg L^{-1}), sodium (5640 mg L^{-1}), chlorides (4517 mg L^{-1}) and sulfates (426 mg L^{-1}). There was a marked effect of effluent on soil properties, composition of surface and groundwater and plant growth. In general the electrical conductivity of surface soils increased from 3 dS m^{-1} in the water treatment plots to approximately 3.5 dS m^{-1} at the higher effluent application rate. The exchangeable sodium percentage of top soil increased from 34 in the control soils to 39 in soils irrigated with 100% effluent. The impact of salt was also evident from the groundwater data which showed a marked increase in the concentrations of Na (4400–5280 mg L^{-1}) with effluent irrigation. Data on the chromium status of soils and subsurface (piezometer) water samples showed a significant buildup following monsoon events for all treatments. This confirms our hypothesis that Cr mobility is high in contaminated soils particularly following heavy rainfall. Effluent irrigation also had a significant impact on plant growth.

THE leather industry is one of the major foreign exchange earners in India. Export of leather and leather products earns more than Rs 7 x 10⁷ (US$2 million) per year. The leather industry directly employs more than one million people apart from the workers in the cottage-based sector (i.e. farmers) of the leather industry.

It is estimated that approximately 17 000 t of hides and skins are daily converted into leather.

This process uses about 35–40 L H_2O kg⁻¹ of leather processed, which implies that approximately 680 x 10⁶ L of waste water are generated daily. The waste water, after treatment, is currently being discharged either into rivers or onto land. This has led to severe degradation of soil and of the quality of both surface water and groundwater (Mahimairajah et al. these Proceedings) in many parts of India. Contaminants in waste water include high concentrations of salt and chromium (Cr). Because of the extensive contamination of land and groundwater, the regulatory body in the Tamil Nadu state has imposed strict guidelines on land- and river-based effluent and waste disposals, stating that the concept of 'zero discharge into

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Table 1. Characteristics of the treated effluent and water used for irrigation

	Treated effluent	Water
pH	9.83	7.5
EC (dS m^{-1})	18.3	1.08
Total dissolved solids (mg L^{-1})	13245	1168
Na (mg L^{-1})	5640	21
K (mg L^{-1})	8.2	4
Cl (mg L^{-1})	4517	290
Sulfates (mg L^{-1})	426	45
Cr (mg L^{-1})	2.94	BDL

BDL = below detection limit

rivers' has to be implemented in the near future. For this reason, the tanning industry, in collaboration with UNIDO (United Nations Industrial Development Organization) and Central Leather Research Institute scientists, has developed Cr-recycling technology. The technology minimizes the concentration of Cr in the treated effluent although the concentration of solute is not reduced. Uncontrolled disposal of such effluent can lead to salinisation of soil and water resources. Secondary effluent has been effectively used for tree production in other countries, so we developed the current project to assess the potential for using tannery waste effluent as an irrigant for tree plantations, especially on land currently declared contaminated. Bearing in mind the salt content of the effluent, we selected sites where groundwater has medium to high salt content.

Materials and Methods

Site, baseline sampling and chemical analyses

One of the major objectives of this study was to investigate the potential for salt movement and subsequent salinisation of surface water and groundwater. First, the groundwater quality was surveyed at selected locations representing the areas most affected by tannery effluents. Special care was taken during the selection of sites to ensure that a wide range of soil types, geological formations and watertable depths were represented. Data from this study revealed an appreciable variation in salinity and Cr content (Mahimairajah et al. these Proceedings). Based on this information, the field trial site was selected— at Ranipet Common Effluent Treatment Plant, Ranipet, Vellore district, in Tamil Nadu.

Soils were sampled at 10 cm intervals to 90 cm depth, and analysed for pH and electrical conductivity (EC) in a 1:5 soil:water suspension after shaking for 16 h end-over-end, and for organic carbon (Walkley and Black 1934), exchangeable cations, cation exchange capacity and total Cr (Table 1). These data formed the benchmark for comparisons made at the end of the field trial. Treated effluent from the Common Effluent Treatment Plant and the water used for irrigation were also analysed for pertinent characteristics.

Groundwater samples were taken at the start of the study, to form a baseline data set, and then at one month intervals. The samples were passed through a 0.45 µm millipore filter, transferred to the laboratory on ice, and analysed for pH, EC, total dissolved solids, Na, K and total Cr. Total Cr concentrations in groundwater samples and soils were determined following digestion with aqua regia (Mahimairajah et al. these Proceedings). Chromium in the digest was determined using atomic absorption spectrophotometry in air acetylene flame.

Experimental design

The field experiment was laid out in a split-plot design. The main plot consisted of effluent concentrations: high = 100% effluent; low = 50% effluent + 50% water; control = 100% water. The sub plot was tree species: *Acacia leucophloea, Casuarina equisetifolia* and *Eucalyptus tereticornis.* The tree seedlings were transplanted to a spacing of 2 m x 2 m with five replications. Each plot size was 8 m x 4 m. A buffer space of two metres was provided between main plots.

Growth study

Commercially available two-month-old tree seedlings were used for all the growth studies. The seedlings were initially examined to ensure uniform tree height and health as evident from the number of branches and shoot quality. The plants were then transferred into pre-dug holes. Following transplanting, all the plants were watered to field capacity until the seedlings became established, and this continued for 10 weeks by which time new shoots had started to emerge in all plants. At this stage, pertinent properties (e.g. stem girth, height) of the plants were established as the baseline data set.

Table 2. Initial soil properties at the study site

	Depth (cm)			
	0–15	15–30	30–60	60–90
pH (1:5 soil:water)	9.41	9.54	9.75	9.35
EC (dS m^{-1})	3.11	2.42	1.96	1.91
N (kg ha^{-1})	138	103	90	75
P (kg ha^{-1})	17.1	15.7	15.5	9.3
K (kg ha^{-1})	260	210	240	240
Org. carbon (%)	0.43	0.38	0.32	0.27
Cr (mg kg^{-1})	22.7	12.8	33.4	52.2
Exchangeable cations (cmol kg^{-1})				
Ca	2.8	3.0	3.2	3.0
Mg	2.0	1.9	2.1	1.8
Na	3.6	3.9	4.1	3.9
K	0.70	0.78	0.69	0.58
CEC (cmol kg^{-1})	10.4	10.9	11.2	10.3
ESP	34.6	35.8	36.6	37.9
Clay	24.3	29.9	21.5	
Silt	13.2	16.3	15.0	
Fine sand	32.1	23.6	25.4	
Coarse sand	30.5	34.2	38.2	
Textural class	SCL	SCL	SCL	
USDA classification: Typic Ustropets				

The plants were then subjected to effluent application at the concentrations detailed above. Initially 10 L of the effluent were applied manually by transferring water onto the tree roots in a basin-shaped hole dug around the tree. The tree plantation was irrigated when 60% of available soil moisture had been depleted. This approach prevented lateral loss of the effluent. Following three months of manual irrigation, flood irrigation was imposed on the plantation as described below. During the growth study the soil between plants was sampled regularly for assessment of soil chemical characteristics.

Flood irrigation

To facilitate flood irrigation, each water or effluent treatment strip was subdivided into five beds representing one replication. Each bed was 8 m x 12 m (96 m^2) with 24 plants, and levelled so that there could be uniform distribution of the water or effluent. Irrigation was facilitated by use of PVC piping running along the centres of the five beds in each strip, with a controlled opening in the middle for all the 20 beds.

The water and effluent were stored in separate 2000 L water tanks on a platform raised 1 m off the ground. The water and effluent were pumped to storage tanks by two 1 hp (746 W) motors, fixed in the water storage tank of the Central Effluent Treatment Plant and in the effluent outlet discharge point, and connected to the water or effluent storage tanks by flexible hosepipe.

Solute movement

A nest of piezometers was installed within the trial to monitor watertable level and water quality. Changes in watertable depth were also used as an indicator of gradient in subsurface water movement. Samples were collected for pH, EC, major anions and cations, and for heavy metals especially Cr. The piezometer depths were chosen to enable sampling of both the unsaturated zone and the groundwater (deep piezometer) to quantify the distribution of salts and heavy metals including Cr. Piezometer samples were taken every 30 days; however, during the first three months of our study, there was no water in the shallow piezometers.

Routine soil analyses and plant measurements

Routine soil samples were taken periodically to 60 cm depth at 10 cm intervals, from sites between the trees. Samples were analysed for pH, EC, exchangeable Na and K and total Cr as described above. Biometric observations for the tree plantation, namely plant height and stem girth, were made every month after the plant roots were established.

Results and Discussion

Effluent and irrigation water quality

Table 1, the mean chemical composition of the effluent used for irrigation, shows that the effluent is highly saline with an EC of 18.3 dS m^{-1} and total dissolved solids exceeding 13 000 mg L^{-1}. The mean pH of the effluent exceeded 9.5; the water was weakly alkaline. Although most of the Cr is removed during the recycling process, the effluent still contained Cr in excess of 2 mg L^{-1}.

Baseline soil properties

The surface and subsurface soils at the study site were strongly alkaline (pH > 8) with EC ranging from 3 dS m^{-1} in the surface horizon to 1.9 dS m^{-1} at depths exceeding 60 cm (Table 2). Consistent with
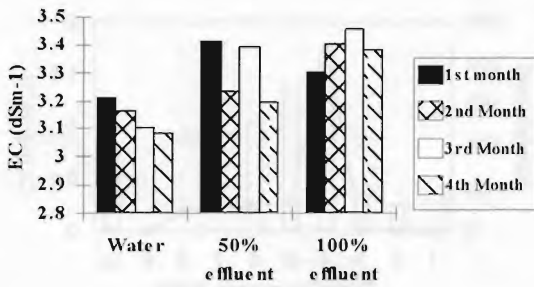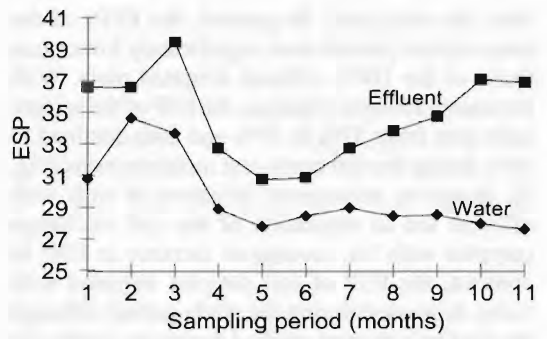
Figure 1. Effect of effluent irrigation on the electrical conductivity of surface soils.

Figure 2. Effect of effluent irrigation on ESP of the surface (0–15 cm) soils during the first 11 months of irrigation

the high exchangeable sodium status, the exchangeable sodium percentage (ESP) of the soils exceeded 30. According to USDA and Australian soil classifications, an ESP of >15 (in USA) and >6 (in Australia) indicates soils which have a dispersive sodic nature. This suggests that the study site is highly sodic and extreme care must be exercised during effluent applications to minimise the sodic effect on soil properties and plant growth. In keeping with the low fertility status of soils from the region, the site was low in organic carbon (0.43%), medium in nitrogen and phosphorus (138 kg N ha^{-1} and 17.1 kg P$_2$O$_5$ ha^{-1}) and low in potassium (260 kg ha^{-1}; Table 2). The soil has a sandy clay loam texture and is a Typic Ustropet by USDA classification.

