



REULATO RIO
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Organic pollutants and heavy metal contaminants in wastewater discharges and sediments from the Riachuelo river, Argentina 2000

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EXECUTIVE SUMMARY

The Matanza-Riachuelo Basin runs through a highly industrial and urbanised area of Argentina, to the south of the city of Buenos Aires. In 1997 and 1998, samples were collected from the river system and from point discharges to the river via storm water and sewage channels as well as from industrial discharge pipes. Analysis of these samples showed widespread contamination with heavy metals and organic pollutants.

Greenpeace revisited the Riachuelo river in August and September 2000 and collected a number of samples to determine the current contamination of certain areas. The analysis of these samples for organic contaminants and heavy metals demonstrated the following:

- The contamination of this area with anthropogenically derived chemicals described in the previous reports has clearly not improved and in some cases the situation has become worse. This is true both for pollution from organic compounds and a number of heavy metals.
- The river sediments at the locations revisited contain many of the organic pollutants previously detected, as well as a number of additional persistent and toxic compounds, including polychlorinated biphenyls (PCBs). The levels of many toxic metals that were present at high level in the samples collected in 1997 have increased at all three locations, indicating the ongoing discharge of these metals.
- Both tanneries sampled, GRD and Americo Gaita, continue to discharge high concentrations of the toxic metal chromium, a well known tannery pollutant. The sediments at both locations also remain contaminated with chromium.
- In addition to the inputs of hazardous substances from industrial effluents, discharges of combined urban runoff water and sewage wastewaters are contributing to the inputs of organic pollutants and heavy metals to the Riachuelo. The situation at the location sampled has deteriorated since 1997, with additional persistent toxic organic compounds being identified and the levels of many heavy metals increasing.

Many of the chemicals identified are toxic at low concentrations, and some have the potential to bioaccumulate. Some of the chemicals discussed in this and the previous reports are highly persistent, and will therefore remain in the environment for a considerable time after their discharge ceases.

Recommendations made in the previous report regarding long-term solutions based on clean production alternatives, renewable resources and pollution prevention clearly remain unaddressed, and this is resulting in increasing decay of the Riachuelo river.



1 INTRODUCTION

The Matanza-Riachuelo Basin runs through a highly industrial and urbanised area of Argentina, to the south of the city of Buenos Aires. In 1997 and 1998, samples were collected from the river system and from point discharges to the river via storm water and sewage channels as well as from industrial discharge pipes. Analysis of these samples showed widespread contamination by a large range of organic pollutants and heavy metals. Details of this survey are given in the following reports;

Matanza-Riachuelo Basin Part 1; Identification and environmental significance of organic pollutants and heavy metal contaminants found in water and sediments collected from the Matanza-Riachuelo Basin, Argentina 1997. (Stephenson *et al.* 1998).

Matanza-Riachuelo Basin Part 2; Identification and environmental significance of organic pollutants and heavy metal contaminants found in industrial wastewaters and sediments collected from the Matanza-Riachuelo Basin, Argentina 1997-1998. (Stephenson & Labunska 1998a).

Matanza-Riachuelo Basin Part 3; Identification and environmental significance of organic pollutants and heavy metal contaminants found in storm water, urban runoff and domestic sewage channels, discharging to the Matanza-Riachuelo Basin, Argentina 1997. (Stephenson & Labunska 1998b).

Greenpeace revisited the Riachuelo river in August and September 2000 and collected further samples to determine the current contamination of certain areas.

2 SAMPLING PROGRAM

Nine samples were collected, including two industrial discharges and associated sediments, one sample of combined runoff water and sewage discharge and associated sediment, and three samples of river sediments. A detailed description of sample collection, preparation and analytical procedures is presented in the previous reports.

Details of the samples collected for the current report and samples collected at the same locations as described in the previous reports are given in Table 1. In this table, the samples are arranged in order from those collected furthest upstream to those collected furthest downstream.



Sample Number (2000)	Sample Number (1997/98)	Sample Description	Sample Location
AM0179	AG7029	River sediment	Southwest bank of the Riachuelo River at La Noria Bridge, Lomas de Zamora
AM0175	AG7035b	Industrial wastewater	Discharge pipe of Americo Gaita leather tanneries to the Riachuelo river, Lanus (collected at the main entrance of the plant)
AM0176	AG7035c	Sediment	Below the Americo Gaita leather tanneries discharge pipe, Lanus (collected at the main entrance of the plant)
AM0177	AG7014	Combined wastewaters	Combined discharge pipe to the Riachuelo River, at the Octagon, Lanus
AM0178	AG7015	Sediment	Below the combined discharge pipe to the Riachuelo River, at the Octagon, Lanus
AM0180	-----	River sediment	Northwest bank of the Riachuelo River near Pompeya Bridge, Lomas de Zamora
AM0048	AG7017	Industrial wastewater	Discharge pipe of GRD leather tanneries to the Riachuelo River, Avellaneda
AM0049	AG7016	Sediment	Below the GRD leather tannery discharge pipe, Avellaneda
AM0181	AG7006	River sediment	Riachuelo River near Avellaneda Bridge, Buenos Aires

Table 1. Description of samples collected from the Riachuelo River and environs, Argentina, 1997, 1998 and 2000.

3 RESULTS AND DISCUSSION

The results of the organic screen analysis and the heavy metals analysis are presented in Table 2, including a breakdown of the groups of organic compounds reliably identified in the samples. For the groups of organic compounds reliably identified; ✓ (#) signifies compounds identified using general GC/MS screening method, with the number of compound given in parentheses for groups with more than one compound; * signifies compounds identified only at trace concentrations using a selective ion monitoring (SIM) method. Metal concentrations are given in mg/kg dry weight for solid samples and ug/l for liquid samples.

More information on the common sources, environmental behaviour and toxicological outlines for many key pollutants detected during this study are given in the previous reports. Information on additional key pollutants is given in Appendix 1.



Sample number	AM0179	AM0175	AM0176	AM0177	AM0178	AM0180	AM0048	AM0049	AM0181
Description	river sediment	industrial wastewater	sediment	combined wastewater	sediment	river sediment	industrial wastewater	sediment	river sediment
Location	Riachuelo River, La Noria Bridge	Americo Gaita discharge pipe	Americo Gaita discharge pipe	Combined discharge pipe, the Octagon	Combined discharge pipe, the Octagon	Riachuelo River, Pompeya Bridge	GRD discharge pipe	GRD discharge pipe	Riachuelo River Avellaneda Bridge
Metals	(mg/kg)	(ug/l)	(mg/kg)	(ug/l)	(mg/kg)	(mg/kg)	(ug/l)	(mg/kg)	(mg/kg)
Cadmium (Cd)	1	<20	<1	<20	5	5	<20	<1	2
Chromium (Cr)	170	213	2051	<20	164	1648	10332	66904	1099
Cobalt (Co)	10	<20	5	<20	22	8	<20	<2	10
Copper (Cu)	250	<20	19	52	242	325	<20	17.4	229
Lead (Pb)	201	<30	36	<30	540	407	<30	14.3	211
Manganese (Mn)	386	<10	371	190	246	236	1539	7	327
Mercury (Hg)	1.76	<1	<0.05	<1	0.94	2.30	2.2	0.79	0.89
Nickel (Ni)	41	<20	15	<20	34	46	<20	2.9	40
Zinc (Zn)	938	24	108	91	18539	936	43	186.5	927
No. of organic compounds isolated	116	183	140	220	93	142	63	85	206
No. of organic compounds reliably identified	26(22%)	60(33%)	33(24%)	56(25%)	7(8%)	34(24%)	16(25%)	25(29%)	57(28%)
ORGANOHALOGEN COMPOUNDS									
Benzene, 1,2-dichloro-						✓		✓	*
Benzene, 1,4-dichloro-	✓	✓	*	✓	✓	✓		*	*
PCB-138						✓			*
PCB-153						✓			*
PCB-180						✓			
Pentachlorobiphenyl isomers						✓(3)			
Hexachlorobiphenyl isomers (other than 138 & 153)						✓(3)			
Hexachlorocyclohexane, beta-			✓						
POLYAROMATIC HYDROCARBONS									
Naphthalene &/or derivatives	✓(3)	✓(16)	✓(8)	✓(12)	✓(2)	✓(2)	✓(6)	✓(3)	✓(12)
Anthracene &/or derivatives				✓(2)					✓
Phenanthrene &/or derivatives				✓				✓	✓(3)
Pyrene &/or derivatives						✓			
9H-Fluorene &/or derivatives		✓							
ORGANOSULPHUR COMPOUNDS									
Benzothiazole, 2-(methylthio)-		✓							
PHENOLIC COMPOUNDS									
BHT			✓			✓		✓	✓
Phenol, 4-methyl-		✓				✓			
PHTHALATE ESTERS									
DEHP		✓		✓		✓			
DEP				✓					
DBP				✓					
OTHER AROMATIC COMPOUNDS									
Alkylated benzenes		✓(22)	✓(3)	✓(3)	✓(6)				✓(9)
Biphenyl &/or derivatives		✓							
1H-Indole &/or derivatives		✓					✓(2)		
1H-Indene &/or derivatives					✓				
Galaxolide (Musk 50)					✓	✓			
ALIPHATIC HYDROCARBONS									
Linear	✓(21)	✓(15)	✓(18)	✓(18)	✓(24)	✓(16)	✓(8)	✓(17)	✓(23)
Cyclic	✓		✓	✓	✓(5)			✓	✓(4)