Effect of effluent on soil properties

There was a significant effect of irrigation on the EC, exchangeable cations and pH of the soil during the 11 months of the plant growth study. In general, the EC of soils increased by 0.2 0.3 units after the high concentration effluent treatment compared to the control treatment in which the soil EC showed a consistent decline with time. The increase in EC was coupled with a significant (P 0.005) increase in the ESP of effluent irrigated soil. This is not surprising because the effluent used for irrigation had high contents of total dissolved solids (13 245 mg L^{-1}), sodium (5640 mg L^{-1}), chlorides (4517 mg L^{-1}) and sulfates (426 mg L^{-1}). At the application rate used here (10 applications per month), approximately 1 324 500 mg of solute was added per plant species, or approximately 3 t solute ha^{-1} per month added at the highest rate of effluent application. Accumulation of salt was also

evident from the EC and the exchangeable cation status of the soils. The exchangeable cations increased for the first four months and then declined during the north-eastern monsoon rain. Continued effluent irrigation resulted in appreciable increase in both EC and exchangeable cations even after the north-eastern monsoon season (Fig. 1). In contrast to the effluent treated soils, both the EC and the ESP of soils irrigated with water showed a consistent decrease with increasing period of irrigation, indicating possible loss of salt through leaching in the percolating water. As the soils at the site were loamy sands, the enhanced percolation during irrigation could result in the leaching and subsequent deposition of salt in the subsurface environment. Examination of the ratio of Na added in effluent to the change in exchangeable Na values,

$$\delta Na_{exch} = Na_{treat} - Na_{exch-native},$$

during the first six months of the study indicates that there is a net accumulation of Na (ratio >1) in effluent treated soils. However, when the samples were taken at the end of three months, δNa_{exch} showed a ratio of 1, indicating leaching of Na from the surface soils during the north-eastern monsoon. Similar changes in the Na status of soils were also evident from the ESP and SAR of the water in the shallow piezometers at the trial site (see below).

Sodicity

The changes in the exchangeable cation status of the soils led to a marked increase in the ESP of both the surface and the subsurface soil samples

from the trial plots. In general, the ESPs of the control plots (water) were significantly lower than those of the 100% effluent irrigated plots. With increasing effluent irrigation, the ESP of the surface soils rose from 37% to 39% and then declined to 30% during the wet north-east monsoon rains (Fig. 2). However, subsequent irrigation of soils with effluent led to saturation of the soil exchange complex with Na, causing an increase in ESP. In contrast, the ESP of soil samples irrigated with water decreased during the study period although the decline was most marked during the north-east monsoon period. The effect of irrigation was also evident from field observations that showed dispersion and extensive waterlogging of soils typical of sodic soils following the north-east monsoon. Waterlogging of soils may be attributed to the reduction of the soil EC below the threshold level required to maintain soil structure. The observed decline in soil structure following the north-east monsoon indicates that precautions must be taken to develop irrigation strategies that minimise the effect of sodicity. Further work should assess the dispersion charactersitics of these soils using the Emerson disperson soil test, as discussed in Naidu et al. (1996).

Chromium movement through the soil profile

The total Cr concentration in the piezometer water samples ranged from below detectable limit (BDL), during the first three months of irrigation, to approximately $2 \, \mu g \, L^{-1}$ (Fig. 3) during the north-east monsoon rainy period. This trend is similar to that shown by data of Naidu et al. (1996) on Cr in piezometer water samples at the tannery waste-contaminated sites in Adelaide, Australia. Consistent with our findings, those investigators report that the concentration of Cr in subsurface water samples increased during the peak rainfall period, indicating substantial leaching of Cr in the percolating water. Speciation of Cr in the leachates (piezometer water) indicated that approximately 80% of Cr was present as Cr(VI), with the rest present in association with colloid particles. These results indicated firstly that Cr(III) added during the tanning process is oxidised to Cr(VI) in the soil environment, and secondly that Cr may move in association with solid colloid particles. Thirdly, the Cr(VI) is extremely mobile in soils of the Tamil Nadu district. The high mobility of Cr(VI) together with the potential for Cr(III) oxidation need careful
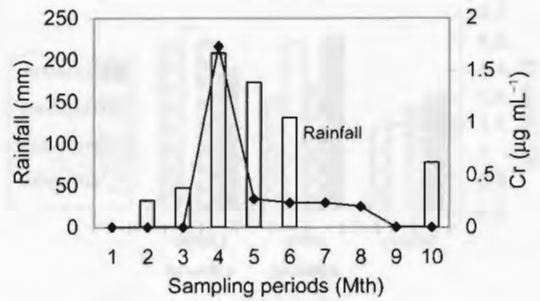
Figure 3. Distribution of total Cr ($\bullet$) and rainfall during the study period at the effluent irrigation trial site

consideration by the regulatory authorities during the establishment of guidelines for tannery waste effluent disposals.

Movement of sodium

The concentrations of Na in soil water at 2 m depth increased for the first three months. With continuous leaching, the Na had moved to deeper soil layers. The concentrations of Na in the water table were high ($4400–5280 \, mg \, L^{-1}$) reflecting the saline nature of the groundwater. However, it is noteworthy that the trend was in sharp contrast to that observed for Cr, which was not detected in piezometer water samples until the north-east monsoon. However, in keeping with the sodium absorption ratio (SAR), the concentration of Na decreased during the north-east monsoon period, suggesting either leaching of sodium beyond the 2 m depth or dilution of Na with a large volume of water.

Groundwater quality

The changes in the soil EC and the ESP are reflected in the chemical composition of the shallow water and groundwater. For instance, the EC of the shallow and deep piezometer samples in the high effluent plots increase with time (up to three months) (Table 3). However, as with the soil EC and exchangeable Na status, the EC and the TDS in the piezometer samples decreased during the north-east monsoon period when the rainfall exceeded 415 mm. The decrease in solute concentration in the shallow piezometer samples may be attributed to the dilution of the solute during the high rainfall period. It is also likely that salt was leached from the system in lateral water flow
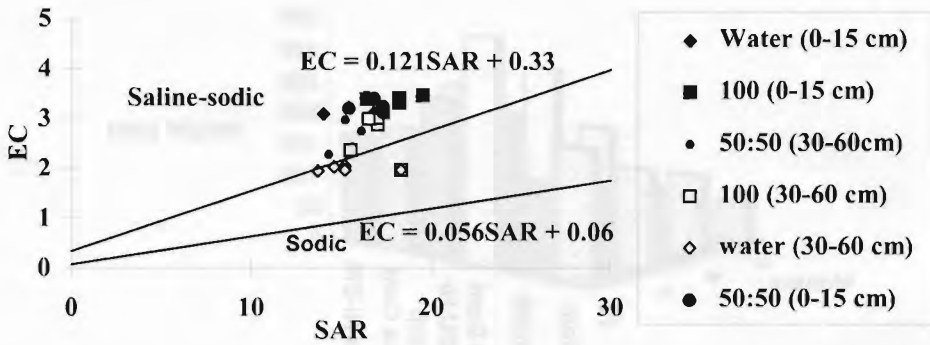
Figure 4. Effect of irrigation on the relationship between SAR and EC of surface and sub-surface soils from the field plots; the lines show theoretical values

because the field sloped towards the Palar River. When the SAR of the soil water was calculated and expressed by the stability phase diagram of Rengasamy et al. (1984) it was evident that irrigation of soils with water caused a slow drift of the SAR towards that of sodic soils, while irrigation with 100% effluent increased both the SAR and the EC, causing the soils to become saline–sodic (Fig. 4). The effects of effluent on soil sodicity and on the quality of subsurface water will perhaps be more evident following the long-term irrigation study which is underway now.

Plant growth

There was a significant effect of effluent applications on the growth of trees. Irrespective of the plant species, effluent applications resulted in a significant decline in tree height (Fig. 5). In

general, the tree height declined by 5–10% depending on the plant species. Nevertheless, none of the plants showed growth constraints reflecting either toxicity or any other adverse impact of effluent. Given that nutrient applications led to appreciable increases in the nutrient status of the soils, with no visible signs of nutrient deficiency, it is likely that any reduction in growth results from osmotic effects caused by the increased salt concentration of the soil water that serves as the nutrient reservoir for plants.

Further long-term study is required to confirm the effect of salt on the growth of plants. Among the tree species, *Eucalyptus* was highly sensitive to effluent irrigation. *Acacia* and *Casuarina* were able to withstand effluent irrigation to a certain extent. This could be seen in the reduced plant growth with effluent irrigation compared to the

Table 3. Change in chemical composition of groundwater (at 2 m) during the first four months of the study

|	Water treatment				50:50 effluent:water				100% effluent treatment			
	1st mth	2nd mth	3rd mth	4th mth	1st mth	2nd mth	3rd mth	4th mth	1st mth	2nd mth	3rd mth	4th mth
pH	7.51	6.91	6.97	6.99	7.35	6.96	7.26	6.79	7.32	6.94	7.22	6.88
EC (dS m^{-1})	13.98	17.94	17.18	13.00	15.8	17.27	17.1	15.0	18.25	18.78	19.00	15.2
TDS (mg L^{-1})	13636	13017	14175	13444	14282	14980	14688	14874	17314	18293	16955	16504
Na (mg L^{-1})	4480	4800	4600	2400	4560	4960	4640	3133	4580	5280	5160	3125
K (mg L^{-1})	9.1	9.5	9.2	10.0	9.0	10.1	9.0	7.3	8.7	10.4	12.5	7.7
Ca (mg L^{-1})				631				837				687
Mg (mg L^{-1})	–	–		422	–	–	–	412	–	–	–	418
SAR				18.2				22.1				24.7
Cr (mg L^{-1})	BDL	BDL	BDL	1.57	BDL	BDL	BDL	1.94	BDL	BDL	BDL	1.7
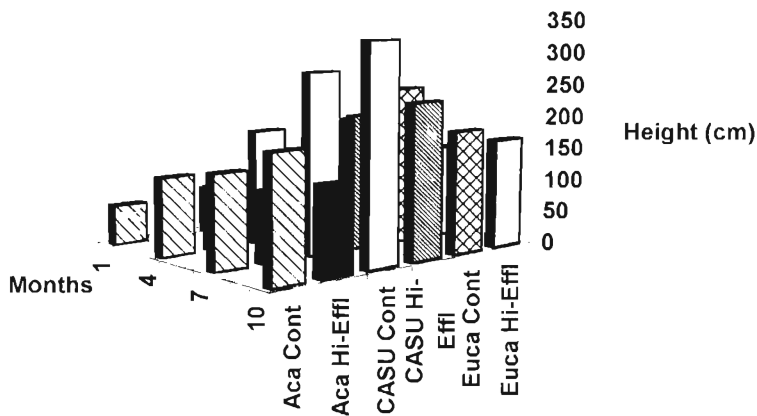
Figure 5. Effect of effluent applications on the tree growth

control. The pronounced effect of effluent was also reflected in the stem girth of the trees. The stem girth was significantly reduced with increasing effluent concentration.

Conclusion

It is evident from the above study that effluent applications to soils lead to marked changes in soil and groundwater quality and in the growth of commercial tree species. In general, the EC of surface soils increased from 3 dS m^{-1}, in the plots irrigated with water, to 3.5 dS m^{-1} at the higher of the two effluent application rates. A similar effect of effluent was observed in the surface and subsurface soil ESP and SAR of the piezometer water samples. Comparison of the EC and SAR of surface and subsurface soils, using the model of Rengasamy and Olsson (1991), indicates that irrigation with water leaches salt from the surface soils, leading to subsurface sodicity. Consequently, application of water shows a gradual tendency to displace salts beyond 60 cm and the subsurface soil tends to become sodic. This contrasts with the high effluent treatments in which soils either

maintained their saline–sodic nature or showed a gradual build up of salt. Data on the Cr status of soils and subsurface (piezometer) water samples show a significant buildup of Cr in the groundwater following the north-east monsoon period in all treatments. This confirms our hypothesis that Cr mobility is high in contaminated soils particularly following heavy rainfall. Effluent irrigation also had a significant impact on plant growth.

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Tannery Sludge Disposal Using Earthworms and Microorganisms: Preliminary Investigations

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Abstract

The large volumes of solid and liquid wastes produced by tanneries have a negative impact when discharged onto land and surrounding water bodies. There is now increasing demand for the production of sludge that has minimal impact on land and water bodies. The present study investigated the role of earthworms and microbes in sludge decomposition under field conditions. Treatments were established to study the efficiency of these organisms acting separately as well as in combination for the decomposition of sludge. Composting led to a marked increase in the concentrations of nitrogen (N), phosphorus (P) and potassium (K). A sludge bed with added earthworms and microbes produced increased N and P, while the maximum increase in K (two-fold) was recorded in the sludge bed that included sawdust and microbes. Appreciable reductions in pH, electrical conductivity and C:N ratio were also observed in all the treatments. In 120 days of composting, the C:N ratio was reduced below the preferred level of 20, except in the control beds. The chromium content of the sludge was also reduced by 40%. Counts of microbial populations during the composting process revealed marked changes in the populations of bacteria and fungi, and some changes in the actinomycete population.

THERE are about 75 large and 1008 small tanneries that generate more than 50 000 t yr^{-1} of solid and liquid waste in India (Ramasamy, these Proceedings). Disposal of such waste has led to extensive contamination of soil and groundwater in the immediate vicinity of the tanneries (Mahimairajah et al. these Proceedings) in many locations around Tamil Nadu.

Although the sludge is rich in nutrients, it contains high concentrations of salts in addition to chromium (Cr). The Cr is of particular concern in 90% of tannery wastes, because chrome tanning is the preferred process in many tanneries in India. In contrast to Cr tanning, the vegetable tanning process produces sludge that is rich in salt and organic compounds originating in the plants. While it is the high salt and Cr content that make the Cr tanning sludge unattractive for land-based application, it is the organic compounds together with the high salt content that make the vegetable tanning sludge unsuitable for land-based application. As reported by Mahimairajah et al. (these Proceedings) and Naidu et al. (these Proceedings), land-based disposals could lead to contamination of soil, surface water and sub-surface water. Given the large foreign exchange this industry generates, the Government of India would like to support tannery operations. However, because of the negative impacts of the current sludge disposal methods, the Government is placing increasing restrictions on land-based waste disposal. Therefore the survival of this industry requires development of appropriate waste disposal technology which has minimal impact on

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Table 1. Treatment details and pertinent properties of the sludge mixture at the start of the decomposition study

Treatment		pH	EC (dS m⁻¹)	total Cr (mg kg⁻¹)	Organic C (%)	total N (%)	avail. P (mg kg⁻¹)	exch. K (mg kg⁻¹)	C:N ratio
T1	S + control	7.70	12.62	82.0	7.19	0.18	0.125	530	40.02
T2	S + soil control	7.70	12.60	79.3	7.86	0.18	0.125	530	42.88
T3	S + soil + EW	7.61	12.89	77.6	7.18	0.19	0.141	580	38.11
T4	S + soil + EW + MO	7.66	12.64	77.0	7.45	0.18	0.115	580	41.47
T5	S + MO	7.76	12.76	80.6	7.38	0.19	0.125	580	39.14
T6	S + SD control	7.68	16.62	83.0	12.81	0.09	0.141	530	129.4
T7	S + SD + MO	7.69	16.29	88.3	12.99	0.06	0.125	505	133.55

where S sludge. EW earthworms, MO microbes, SD sawdust

the environment. With this background in mind, we investigated the possibility of converting the sludge into manure and its potential use in agriculture. The experimental study was sub-divided into two phases: phase I focused on vegetable-tanning sludge while phase II focused on Cr-tanning sludge. For the phase II study, our aim was to investigate the changes in the nature and the potential bioavailability of Cr following the decomposition of sludge. In this paper we report the results from our phase I study.

The experiment was initiated using earthworms and microorganisms, which are major groups of decomposers of carbon-rich wastes (Edwards and Lofty 1977). The earthworms and microbes break down complex materials into simpler substances by releasing enzymes and various organic acids (Jeuniaux 1969). They are also known to accumulate heavy metals in their tissues (Ireland 1983). For these reasons, these organisms were selected to investigate the possibility that they could decompose sludge to a quality that can be used on productive land.

Materials and Methods

The experiment was conducted using vegetable sludge at the Ranipet Common Effluent Treatment Plant. One-month-old sludge was crushed to approximately 1 cm size prior to its use in the incubation studies. The treatment combinations of sludge, sawdust, earthworms and microbes are listed in Table 1.

Sawdust was included in the experiment because it increases the air space in the sludge bed, thereby favouring microbial activity, and it also serves as the carbon source for the microorganisms (Wani

and Lee 1995). Moreover, in Cr-tanning sludge, the dissolved organic compounds in sawdust may enhance the reduction of any hexavalent Cr to non-toxic trivalent Cr.

The experiment was done on large unreplicated beds and replicate samples were taken from five points in each bed every 30 days.

Preparation of sludge beds for composting

Vermiculture beds

The worm beds were 1 m x 1 m in area and 0.3 m high. First, a thin layer of fine sand was spread (for water infiltration); above this, field moist soil was added to a height of 15 cm to serve as the worm bed. Then 300 earthworms (150 each of *Perionyx excavatus* E.Perr. and *Eudrilus eugeniae* Kinsperg.) were introduced. These two species were selected because they are common in Indian soils and are also very good decomposers of
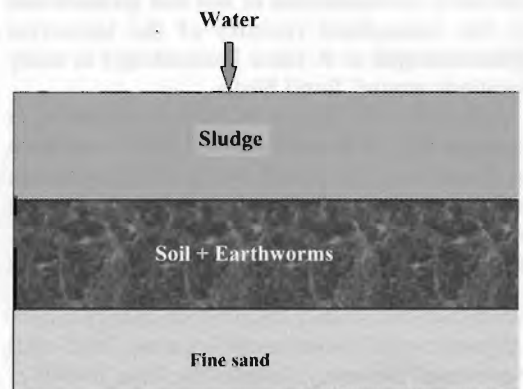
Figure 1. Schematic diagram of the vermiculture bed
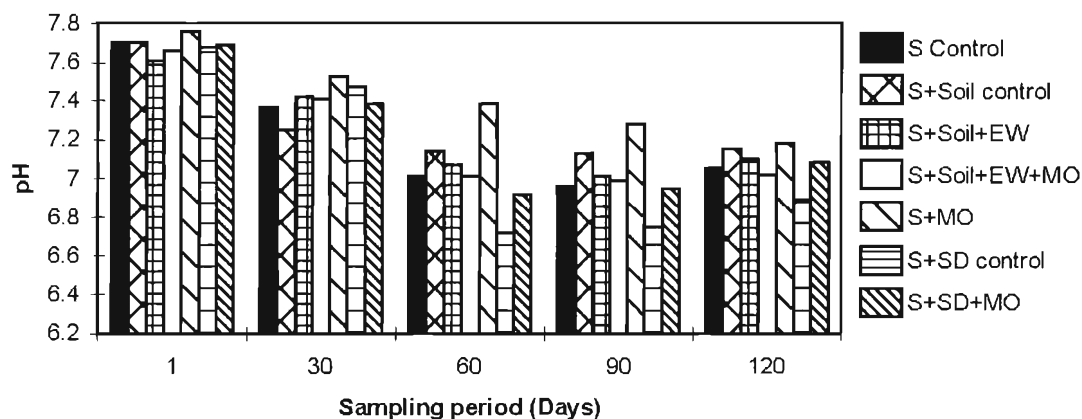
Figure 2. Changes in pH during composting

organic wastes. When all the worms had burrowed into the soil, approximately 10 cm depth (30 kg) of 1 month old crushed sludge was added.

In treatment T4, 150 earthworms were introduced and a mixed microbial inoculum consisting of *Bacillus* sp., *Pseudomonas* sp., nitrogen fixing *Clostridia*, *Penicillium* and *Streptomyces* was sprayed over the sludge at 10% wt/vol basis. This is the rate which is normally used for microbial composting of organic wastes. Although native earthworms are associated with microorganisms, the additional mixed microbial inoculum was introduced to test whether it enhanced the capacity of the system to decompose sludge.

Microbial treatment beds

Like the vermiculture beds, sludge beds were prepared to 1 m x 1 m x 0.3 m in size. About 30 cm (60 kg) of sludge was added to each bed. For treatments T6 and T7, 15 kg of sawdust was thoroughly mixed with 45 kg of sludge on a 1:1

Table 2. Characteristics of soil and sludge samples

	Soil	Sludge
pH	9.78	7.6
EC (dS m⁻¹)	3.06	12.6
Organic carbon (%)	0.3	7.4
Nitrogen	127 kg ha⁻¹	0.18%
Phosphorus	17 kg ha⁻¹	0.18 mg L⁻¹
Potassium	210 kg ha⁻¹	580 mg L⁻¹
Chromium (mg kg⁻¹)	23	77

vol:vol basis. Microbial inocula, as used for the earthworm beds, were sprayed over the beds at 20% wt/vol basis. For all the treatments, suitable controls were maintained.

The beds were watered daily for the first three weeks, by which time the sludge had become hydrophilic. After that, the beds were watered every alternate day to maintain a moisture level between 50% and 60%.

Samples were collected every 30 days, to study the changes that occur during composting. The samples were air dried, mixed and homogenised, and analysed for pH, electrical conductivity (EC), organic carbon, nitrogen (N), phosphorus (P), potassium (K), chromium (Cr) and the microbial population, using standard methods.

Laboratory analyses

The pH and EC of the sludge mixture were analysed after end-over-end shaking of a 1:5 sludge:water mixture. The organic carbon content of the sludge samples was analysed by the wet oxidation method (Walkley and Black 1934). Total nitrogen was estimated by the Kjeldahl method. Available phosphorus and exchangeable potassium were estimated by the methods of Olsen et al. (1954) and Stanford and English (1949), respectively. The prime heavy metal in the tannery sludge, Cr, was analysed in the atomic absorption spectrophoto-meter (Varian Spectra A2000) after a known weight of sample had been digested in aqua regia at 120°C for 2 h, then made up to a
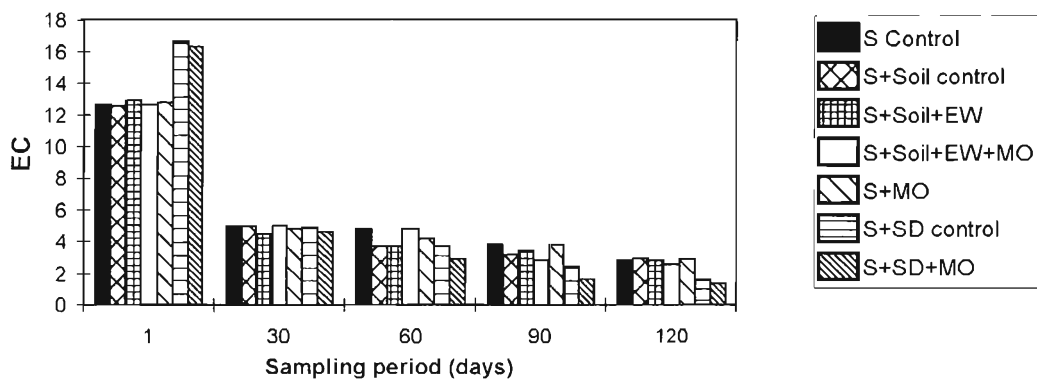
Figure 3. Changes in electrical conductivity during composting

known volume, and filtered; the value was read at 358 nm. The microbial population was assessed by the viable count method. Sludge samples (1 g) were serially diluted to 10^6 for bacteria, 10^3 for fungi, and 10^3 for actinomycetes, and the colony-forming units were counted. Table 2 gives the baseline data for the soil and sludge used for this study.

Results and Discussion

Analysis of this preliminary investigation revealed encouraging decomposition results. There was an increase in the major plant nutrients, and a favourable reduction in the C:N ratio, pH, EC of the compost samples.

pH and EC

There was a significant decrease in the pH of the sludge mixtures during 90 days of incubation. The maximum decrease in pH (7.7 to 6.8) was recorded for the sawdust sludge mixture (Fig. 2). This decrease in pH during composting may be attributed to the release of various organic acids by microorganisms for particle breakdown (Wani and Lee 1995). Cell lysis and ammonia release may have contributed to a pH increase in the later stages. Leachates from sawdust are often high in dissolved organic carbon and acids, so this may also contribute to the observed reduction in the pH.