Table 2. Organic chemicals and heavy metals identified in samples from the Riachuelo River and environs, Argentina, 2000. See text for details.



The river sediments exhibit severe contamination with heavy metals, in part discharged via the effluents sampled. Moreover, certain of the samples contained highly toxic and persistent organochlorines. These are discussed in more detail below.

The majority of the samples collected for both this report and the previous reports also contained a wide range of common pollutants. These include hydrocarbons, alkyl benzenes and polyaromatic hydrocarbons (PAHs), 1,4- and 1,2-dichlorobenzene and as butylated hydroxytoluene (BHT). Additional information on these organic compounds is given in the previous reports (Stephenson *et al.* 1998, Stephenson & Labunska 1998a & b).

The hydrocarbons, alkyl benzenes and polyaromatic hydrocarbons (PAHs) are components of crude oils or petroleum products and as such are very widespread environmental pollutants (Mackay 1988, Wang & Fingas 1995).

The persistent organochlorine, 1,4-dichlorobenzene, was also detected in the majority of samples, including two of the three wastewaters. The main use of 1,4-dichlorobenzene is in the production of room deodorants and sanitary deodorant blocks, and as such is an extremely common pollutant in sewage wastewaters. It is most likely that this is the source of 1,4-dichlorobenzene at these locations, although other sources cannot be ruled out. Other uses of this compound include its use as an insecticide, an intermediate in organic synthesis, in extreme pressure lubricant and in the manufacture of poly(phenylene sulphide) resin (Bryant 1993, CEC 1986).

1,2-dichlorobenzene was also detected in three sediment samples collected for this study: AM0049, AM0180 and AM0181. This is an isomer of 1,4-dichlorobenzene and is often manufactured together with it (Bryant 1993, CEC 1986). 1,2-dichlorobenzene is mainly used in degreasing for the metal and automotive industries (Meek *et al.* 1994). However, in light of wide-ranging occurrence of 1,4-dichlorobenzene in this location, it is possible that the presence of the 1,2-isomer is due to its presence as a contaminant in 1,4-dichlorobenzene used to prepare sanitary deodorant.

The compound 2,6-bis(1,1-dimethylethyl)-4-methylphenol, also known as butylated hydroxytoluene (BHT), was identified in four sediment samples; AM0049, AM0176, AM0180 and AM0181. This compound was also detected in a large number of the samples collected for the previous reports. This compound is frequently employed as an antioxidant in food products and in the production of plastics, petrochemicals and some cosmetics (Merck 1989). Due to its presence in many consumer products, it is frequently found in domestic sewage and sewage sludge.