In general, the EC of the composting mixture ranged from 12 dS m^{-1} in the sludge–soil bed to
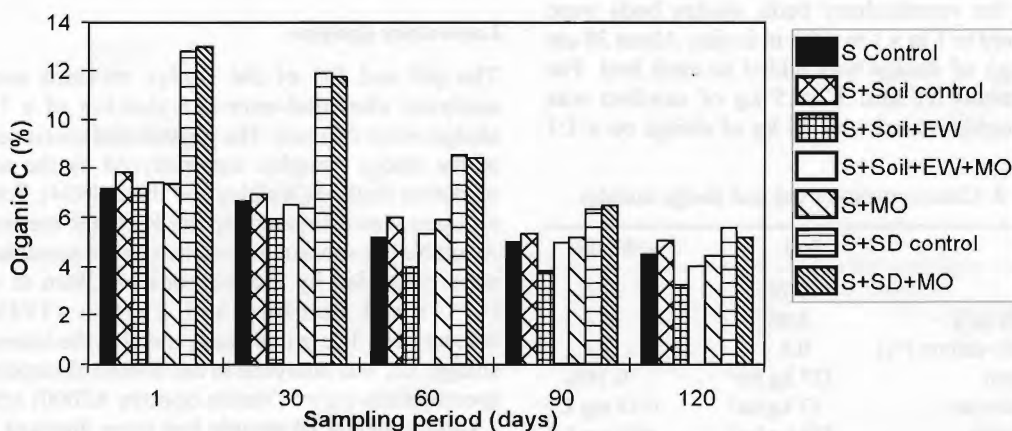
Figure 4. Effect of time on changes in organic carbon during composting of tannery sludge
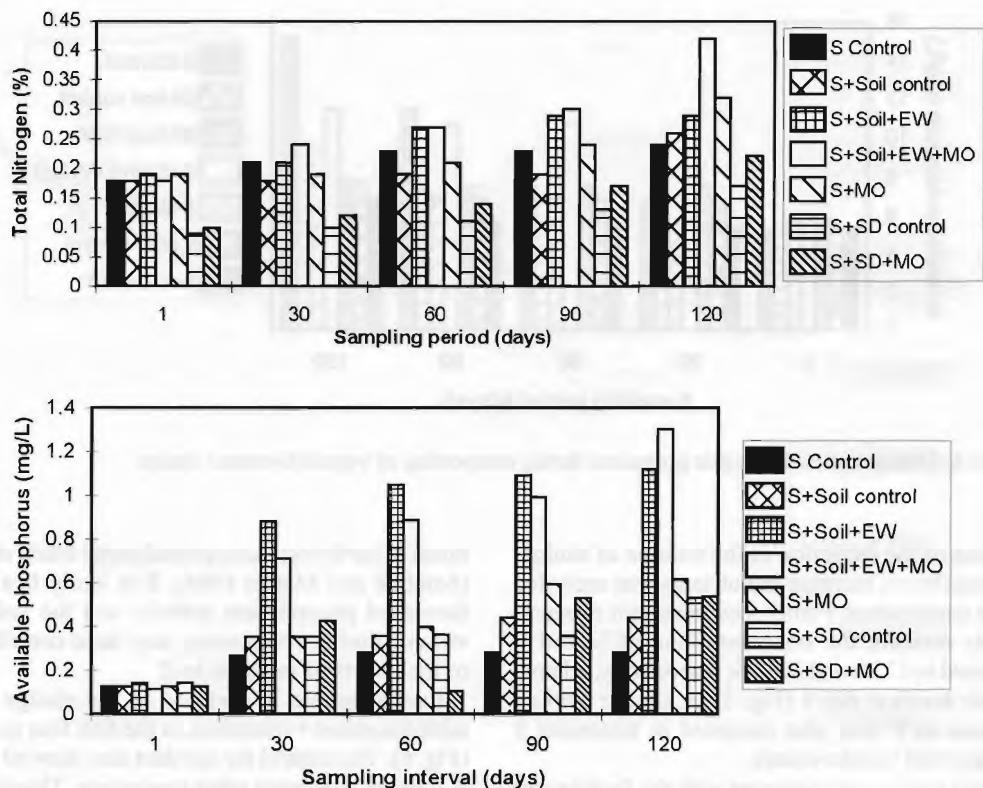
Figure 5. Changes in the total nitrogen (top graph) and available phosphorus (lower graph) during composting

16 dS m⁻¹ in the sawdust–sludge mixture at the start of the study. Just as with pH, the EC of all the composting mixtures decreased with increasing period of incubation; the most marked changes were recorded at the end of 30 days (Fig. 3).

The decrease in EC may be attributed to salt percolating out in the water that was added to the beds during the incubation period. Our subsequent column studies in the laboratory revealed large concentrations of salt in water leachates of the sludge mixture.

Organic carbon

The total organic carbon content of the composting mixture varied substantially between the treatments (Fig. 4). As expected, the highest organic carbon content was recorded for the sawdust sludge mixture and the lowest for the sludge soil mixture. With increasing periods of composting the total carbon content decreased by between 38%

(control) and 60% (sawdust mixture). Reduction in carbon content during composting is not surprising because carbon serves both earthworms and microorganisms as an energy source for their tissue build-up.

The marked reduction in the carbon content of sawdust is interesting because sawdust is not easily decomposed because of its wide C:N ratio; however, in the presence of sludge the decomposition is fast. This finding is important because two different wastes are being converted into compost in a single process. However, much work needs to be done to assess the optimum conditions for effective and rapid decomposition of the sludge in combination with the sawdust.

Nutrients

In contrast to pH, EC and organic carbon, the concentrations of the major plant nutrients, N, P, and K, increased in the compost samples, primarily
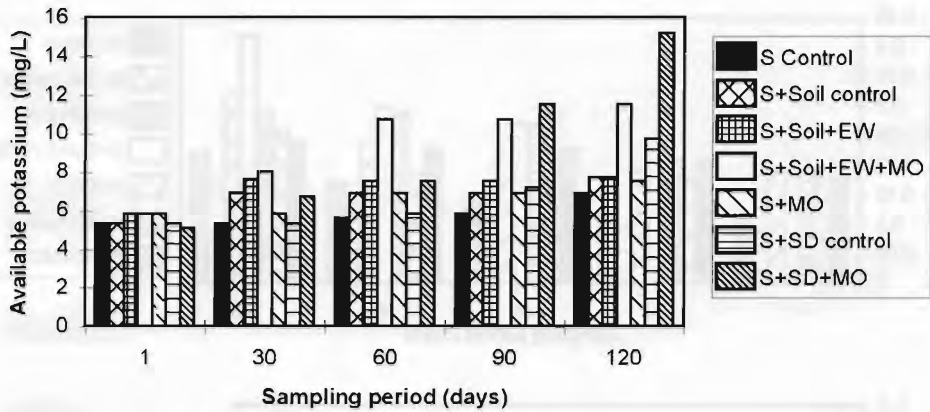
Figure 6. Changes in exchangeable potassium during composting of vegetable-tanned sludge

because of the reduction in the volume of sludge. The maximum increase in nutrients was recorded in the earthworms + microbes treatment mixture. In this mixture the concentrations of N and P increased by 133% and 1032%, respectively, relative to their levels at day 1 (Fig. 5). A similar marked increase in P was also recorded in treatment 3 (sludge+soil+earthworms).

These results are consistent with the finding that earthworms increase the concentration of P by their activity (Dorcas et al. 1991). Many studies indicate that earthworms alone (Satchell and Martin 1984) and in combination with microbes (Kucey 1983) induce phosphatase activity thereby increasing the solubilisation of bound P and making it available to plants. Increased phosphatase activity was also

noted in earthworm-composted paper waste sludge (Satchell and Martin 1984). It is likely that both increased phosphatase activity and the reduced volume during composting may have contributed to the observed increase in P.

Exchangeable K doubled in the sludge with added sawdust + microbes, in the first four months (Fig. 6). The control for sawdust also showed more K content than most other treatments. Though the reason for this is not known, it is possible that there is a contribution to K from the sawdust itself.

C:N ratio

The C:N ratio is the conventional index used to establish the maturity of compost. The C:N ratio steadily decreased during composting (Fig. 7).
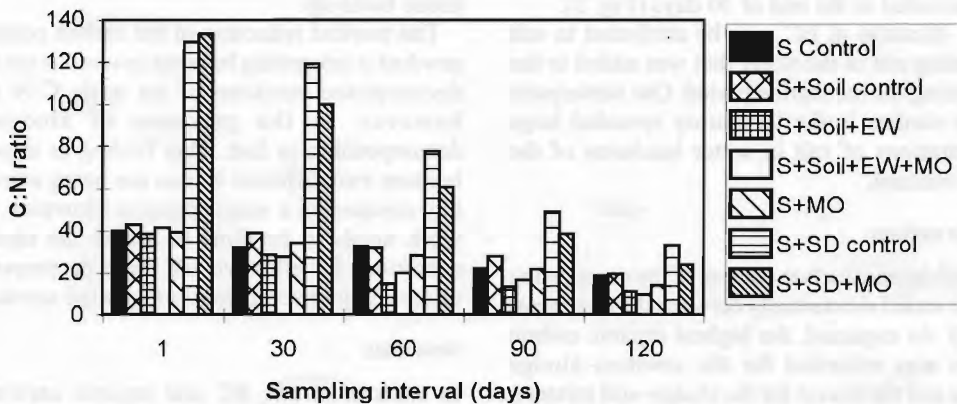
Figure 7. Effect of composting on the C:N ratio during 90 days of incubation
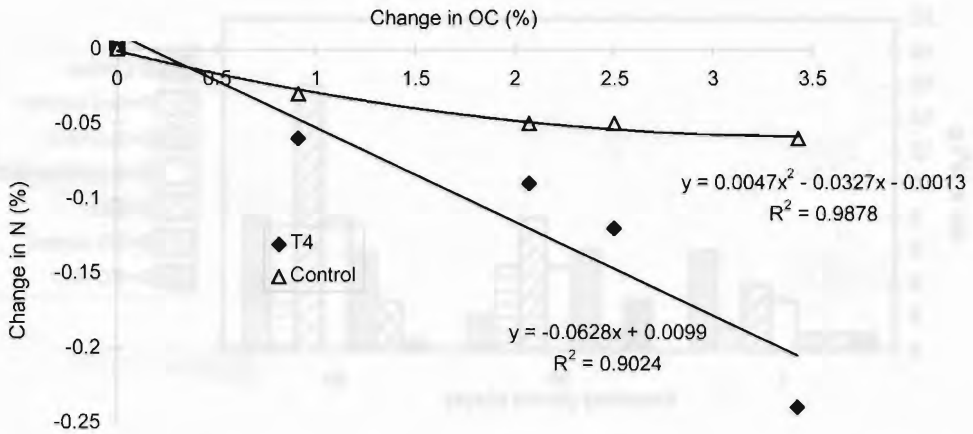
**Figure 8.** Changes in organic carbon (OC), related to the changes in total N content

Maximum reduction (82%) was observed in sludge with added sawdust + microbes, while the sludge with earthworms and microbes produced 76% reduction.

Comparison of the C and N data from treated and control plots reveals a marked decrease in total organic carbon in the treatment plots relative to the control plots (Fig. 8; only typical results are presented). Concurrent with the decrease in organic carbon, there was an increase in total N indicating that mineralisation of organic carbon contributes to the increased N during the composting process. The reduction in C:N ratio is due to the conversion of carbonaceous materials into cell biomass, CO_2, water and humus, and thus

the ratio between carbon and nitrogen reduces progressively with the age of composting (Kalaiselvi and Ramasamy 1996).