3.1 Tannery discharges

The direct industrial discharges to the Riachuelo river and their associated sediments were collected from the GRD and Americo Gaita leather tanneries. The toxic metal chromium is one of the commonest and most damaging of the environmental pollutants associated



with the tanning industry. A detailed discussion of the tanning process, including the associated environmental problems is given in Appendix 2. More information on the common sources, environmental behaviour and toxicological outlines for chromium is given in Appendix 1.

In addition, both the wastewater samples (AM0048 and AM1075) and the associated sediments (AM0049 and AM0176) contained a similar range of organic contaminants to those detected in the samples collected previously. The majority of these were hydrocarbons, alkyl benzenes and PAHs.

3.1.1 GRD leather tanneries

In addition to the organic compounds discussed above, the wastewater and sediment samples collected both previously and for the current study contained a number of toxic metals at elevated concentrations. In particular, there is evidence of severe and continuing contamination with chromium.

The wastewater and sediment samples collected from this location in 1997 (AG7016 and AG7017) contained high concentrations of chromium. The wastewater (AG7017) contained 7530 ug/l and the sediment (AG7016) contained 2883 mg/kg. The concentrations in the samples collected for the current survey contained this toxic metal at even higher concentrations: 10332 ug/l in the wastewater (AM0048) and 66904 mg/kg in the sediment (AM0049). The concentration of chromium in the sediment collected for this study is more than twenty times the concentration found in the sample collected previously. The continued discharge of large quantities of chromium in the wastewaters from the GRD tanneries is clearly contributing to the very large increase in the concentration of chromium found in the sediment collected for this study compared to that collected in 1997.

Typical background concentrations of chromium are 1.3 ug/l in freshwater and 1-500 mg/kg for freshwater sediments (ATSDR 1997). The concentration of chromium in the wastewater sample AM0048 is 7948 times typical freshwater concentrations, and the concentration in the sediment sample AM0049 is 134 - 66904 times background concentrations.

Chromium is a well known pollutant in wastes from leather tanneries, and based on data obtained from the Argentine Secretary of Natural Resources and Sustainable Development (Programa de Obras 1997), tannery wastes seem to be one of the most likely sources of chromium in the Matanza-Riachuelo Basin (see Appendix 2).

3.1.2 Americo Gaita leather tanneries

The wastewater and sediment samples collected from the discharge point of the Americo Gaita leather tanneries (AM0175 and AM0176), as well as those collected previously



contained the toxic metal chromium at significant concentrations. The wastewater (AM0175) and sediment (AM0176) samples contained chromium at 213 ug/l and 2051 mg/kg respectively. The wastewater and sediment samples collected from this location in 1997 (AG7035b and AG7035c) also contained high concentrations of chromium. The wastewater (AG7035b) contained 1590 ug/l and the sediment (AG7035c) contained 4918 mg/kg.

The concentrations of chromium in the samples collected for this study are significantly lower than those found in the previously collected samples, suggesting that additional treatment of the wastes from Americo Gaita leather tanneries may be taking place. However, the concentrations in the wastewater and associated sediment samples are still high. Typical background concentrations of chromium are 1.3 ug/l in freshwater and 1-500 mg/kg for freshwater sediments (ATSDR 1997). The concentration of chromium in the wastewater sample AM0175 is 164 times typical freshwater concentrations, and the concentration in the sediment samples AM0176 is 4-2051 times background concentrations.

Organic contamination at this site included compounds discussed in Section 3.1. In addition, the effluent contained the phthalate ester, di(2-ethylhexyl)phthalate (DEHP), and the sediment from this site contained the toxic and persistent organochlorine compound beta-hexachlorocyclohexane (beta-HCH). These compounds were not detected in the samples collected in 1997 (AG7035b and AG7035c).