Chromium

The total Cr content of the sludge was 78 mg kg^{-1} which is high considering that the sludge used is from vegetable tanning. The presence of Cr can be attributed to the disposal of Cr-tanned effluent in the common effluent treatment plant. The sawdust used for the study contained 19 mg Cr kg^{-1}, also. Results of Cr analysis in the composts show that there was reduction in volume as composting progressed. There was a small reduction of Cr in the first 30 days, but after that, Cr content fell by
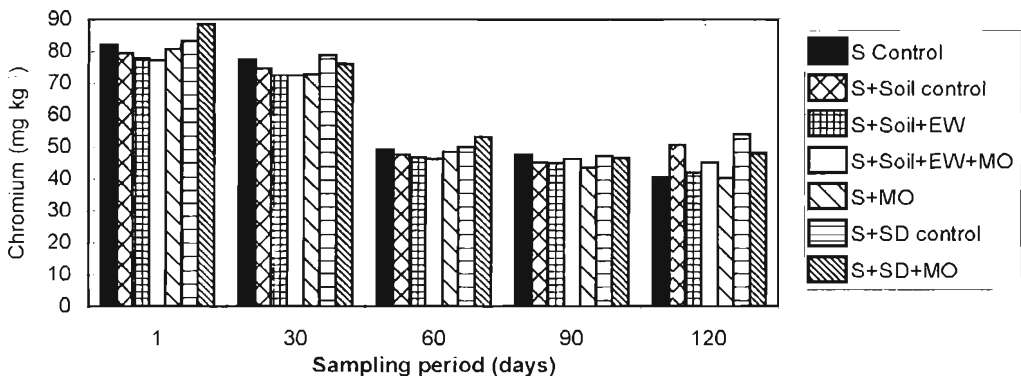
Figure 9. Changes in Cr content of the sludge during composting
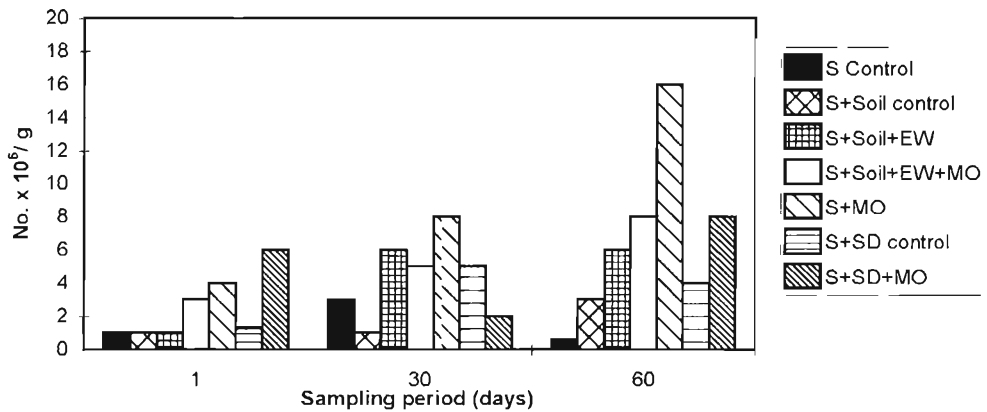
Figure 10. Changes in bacterial population during composting of tannery sludge

up to 40%. After 60 days, the concentration of Cr was more or less similar in all treatments (Fig. 9).

The reason for the observed decrease in Cr with composting is not clear, although accumulation in earthworm and microbial tissue may be considered as possible mechanisms. In an earlier laboratory study we found a Cr concentration of 35 mg kg⁻¹ in earthworm tissue. Before the Cr concentrations in earthworm tissue were assessed, the Cr in the earthworms' gut contents was removed by filter paper feeding. Chromium accumulation by earthworms was also reported by Hartenstein et al. (1980). Chromium forms complexes with organic matter and becomes unavailable for extraction at low pH, but in this study the pH was near neutral; therefore, it is unlikely that complexation occurred. The mechanism, and especially the roles played by the soil enzymes, organic acids and microbial enzymes, needs to be studied in detail to better understand the process of Cr reduction during the composting process. Another reason for the reduction in Cr may be leaching in the percolating water. Our subsequent studies with water extracts of sludge material showed soluble Cr ranging from 1 to 2 mg L⁻¹.

Microbial population

There was a significant increase in the number of bacteria and fungi, while the population of actinomycetes reduced after an initial increase (Fig. 10). *Pseudomonas*, *Bacillus*, *Penicillium*, *Aspergillus*, *Beijerinckia* and *Streptomyces* were the main organisms observed.

The presence of these microorganisms was not treatment-specific. In sludge beds that did not receive any microbial inoculum, *Pseudomonas* and *Beijerinckia* were found to be common organisms. However, the maximum number of micro-organisms was present in the beds into which microbial culture had been introduced, especially the sawdust-mixed beds. Though there were fewer bacterial colonies here, the bacterial population was larger, taking into account the dilution factor. Fungi followed bacteria in population numbers and actinomycetes were the smallest population. Sawdust reduced the compaction in compost beds and thereby increased aeration, which may have resulted in better aerobic microbial activity. Microbial colonisation in uninoculated beds indicated that the sludge serves as carbon source to the native population. It is unusual to see a reduction in the population of actinomycetes during composting because of their ability to withstand heat. Competition by bacteria and fungi for nutrients might have excluded actinomycetes.

Conclusion

It is evident from our preliminary study that there is scope for increasing the nutrient content of vegetable tanning sludge using earthworms and microorganisms. However, based on the preliminary data, it is is not possible to explain the roles of these two organisms during the composting of tannery sludge. Different sets of treatments, using chrome-tanning sludge as well as vegetable sludge are currently being studied. The responses

of crops and the bioavaiability of Cr as assessed by plant uptake are being tested. Based on these detailed studies the potential for long-term field scale composting will be determined with a view to using composted material as a source of plant nutrients.

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Developmental Studies on Bioreactors with Immobilised Biomass for the Removal of Chromium in Tannery Effluent

T. Emilia Abraham[1] and Saswathi Niyogi[1]

Abstract

Discharge of toxic chromium (Cr), from industries such as ore mining and processing, textiles, leather and tanning processes, steel processing and battery processing, into the main stream of effluents is hazardous. Chromium compounds from industrial effluents accumulate in sludge and have created other environmental problems. Biological remediation of these contaminants could reduce the hazards. The biological systems of plants, animals and microbes have certain functional groups in their cell walls or cell membranes which could react with heavy metals in anionic or cationic forms. Good bioadsorption beads have been prepared by immobilising dead biomass of a fungus in a polysulfone matrix which can withstand more than 15 adsorption–desorption cycles. These beads can be used in a packed bed or in a fluidised bed reactor without any particle damage. The beads can take up 35–60 mg g^{-1} of Cr in 4–24 h. The biofix beads are useful for treating Cr(VI) at concentrations from 10 to 100 mg L^{-1}; they are efficient at a stirring speed of 100 rpm, at pH 2. The adsorption characteristics fit the Langmuir isotherm better than the Freundlich isotherm.

HEAVY metals and radio nuclides are discharged into the environment and municipal sewers by various industries during rapid industrialisation. They constitute one of the major causes of land and water pollution. These metals include chromium, copper, lead, zinc, cadmium, nickel, etc. The cumulative toxicity and environmentally detrimental effects of heavy metals have stimulated increased investigation into their removal from industrial wastes. The chromium (Cr) present in effluent is primarily in the trivalent, Cr(III), and hexavalent, Cr(VI), forms. Chromium(VI) is considered to be toxic, carcinogenic and mutagenic in animals and hence deserves special attention (Roe and Carter 1969). Several industrial products and activities, such as dyes and pigments, film and photography, galvanometry, metal cleaning, electroplating, leather making and the mining

industries release undesirable amounts of Cr(VI). The permissible concentration of Cr in drinking water is 0.05 mg L^{-1} and not more than 2 mg L^{-1} in effluent. Removal of this metal from waste water by conventional physical and chemical methods such as precipitation- filtration, ion-exchange, reverse osmosis, oxidation reduction, electrochemical recovery, membrane separation, etc., is found to be ineffective and more expensive when the metal ion concentration in the polluted environment is in the range 10–100 mg L^{-1} and the set value is usually less than 1 mg L^{-1} (Zagie 1975; Patterson 1977).

In recent years, biosorption of heavy metals has been recognised as a potential alternative to existing technologies for removing heavy metals from industrial effluents, because this process can remove metal ions at concentrations lower than 10 mg L^{-1}. Various types of microbial biomass algae, fungi, bacteria and yeasts—have been reported as potential metal sequestering biosorbents (Tsezos and Volesky 1981; Kuyacak and Volesky 1989a; Ting and Teo 1994; Philip et

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al. 1995). The biosorptive capacity of dead fungal cells has been studied extensively and may be often greater than, equivalent to, or less than that of living cells (Urrutia Mera et al. 1992). Dead biomass in industrial applications enjoys certain advantages over living cells because of its ease of handling and ability to withstand toxicity and adverse operating conditions. Moreover, it can be procured from industrial sources as waste product from established fermentation processes. Inactivated biomass of the filamentous fungus *Rhizopus arrhizus* has been reported to be effective in scavenging heavy metals such as strontium, cadmium, copper, zinc, nickel, uranium, thorium, chromium and lead (Tsezos and Volesky 1982a,b; Brady and Tobin 1994; Fourest et al. 1994; Nourbaksh et al. 1994; Sag et al. 1995a).

Studies on the mechanism of removal of Cr ions by dead biomass have shown that the cell wall is the primary site of metal ion accumulation, and a variety of ligands (carboxyl, amino, hydroxyl, phosphates and sulfhydryl groups) located in the cell surface are known to be involved in metal binding. Chitin and chitosan, present in high concentration in the fungal cell wall, are also thought to be important sites of metal chelation and therefore important for Cr uptake (Tsezos and Volesky 1982a,b; Tobin et al. 1984; Holan et al. 1993).

Use of non-living biomass in its native form for large scale processes is limited because of the small particle size and low mechanical strength of the biomass. Moreover, the separation of biomass and effluent is difficult and expensive (Tsezos 1986). Therefore, immobilisation of biomass is necessary for an industrial biosorption unit. This yields mechanically strong, rigid particles with a high density, and of a size that allows easy operation of reactors. In addition, minimum clogging under continuous flow conditions, efficient regeneration of biosorbent and recovery of metal, and easy separation of biomass from effluent can be achieved (Gadd 1991).

Several reports are available on the use of immobilised biomass for the removal of metal contaminants from industrial effluents. Calcium alginate, a popular entrapment agent in immobilisation technology, has been one of the most extensively investigated biopolymers for binding heavy metals in diluted aqueous solution (Sag et al. 1995b; Lu and Wilkins 1996).

Polyacrylamide gel has been used successfully as an immobilising matrix for the removal of various metals (Wong and Kwok 1992; Wong et al. 1993; Andres et al. 1995). Polysulfone-entrapped biomass (mostly sphagnum peat moss) has been reported to be effective for the removal of heavy metals from mining waste water (Seidel and Jeffers 1991; Trujillo et al. 1991). Other matrices such as polyurethane, polyvinyl chloride, silica gel and adsorbent resins, have been evaluated for their metal uptake capacity (Tengerdy et al. 1981; Feiler and Darnell 1991; Zhou and Kiff 1991; Philip et al. 1996; Hu and Reeves 1997). Hu and Reeves (1997) have developed a technique using *Pseudomonas aeruginosa* biomass entrapped in porous polyurethane-based materials for the removal of uranium from acidic waste water. *Rhizopus arrhizus* biomass immobilised in reticulated polyester foam has been reported capable of binding cupric ions (Zhou and Kiff 1991). Tsezos and Deutschman (1990) have shown higher uptake efficiency of uranium by the same organism entrapped in polyvinyl formaldehyde. The same immobilised biosorbent has been successfully used for the removal of radium and uranium from process streams at pilot plant scale (Tsezos et al. 1989).

The metal-sequestering cycle which results in binding of the metal in the solid biosorbent material should be followed by a cycle which results in the release of the metal in a concentrated form. This part of the process, similar to the ion exchange process, is based on eluting the metal by a small volume of an appropriate solution which, ideally, regenerates the biosorbent for subsequent reuse. A successful biotechnological remediation process, therefore, would depend on the coupling of effective removal of soluble metal ions from the aqueous environment and subsequent recovery of these metals to enable regeneration of biomass for use in multiple adsorption–desorption cycles. This would lower biomass treatment costs for users and enhance profitability for biosorbent producers. An appropriate immobilisation technique would increase the number of sorption–desorption cycles and biosorbent life span. Dilute mineral acids such as HCl, H_2SO_4 or HNO_3 could be used for desorption of metal from loaded biomass (de Rome and Gadd 1987; Luef et al. 1991; Zhou and Kiff 1991; Holan et al. 1993; Pons and Fuste 1993).

Among all these acids, dilute HCl has been found to be the most effective eluent. Various reagents, such as sodium carbonate, sodium bicarbonate, EDTA, thiourea, citrate, ammonia, calcium chloride and nitrilotriacetic acid have been reported for elution of metals bound to the biosorbent (Kuyacak and Volesky 1989b; Xie et al. 1996; Hu and Reeves 1997).

The present work is aimed at developing economically viable bioreactor systems using immobilised microbial biomass to remove Cr from effluent. During industrial operations, use of biomass in native form causes problems such as blockage of flow lines and clogging of filters. Application of immobilised biomass solves such problems.

Dead biomass of *Rhizopus arrhizus* was encapsulated in various polymeric matrices such as alginate, polyacrylamide, polyvinyl alcohol (PVA) and polysulfone, and the metal binding efficiencies of the matrices plus biomass were evaluated so that a suitable biofix particle could be developed for removing Cr(VI) from industrial effluents. The effects of initial pH, biomass loading, temperature, contact time, initial metal ion concentration on adsorption of Cr(VI) and other aspects were investigated. Isotherms for the adsorption of Cr by native and by immobilised biomass were developed from optimum conditions, and the adsorption phenomena were explained by use of classical isotherm equations (Freundlich and Langmuir). The Cr removal efficiencies of immobilised beads in a stirred tank reactor and a fluidised bed reactor were evaluated.

Materials and Methods

Organism media and growth conditions

Rhizopus sp. was procured from NCL, Pune, and grown at pH 6.8 in liquid medium consisting of bacteriological peptone 10 g L^{-1}, sucrose 20 g L^{-1}, KH_2PO_4 1 g L^{-1}, $NaNO_3$ 1 g L^{-1}, and $MgSO_4.7H_2O$ 0.5 g L^{-1}. It was kept in static condition at room temperature for six days. Then it was killed by autoclaving for 1 h at 15 lbs (121°C) and washed twice with deionised distilled water and dried in an oven at 90°C for 6–8 h. The dried biomass was thoroughly powdered into uniform particle sizes.

Preparation of immobilised biomass

Four matrices—alginate, polyacrylamide, PVA and polysulfone—were used for entrapment of dead

biomass of *Rhizopus arrhizus*. In each case, blank beads were also prepared with no loading of biomass.

Sodium alginate was obtained from the CDH company. The PVA (MW 125 000) was supplied by S D Fine chemicals. Acrylamide, N'N'-methylenebis(acrylamide) and dimethyl formamide were purchased from SRL chemicals. Polysulfone resin (MW 30 000) was obtained from Aldrich chemicals. Ammonium persulfate and N,N,N',N'-tetramethylethylenediamine were purchased from Sigma chemicals.

Synthetic effluent was prepared so it resembled the effluent being discharged from the tannery industry: $NaHCO_3$ 2g L^{-1}; glucose 5g L^{-1}; NaCl 10 g L^{-1}; Na_2SO_4 2.5 g L^{-1}; $K_2Cr_2O_7$ 100 ppm. The pH of the solution was 8.3.

Entrapment of biomass in gels

Alginate beads

Alginate (2%) was mixed with 2% dry powdered biomass and made into beads in $CaCl_2$. The resultant beads were cured for 6 h and stored in 0.2% $CaCl_2$ at 4°C.

Polyacrylamide beads

Acrylamide/N'N'-methylenebis(acrylamide) (10% wt/vol) was mixed with 2% biomass. Polymerisation was initiated by ammonium persulfate and N,N,N',N'-tetramethylethylenediamine. The resultant slab gel (4 mm thickness) was cured for 4–6 h and cut into small cubes and stored at 4°C.

PVA beads

The PVA (4%) was mixed with 2% biomass. The mixture was extruded into 4% $CaCl_2$ solution as spherical particles and polymerisation was achieved by repeated freezing and thawing.

Polysulfone beads

Biomass (2%) was added to 10 g of polysulfone in dimethyl formamide solution, and the slurry was extruded as spherical beads. The beads were cured in water for 16 h.

Preparation of Cr(VI) solution

A stock Cr(VI) solution of 1000 mg L^{-1} was prepared in distilled water. It was used as the basis for Cr solutions containing 50–300 mg L^{-1}. The range of pH studied was 2.0–9.0. The pH of the

solution was adjusted to the required value with HCl (1N) or NaOH (1N) before immobilised biomass was added.

Metal adsorption studies

The metal adsorption efficiencies of fungus immobilised in alginate, polyacrylamide, PVA and polysulfone were studied by adding an adequate quantity of beads containing 100 mg of biomass (dry wt) to 50 mL of Cr solution (100 mg L^{-1}, pH 2.0. at 100 rpm) at ambient temperature for 24 h. Samples were taken at regular intervals and analysed for presence of Cr(VI) ion in the residual solution. The effects of pH (2 to 9), biomass loading (0.2 to 10%), duration of adsorption (0.5 to 24 h), agitation (50 to 200 rpm) and the initial metal ion concentration (50 to 300 mg L^{-1}) were studied in the Cr(VI) solution.

Analysis of Cr(VI) ions

The concentration of residual Cr ions in the adsorption medium was determined spectrophotometrically at 540 nm using diphenyl carbazide as the complexing agent (Nourbaksh et al. 1994). A calibration curve was prepared in the range 1–10 mg L^{-1}.

Reactor operations

The process of metal recovery using microbial biosorbent is basically a solid liquid contact process consisting of a metal uptake cycle and metal desorption. Appropriate contact between the solution and the solid can be accomplished in a reactor: for example, a stirred tank, a packed bed or a fluidised bed reactor, as in this study.

Stirred tank reactor

The granular biosorbent was kept in contact with the metal-bearing liquid by stirring it, to maintain a homogeneous suspension and good mass transfer. To study the effect of turbulence in the reactor on the adsorption capacity the speed was varied (75–200 rpm). Immobilised beads containing 2 g of biomass were added to 500 mL of synthetic effluent having a Cr concentration of 100 mg L^{-1} at pH 2.0 (liquid: biomass ratio of 1:50). The experiments were monitored for 8 h and samples were collected every hour and analysed for residual metal ion concentration. Experiments were also conducted by varying the liquid:biomass ratio to 1:10 and 1:16.66.

Packed bed reactor

The fixed bed reactor is a column in which the bioadsorbent granules (particle size 3 mm) are packed and do not move. When the whole bed becomes exhausted and saturated, the bioadsorbent is regenerated, in situ or separately. A serious drawback of this column is the sensitivity to suspended foreign matter in the influent, which clogs the bed. A packed bed of biofix beads (60 cm x 10 cm glass column) was used for the study. The Cr solution was pumped in from the bottom of the column. The residence time was varied to study the efficiency of the reactor.

Fluidised bed reactor

Fluidised bed reactors (FBRs) offer an attactive kinetic alternative to packed bed reactors because they use solution containing suspended matter. However, conditions in FBRs are difficult to control. In this study, the immobilised biomass particles of absorbent (*Rhizopus*) were fluidised in a 2.5 cm diameter column by a stream of the synthetic effluent continuously flowing upward to achieve a high degree of mixing. Fluidisation was attained by supplying compressed air through the bottom of the column. Studies were conducted by varying the liquid:biomass ratio (as was done for the stirred tank reactor, i.e. 2 g, 6 g and 10 g biosorbent in 100 mL of solution). Synthetic effluent containing 100 mg Cr L^{-1} at pH 2 was continuously fed into the column for 4 h. The samples eluting out of the column were monitored for metal ion concentrations at regular intervals.

Results and Discussion

Screening of polymeric matrices for immobilisation of *Rhizopus arrhizus*

Preliminary experiments were carried out to determine the metal binding efficiencies of biosorbents immobilised in the PVA, polysulfone. polyacrylamide and alginate matrices. The metal adsorption efficiencies of encapsulated biomass beads were compared with the native biomass. The results are presented in Table 1. Both polysulfone and PVA matrices were identified as superior candidates for fungal immobilisation in our study. Experimental results showed a higher effectiveness factor (>0.9) in both cases. Both matrices exhibited improved adsorption efficiency (~63%) in comparison to alginate-entrapped biomass (55%).

Table 1. Evaluation of Cr(VI) removal by polymeric matrices with or without immobilised *Rhizopus arrhizus*

Polymeric matrix	% Removal of Cr(VI) after 24 h of incubation	Cr(VI) loading (mg g^{-1} of dry biomass)	Effective factor
Free biomass (control)	69.604	34.802	1
PVA with biomass	63.513	31.756	0.912
PVA without biomass	6.116	0.441	0.087
Alginate with biomass	55.015	27.507	0.790
Alginate without biomass	4.412	0.455	0.063
Polyacrylamide with biomass	21.465	10.732	0.308
Polyacrylamide without biomass	9.380	0.753	0.134
Polysulfone with biomass	65.160	32.676	0.936
Polysulfone without biomass	6.5	0.526	0.0933

100 mg of biomass was used in all cases; initial Cr(VI) ion concentration in the solution was 100 mg L^{-1}

Higher metal uptake capacity was observed in these cases. The metal uptake efficiency of polysulfone-immobilised biosorbents was found to be 33 mg g^{-1} of biomass whereas in the case of PVA beads it was 32 mg g^{-1} of biomass. Biomass entrapped in polyacrylamide gel showed poor chromium-binding capacity in our study. However, polyacrylamide gel was reported to be a successful immobilising matrix for the removal of various metal ions such as copper, nickel, or uranium (Wong and Kwok 1992; Wong et al. 1993; Andres et al. 1995).

Parallel experiments were conducted to evaluate the adsorption efficiency of biomass-free polymeric matrices. Removal of Cr(VI) was found to be negligible in all these cases.

The variation in the metal uptake capacities of the various matrices could be attributed to the differences in porosity of polymeric gels. In the case of PVA- and polysulfone-entrapped biosorbents, higher metal uptake was recorded, perhaps due to the better porosity of the beads which would allow metal ions to be freely transported through the matrix.

Our study found differences in the performances of the native and immobilised biomass. Free biomass showed highest metal loading capacity (35 mg g^{-1} of biomass) and percent adsorption (69%). Biomass after entrapment in immobilising matrices (PVA and polysulfone) had 6–8% lower adsorption capacity than free fungal biosorbent. The binding of metal ions to the fungal cells was presumed to occur exclusively through surface adsorption. The active sites present in the cell wall of free biomass had greater exposure to the metal ions present in solution, which resulted in higher metal uptake. The encapsulated biosorbent adsorbed less metal and this was probably because of the cross linking of the potential metal binding sites with matrices, and masking of the active sites due to immobilisation. Moreover, the rate of the adsorption process could also depend on the rate of mass transfer from the bulk metal solution in the case of immobilised beads. However, the negative effect was found to be negligible compared to the distinct advantage of immobilisation in industrial operation.

There are reports of polysulfone-entrapped biomass being used for removal of mainly cationic metals from industrial effluents (Seidel and Jeffers 1991; Trujillo et al. 1991). However, the use of polysulfone and PVA-immobilised biosorbents for treatment of waste water contaminated by anionic metal ions such as Cr(VI) has not yet been reported.