The phthalate ester, DEHP, is a well known environmental contaminant that has been widely used as a plasticiser in PVC (Kemi 1994, Jobling *et al.* 1995). However, numerous alternative uses of DEHP have also been reported, including use as a solvent in erasable ink, in vacuum pump oil, as a component of dielectric fluids in electrical capacitors, as a concrete additive and as an insect repellent (ATSDR 1997; Jobling *et al.* 1995). Due to the widespread use of this compound, it is not possible to identify the source of DEHP in this sample.

beta-HCH is a component of technical grade hexachlorocyclohexane (HCH) (Safe 1993). Technical grade HCH can be purified to extract the gamma isomer, which has insecticidal properties and is best known under the trade name "lindane". The technical mix has also been used unpurified as an insecticide, under which circumstances it is more usually called technical HCH or BHC. Among the eight possible isomers of hexachlorocyclohexane, alpha-, beta-, and gamma-HCH are the most important isomers in terms of environmental impact, with beta-HCH being the most stable of these isomers. While the presence of beta-HCH could either be due to releases from the manufacturing of technical HCH or lindane, it is possible that its presence at this location is as a result of the use of technical HCH as an insecticide in the past. Additional information on the uses, environmental behaviour, toxicity and legislation for HCH is given in Appendix 1.

While beta-HCH was not detected in the samples collected from this location in 1997, it was identified in a number of samples collected from other areas of the Matanza-Riachuelo Basin (AG7013, AG8004).



3.2 Combined runoff water and sewage discharge

It is believed that runoff discharged to the Riachuelo river water carries large volumes and diverse pollutants from industrial wastes from the chemical, petrochemical, pharmaceutical, metallurgical, food, beverage, leather, textiles, and paper industries of the area (Programa de Obras 1997).

The samples collected from this location both previously and for this report contained a wide range of hydrocarbons, alkyl benzenes, polyaromatic hydrocarbons (PAHs) and 1,4-dichlorobenzene. These compounds have been discussed in Section 3.

A number of additional organic pollutants were identified in the samples collected for this report (AM0177 and AM0178) that were not identified in the samples collected from this location in 1997 (AG7014 and AG7015). Three phthalate ester; di-(2-ethylhexyl) phthalate (DEHP), diethyl phthalate (DEP) and di-n-butyl phthalate (DBP) were detected in the effluent.

It was only possible to reliably identify a small number of organic compounds in the sediment sample AM0178, although a large number of unresolved compounds were detected. Nevertheless, the pollutants identified in the sediment included the synthetic musk Galaxolide (also known as Musk 50 or HHCB). Galaxolide is a polycyclic synthetic musk compound. This class of synthetic musks is increasingly replacing synthetic nitro musks such as musk xylene (MX) and musk ketone (MK). Worldwide production of polycyclic musks is estimated at 6000 tonnes per year. Like MX and MK, polycyclic musks are detectable in many aquatic systems, particularly those receiving sewage (Rimkus 1999).

This highly persistent compound has a structure very similar to that of a natural human pheromone and is also absorbed directly through the skin and therefore may pose a health risk, though the full potential health impacts of this compound have yet to be fully investigated (Kallenborn et al. 1999).

Phthalate esters are used in a very large number of products, and many are well known environmental contaminants. A study published in 1986 showed that the two most abundantly produced phthalate esters were DEHP and DBP (Menzert *et al* 1986). Numerous uses of DEP have also been reported, including use in cosmetics, as a concrete additive, and as a solvent for perfume oils (ATSDR 1997; Jobling *et al.* 1995). The phthalate ester DEHP is discussed in Section 3.1.2, and more information on phthalate esters is given in Appendix 1.

The sediment sample AM0178 contained a number of metals at significant concentrations, most noticeably zinc at 18539 mg/kg, which is 185 times the typical background concentration of 100 mg/kg (ATSDR 1997, Salomons and Forstner 1984). The concentration of zinc in the sample collected at this location in 1997 (AG7015) was only 262 mg/kg.



The sediment sample AM0178 also contained elevated concentrations of copper (242 mg/kg), cadmium (5 mg/kg), mercury (0.94 mg/kg), and lead (540 mg/kg). As for zinc, the concentration of these metals in the corresponding sample collected in 1997 (AG7015) were significantly lower. The sediment sample AG7015 contained copper at 79 mg/kg, mercury at 0.2 mg/kg, and lead at 254 mg/kg. The concentration of cadmium in this sample was below detection limits.