Adsorption isotherm

Adsorption isotherms are graphs of solute concentration in the adsorbed state as a function of solute concentration in the solution at a constant temperature. They are useful for estimating the amount of adsorbent needed to adsorb a given amount of sorbate from the solution. They give valuable information that is useful for the selection of an adsorbent. They also facilitate the evaluation of the feasibility of the adsorption process for a given application (Weber 1985). The metal uptake data (θ) plotted against the final solution concentration (C) at equilibrium yields the
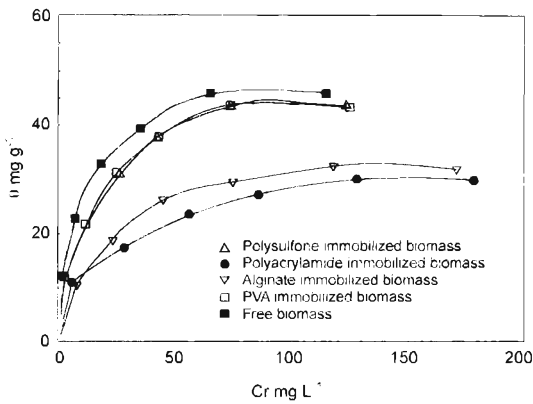
Figure 1. Adsorption isotherm for Cr(VI) removal using free and immobilised biosorbents
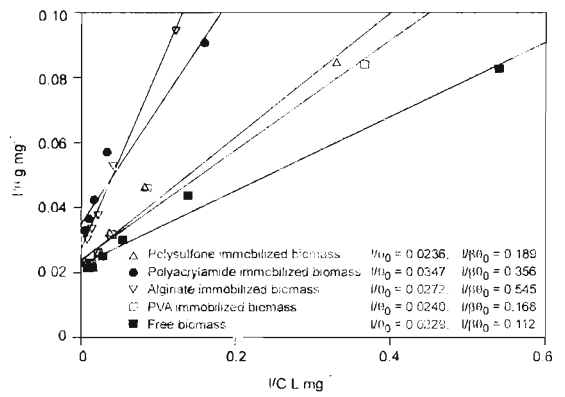
Figure 3. Langmuir adsorption isotherm of free and immobilised biosorbents for Cr(VI) removal

adsorption isotherm. The resulting relationship is most often hyperbolic because the biosorbent uptake value approaches the value of complete saturation of the sorbing material at a high concentration of the sorbed species (Volesky 1990).

The adsorption isotherms of immobilised biofix particles for uptake of Cr(VI) were compared with the isotherms for native biomass (Fig. 1). For each isotherm, initial Cr(VI) concentrations were varied from 50 to 300 mg L^{-1} while the biosorbent in each sample was held constant (4 g L^{-1}). It was observed that the adsorption isotherm of native biosorbent was steeper than that of immobilised biosorbents, indicating more affinity of the sorbent towards the given sorbed species. Of the four

Figure 2. Freundlich adsorption isotherm of free and immobilised biosorbents for Cr(VI) removal

matrices compared, PVA- and polysulfone-immobilised biosorbents had similar adsorption isotherm patterns. Biomass entrapped in polyacrylamide gel showed least metal binding affinity. The highest metal uptake capacity was 45.876 mg g^{-1} with free biosorbent. In comparison, biofix particles immobilised with PVA and polysulfone recorded 43.745 and 43.608 mg g^{-1} of biomass, respectively.

During adsorption, a rapid equilibrium is established between the adsorbed metal ions on the microbial cell (θ) and the unadsorbed metal ions in solution (C), and it can be represented by either Freundlich or Langmuir adsorption isotherms which are widely used to present data for water and waste water treatment applications. The Freundlich isotherm, used to describe the adsorption of solutes from dilute solution, can be given by
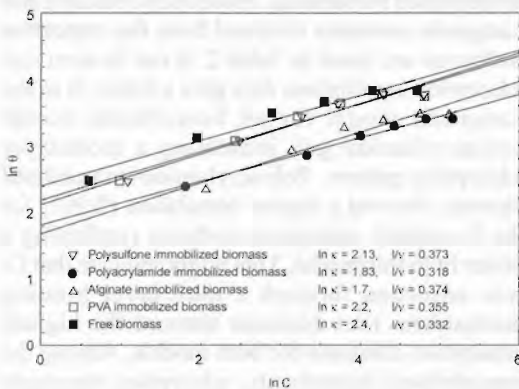
$$\theta = \kappa C^{1/\nu}.$$

This can be linearised by taking the natural logarithm of both sides of the equation to give

$$\ln \theta = \ln \kappa + 1/\nu \times \ln C.$$

The intercept $\ln \kappa$ gives a measure of the adsorbent capacity of the microorganism. The slope $1/\nu$ indicates the effect of concentration on the adsorption capacity and shows the adsorption intensity.

Unlike the empirical Freundlich isotherm, the Langmuir isotherm has a theoretical basis which relies on a postulated chemical or physical

Table 2. Model regression isotherms of free and immobilised biosorbents

Biosorbent	Freundlich model			Langmuir model		
	κ	ν	r^2	θ_0	$\beta\theta_0$	r^2
Free biomass	11.1	3	0.976	43.67	8.93	0.991
Polysulfone + biomass	8.4	2.67	0.981	42.29	5.29	0.987
PVA + biomass	9	2.8	0.977	41.67	5.95	0.985
Alginate + biomass	5.46	2.59	0.963	36.76	1.83	0.998
Polyacrylamide + biomass	6.24	3.14	0.991	28.8	2.81	0.971

Freundlich isotherm model: $\theta = \kappa C^{1\nu}$ where κ and ν are model parameters
Langmuir isotherm model: $\theta = \theta_0\beta C / (1 + \beta C)$ where θ = uptake of species, θ_0 = maximum uptake,
C = equilibrium (final) concentration in solution, β = constant related to energy of adsorption
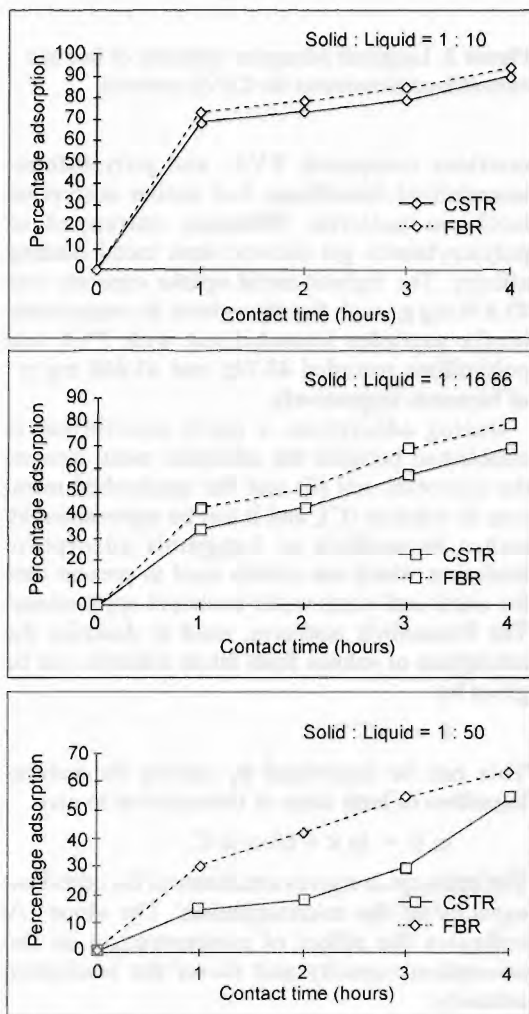
Figure 4. Comparison of the removal efficiencies of a continuous stirred tank (CSTR) and a fluidised bed reactor (FBR)

interaction (or both) between solute and vacant sites on the adsorbent surface, and the heat of adsorption is independent of the fraction of surface covered by the adsorbed solute. The Langmuir isotherm model has the form

$$\theta = (\theta_0\beta C) / (1 + \beta C),$$

where θ = uptake of the species, θ_0 = maximum uptake, C = equilibrium (final) concentration in solution, and β is a constant related to energy of adsorption. The linear form of the Langmuir equation is

$$1/\theta = 1/\theta_0 + [1/\beta\theta_0 \times 1/C].$$

The constants of the Langmuir equation can be determined by plotting $1/\theta$ versus $1/C$. This gives a straight line with slope $1/\beta\theta_0$ and intercept $1/\theta_0$.

In the present study both the models were used for evaluation of the adsorption data. Freundlich and Langmuir adsorption isotherms are presented in Fig. 2 and Fig. 3, respectively, for free and immobilised biosorbents. Freundlich constants and Langmuir constants obtained from the respective isotherms are listed in Table 2. It can be seen that adsorption equilibrium data give a better fit to the Langmuir model for all biosorbents except polyacrylamide gel, indicating a monolayer adsorption pattern. Polyacrylamide-immobilised biomass showed a higher correlation (0.991) for the Freundlich adsorption isotherm confirming a better fit to this model. This might indicate that Cr was adsorbed through a multilayer binding mechanism. Free biomass showed the highest adsorption constants for both models. Among the immobilised biosorbents, adsorption constants were higher for both models in the case of PVA- and polysulfone-immobilised biofix particles. Though the adsorption efficiency was found to be

larger for free biomass than for immobilised biosorbents (PVA and polysulfone), the difference was marginal and would not offset the advantage of immobilisation in industrial applications for removal of heavy metals from effluents.

Reactor studies

Batch experiments in a stirred tank reactor

Removal efficiencies of immobilised absorbents (PVA, polysulfonate and alginate) were tested in batch experiments in stirred tank reactors with 100 mg Cr L^{-1} and 4 g biomass at impeller speeds ranging from 75 to 200 rpm. In all cases the impeller speed of 100 rpm was found to be ideal for adsorption of Cr(VI). At higher impeller speed (200 rpm) a 12% decrease in adsorption was noticed with biomass on PVA and polysulfone beads, mainly due to eddy formation and improper contact between the adsorbent and Cr. A similar trend was observed with alginate-immobilised biomass. The lower impeller speed (75 rpm) also exhibited poor performance. Therefore further studies with immobilised biomass were carried out at 100 rpm only.

Figure 4 shows the adsorption of Cr (100 mg L^{-1}) by immobilised biomass from synthetic effluents in continuous stirred tank and fluidised bed reactors. In both cases the adsorption was more efficient at lower solid:liquid ratios. The fluidised bed reactor was generally more efficient than the continuous stirred tank reactor, especially in more dilute systems (solid:liquid ratio of 1:50). The study showed that with PVA and polysulfone-immobilised beads, about 90% adsorption of Cr(VI) and a metal uptake capacity of 23 mg g^{-1} can be achieved in a four hour contact at 1:10 solid:liquid ratio. The fluidised bed reactor performance was superior to that of the packed bed reactor (data not shown).

Conclusion

This study investigated the development of a suitable biofix particle for the removal of Cr(VI) from industrial effluents by entrapping the dead biomass of *Rhizopus arrhizus* in various matrices. The following important observations were made.

1. Poly(vinyl alcohol) and polysulfone matrices were identified as superior candidates for fungal immobilisation. These matrices had a higher effectiveness factor (>0.9). They exhibited a higher metal uptake capacity (33 mg g^{-1} of biomass) than alginate (27.5 mg g^{-1} of biomass) and polyacrylamide (10.73 mg g^{-1} of biomass).

2. Adsorption equilibrium data gave a better fit to the Langmuir isotherm model for PVA-, polysulfone- and alginate-immobilised biosorbents. In the case of polysulfone-entrapped biomass, the experimental data had a better fit to the Freundlich isotherm model.

3. The optimum agitation speed for Cr(VI) adsorption in a stirred tank reactor in batch process was found to be 100 rpm. Polyvinyl alcohol- and polysulfone-immobilised biomass beads showed 92% adsorption and a metal uptake capacity of 23 mg g^{-1} of biomass after 4 h of contact. In comparison, 59% metal removal was achieved with alginate-immobilised biomass during the same period of time. The corresponding metal uptake was 14.6 mg g^{-1} of biomass.

These observations establish that a good bioadsorbent particle can be obtained by immobilising dead fungal biomass in a polysulfone-matrix, and that it can be used for the removal and recovery of heavy metals from industrial effluents in large-scale operations so as to make the process economically viable.

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Development of Treatment Processes
for Waste Emissions at Their Source

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Abstract

Waste minimisation and recycling has become a high profile concern, both in manufacture and in material processing. The environmental aspects, in particular those associated with food and fibre products, are of vital importance because the associated industries use large volumes of water. The methods of 'cleaner production' enable these industries to address pollution through analysis of their production to discover where improvements can be made. As a result, energy consumption, water and material usage can quite often be reduced, with significant reduction or elimination of waste discharges and emissions while improving productivity. The engineers at the Agricultural Machinery Research and Design Centre (AMRDC) have developed various systems capable of handling the heavily polluted large volume waste treatment requirements of the food and fibre by-product industries. The methods involved are based on classic sizing, sorting and separation principles using appropriate yet often simple concepts. The AMRDC has developed one such system for the treatment of waste water, a portable filtration unit, now referred to as the 'Selective Separation Unit' (SSU), patented in key countries, which has attracted much broad interest. A prototype unit, capable of handling 50 L s^{-1} but able to be readily transported has been demonstrated in a number of difficult industrial situations such as a dried fruit (sultana) processing plant, a plastics recycling plant, a meat processing and by-product recovery plant, and a fruit and vegetable processing plant. In each case, the results have been most encouraging. This paper gives details of developments to date.

For many years, water and waste products have been discharged together into river systems or the sea itself, sometimes after some contaminants have been allowed to settle in holding tanks or dams. A great deal of suspended matter can be separated in the tanks, but because of the associated costs, most industries have dumped all waste streams into either one or a small number of tanks. That produces a troublesome waste stream, making it sometimes difficult to obtain water clean enough for re-use in production. Stream separation and 'at-the-source' treatments are now being more readily adopted by industry, helping to simplify this problem.

Some industries attempt to filter at various stages of production using currently available filters, but because there are normally large volumes of water involved, this is a very expensive procedure. There are large capital costs and maintenance problems associated with conventional filtration systems. In most cases, centrifuges, mechanical screens, pressure filters or rotating drum filters are used.

Stringent legislation is creating many challenges and new and economical methods of waste water treatment have to be found to satisfy the ever increasing safeguards being developed to protect the environment.

Researchers are investigating 'at-the-source' treatment opportunities, or the use of 'cleaner production' methods, but to design and develop improved equipment capable of carrying out the necessary tasks is often difficult. The engineers at

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the Agricultural Machinery Research and Design Centre (AMRDC) of the University of South Australia have developed several systems capable of solving the heavily polluted, large volume waste treatment requirements of the food and fibre industries. The methods are based on classic sizing, sorting and separation principles using appropriate yet often simple concepts that target both the 'dry' and 'wet' processes associated with production.

One system that the AMRDC has developed for the treatment of waste water is a modular filtration system, referred to as the 'Selective Separation Unit' (SSU). This technology has been patented in key countries and has attracted significant interest. It is described later in the paper.

'Cleaner Production' Principles

The philosophy of 'cleaner production' entails the use of revised management practices and processes that minimise environmental impacts associated with production. It can readily be applied to most industry practices. The revised practices not only protect the environment but may also reduce production costs by implementing improvements that increase efficiency, reduce waste of material inputs and increase productivity, while lessening energy usage and waste generation.

There can be added benefits in the food and fibre industries: marketable by-products can be collected; quality of the primary product can be improved; market competitiveness can be increased; and available resources can be recycled and reused. Particular benefits arise when the production system removes contaminants at the first point of identification, rather than trying to handle them at the end of production as a complex waste stream. This point-of-identification approach provides further reductions in waste discharge volumes, potency and the level of treatment required, while increasing financial return.

Cleaner production methods in essence promote higher efficiency for industrial processes, products and services so as to prevent pollution, in many cases for financial gain. Application of these methods, however, requires know-how and the use of modern technology and practices. While the benefits for both the producer and the environment are evident, recognition of a need for cleaner production develops a competitiveness within industries for sustained economic development through state-of-the-art plant improvements.

Sizing, Sorting and Separation

One approach that alleviates waste disposal problems involves the collection of specific by-products or waste constituents as they become apparent in processing. This enables the production system to steadily lower the percentage of waste matter in the final waste stream while reducing the effluent load on waste water discharges. The use, rather than disposal, of wastes creates a means of repayment for the costs incurred, thereby offsetting the total cost associated with the process changes implemented.

A key requirement of this approach is the division of a complex problem into a number of key parameters or smaller problems. This eliminates as many parameters as possible, and thereby simplifies the original problem. For example, consider the fundamentals of production: a raw material is subjected to a number of process operations which require input of energy for plant operations and result in a waste stream and the desired product stream.

Simplification of the final waste problem can be achieved by identifying all sources of waste generated from each process in the operation. Each of these smaller waste problems is addressed by applying the particular procedures or treatments necessary to solve it. In many cases, this allows the waste to be collected before it degrades, with a potential for making by-products.

This method of simplification focuses on solving the waste problem practically, by adopting a versatile array of sizing, sorting and separation techniques that can be implemented in both the 'wet' and 'dry' stages of production. The result can improve product quality and enable the collection of constituent waste contaminants of relatively similar character.

The science of sizing, sorting and separation is very important in the handling of natural products and waste streams. It can be applied both to the handling and to the process operations up to the final stages of industry production, and its outcomes can readily lead to improved raw material handling and enhanced product quality.

The concepts can be divided into two activities, viz. dry sizing, sorting and separation (e.g. removal of coarse particulates from fresh produce) and wet sizing, sorting and separation (e.g. removal of particulates and chemical residues from process water).

The basic principles of sizing, sorting and separation for treatment of wastes and by-products are based upon:

• the distinction of raw materials, intermediary and final products from constituent contaminant matter, by both physical and chemical classification techniques;

• the sorting of each product, by-product or waste contaminant by physical, chemical or biological means or a combination of them, ensuring efficient removal of dissolved or suspended solids.

An immediate outcome of the sorting regime is separation, generally enabled by physical means once the correct sorting principle has been established.

Once the process has been truly understood in terms of the related scientific and engineering principles, a cost-effective solution can usually be applied to specific industry problems. The sizing, sorting and separation method is a way of facilitating cleaner production. It is valuable tool with which engineers can develop cost-effective and environmentally-aware waste solutions for industry. Primary product purification and by-product collection is thus made possible. The 'sizing, sorting and separation' technique is implemented as an integral component of routine sampling and analysis to obtain basic data. The treatment procedures that evolve can prevent undesirable interaction of wastes, further degradation and odorous emissions.

The ability to classify, sort and separate materials to achieve a contaminant free, high quality final product with minimal waste-bearing streams can assist agricultural production systems to add value to their products, and to achieve a 'clean green' image for food and fibre industries.

Solutions to Waste Problems

The best long-term solution is to reduce pollution at its source, or to stop generating waste in the first place through appropriate strategies. In some cases however, some form of 'end-of-pipe' treatment is the only means of preserving production and the environment. In either case it is important that any unit processes are simple and reliable.

Waste water is generally contaminated with inorganic and organic matter and micro-organisms. The traditional aims of treatment are first to remove suspended matter, and then to facilitate the reduction of dissolved matter without added degradation of the water quality. Treatment should therefore begin with the physical removal of grit and other easily separable solid matter associated with the raw material. Effective screening must be correctly implemented for solids recovery and value-added by-product opportunities.

Chemical and biological treatments, while likely to provide further treatment benefits for obtaining improved quality waste water, should be only used once all screenable solids have been separated. All waste treatments should be selected so as to be cost effective and perhaps offer cost benefits as an offset to treatment costs.

As we have said, it is far better to treat pollution through preventative measures by tackling the waste as it occurs. Water monitoring equipment for recording temperature, salinity, flow, and turbidity measurements should be used to provide accurate material balances for a processing plant and thereby identify potential improvement areas. Such measures not only assess the performance both of management and of production workers, but can allow waste handling costs to be reduced, and enhance water conservation and re-use, resulting in possible raw material savings.

After all in-plant waste management opportunities have been explored, decisions can be made about appropriate methods of treatment and disposal of the resultant wastes.

Once the sources and quantities of waste have been established, it is usual to find that there are methods of reducing water consumption and waste. Process re-design and reorganisation can also improve energy consumption, lower product losses, and result in fewer accidents and spills, better public relations and reduced liability.

By-product or resource recovery often creates a range of potential uses, depending on the character and quality of the by-product or resource.

By-product Recovery

Most of the by-products associated with the agricultural, food and fibre industries can be recovered as animal feeds, waste paper, fats and oils, or fertilizers; the water can be used without alteration for land irrigation. Simpler by-products generated through biochemical treatment include biogas and energy derived from combustion of waste.

Examples of by-product recovery include:

- protein from meat, shellfish and by-product processing;
- fruit matter from dried vine-fruit process operations;
- citrus and vegetable meal from canning and juicing operations;
- starch from vegetable and grain processing;
- fats, oils or gelatin from animal offal-containing wastes; and
- solids from food processing operations which can often be used for animal feed, compost, and as soil conditioners.

Implementation of a cleaner production approach can also provide benefits by improving by-product quality in a host of industries.

Abattoirs, tanneries and meat works all offer a diverse range of by-products, both edible and non-edible, and perhaps reflect a typical example of good by-product utilisation. However, a great number of 'cleaner production' opportunities still exist particularly in the recovery of raw materials or chemicals, especially in tanneries. For example, process operations associated with these industries produce appreciable amounts of hair, wool, feathers, fat, oil and protein which are carried away by water streams at a large scale. Losses of these by-products occur in each section of processing, whether it be the processing of meat or its related by-products; they are not only 'dollars down the drain' but also present serious environmental concerns.

Tanneries in particular use large volumes of concentrated liquors in each stage of production. The removal of contaminants from spent liquors therefore provides the opportunity to recycle and re-use chemicals, and also the opportunity for value-adding through by-product recovery. Good management practices and improved waste handling measures not only reduce pollution output by the industry but enable commercial realisation of recognisable by-products and chemical recovery.

Associated meat by-products can be manufactured into industrial chemicals, cosmetics, pharmaceuticals, glue, soap, glycerine, animal feeds, fertilizers, candles, lubricating oils and shaving cream.

Leather, scrap and associated waste generated by skin processors and tanneries, which are uncontaminated by worn parts, nails, adhesives, and so on, offer significant recycling potential for commercial gain, and can also be used as biodegradable fertilizer. Smaller pieces of leather trimmings and shavings of both tanned and untanned waste can be used for the manufacture of gelatin and collagen-based products and for the manufacture of insulation and a range of recycled leather products.

A Cleaner Production Technology: The SSU

The Selective Separation Unit or SSU is a technical breakthrough in the extraction of a lean filtrate from a solid-carrying liquid. It combines simplicity and effectiveness with low capital and operational costs. Its real significance, however, lies in the fact that it can operate under high flow conditions without requiring regular maintenance as conventional 'dead-end' filtration methods do. Thus, the SSU enables in-line recycling opportunities previously not achievable by other filtration solutions for waste treatment.

The system possesses the following advantages:

- minimal floor space required;
- no operator involvement;
- very little power requirement;
- little or no maintenance required;
- no residence time; separation is immediate and in-line with flow;
- system can alter operation to suit contaminant level and flow character;
- relatively small in size and capital outlay;
- virtually zero pressure differential.

In general, the SSU has enormous potential in industry because it may be used for virtually any type of water or effluent in which a predominant liquid volume is to be separated from its suspended solid constituent. The SSU's operating principle relies on the response of the solid contaminants' particle dynamics in response to fluid flow, thereby using counter-flow techniques for the efficient separation of solids. The SSU is in fact a 'self cleaning' filtration unit that can be used in various in-line situations.

The SSU offers two modes of application: (i) particle filtration, from coarse solids down to a particle size of less than 100 μm, e.g. sand; (ii) micro filtration, from particles down to colloidal matter of less than 5 μm, e.g. flocs.

Some examples include: final filtration of effluent before irrigation; insurance filtration during waste water recycling to ensure solids removal; primary/ secondary/tertiary filtration during conventional treatment 'at the source' for solids reduction and water recycling; by-product recovery.

A prototype unit, capable of handling 50 L s^{-1} is readily transportable and has been demonstrated in a number of difficult industries such as a dried fruit (sultana/raisin) processing plant, a plastics recycling plant, a meat processing and by-product recovery plant, and a fruit and vegetable processing plant.

Cleaner production demonstrations are planned for various other industries, including the tanning industry, for a number of potential applications, from stream purification to by-product recovery.

Conclusion

The University of South Australia is now in the process of formulating a marketing strategy to commercialise the technology. A full patent has been granted for world protection of the SSU technology in the light of the commercial opportunity presented. The prototype SSU has received interest from various organisations and government bodies, and is an excellent example of technology which can assist in cleaner production.