For comparison, the typical background concentrations of these metals in uncontaminated freshwater sediments are 45-50 mg/kg for copper, 0.2-0.35 mg/kg for mercury and 20-30 mg/kg for lead (Salomons and Forstner 1984, ATSDR 1997).

The increase in these metals in the sediment samples between 1997 and 2000 suggests the ongoing discharge of wastewaters containing significant concentrations of these metals at this location. However, most metals analysed for were not detectable in the combined wastewater sample AM0177. Those that were detected were at comparatively low concentrations. For instance, zinc was present at a concentration of 91 ug/l. Typically, zinc is found in freshwater at less than 50 ug/l (ATSDR 1997).

The fact that the one sample of wastewater collected from this location in 2000 did not contain high concentrations of metals may be due in part to the high degree of variability in both the volume and composition of the combined wastewater discharge. It may also be indicative of the influence of other discharges on the sediments at this location.

3.3 River sediments

Heavy metals and many persistent organic pollutants will bind predominantly to suspended material, and finally accumulate in the river sediment, thus providing a reliable history of pollution.

The three river sediments collected from the Riachuelo (AM00179, AM00180, and AM0181) contained a large number of organic compounds, though it was not possible to identify a large proportion of these compounds. Of the compounds identified, the majority were hydrocarbons, alkyl benzenes and PAHs.

All three sediment samples contained the common persistent environmental pollutant, 1,4-dichlorobenzene. The two downstream samples (AM0180 and AM0181) also contained the isomeric organochlorine, 1,2-dichlorobenzene, and butylated hydroxytoluene (BHT). These compounds have been previously discussed in Section 3.

The sediment sample collected furthest upstream, at La Noria Bridge (AM0179) did not contain any additional organic compounds that could be identified. A sample of river sediment (AG7029) was collected 200 metres downstream of La Noria Bridge in 1997. The only organic compounds identified in this sample were 1,4-dichlorobenzene, hydrocarbons, alkyl benzenes, and PAHs.



Polychlorinated biphenyls (PCBs) were detected in the two downstream river sediment samples. The sediment sample collected near to the Pompeya Bridge (AM0180) contained three isomers of pentachlorinated biphenyls, five isomers of hexachlorinated biphenyls (including PCB-138, PCB-153, and PCB-180) and one isomer of heptachlorinated biphenyl. The sediment sample collected near to the Avellaneda Bridge (AM0181) contained two hexachlorinated biphenyls (PCB-138 and PCB-153), though at trace concentrations only. The three congeners specifically mentioned (PCB-138, PCB-153 and PCB-180) are often the most abundant in environmental samples due to their resistance to degradation (Bazzanti *et al.* 1997).

The relatively high abundance of PCBs in sample AM0180 compared to the samples collected both upstream and downstream of this location suggests localised inputs to the river close to this location, possibly in the form of transformer oils. It is not possible to determine whether this is from a point discharge or as a result of diffuse inputs.

Polychlorinated biphenyls are a group of highly persistent synthetic organic chemicals for which there are no known natural sources. Many PCB congeners are bioaccumulative, and concentrations of PCBs in biological material may be several orders of magnitude higher than ambient (Jones *et al.* 1988). PCBs can be absorbed through the skin as well as through ingestion and inhalation. For the general population today, food is generally the primary source (Lees *et al.* 1987). A large range of symptoms of PCB toxicity have been reported, including reproductive and developmental toxicity and immunosuppression (Safe 1984). Some congeners, or their metabolites, also exhibit endocrine disruption, including both oestrogenicity and anti-oestrogenicity. A recent report shows that the migratory fish Sabalo (*Prochilodus lineatus*) collected from the Rio de la Plata estuary, of which the Riachuelo river is a tributary, contained PCBs at moderate to high levels, including the PCB-138, PCB-153, and PCB-180 congeners (Colombo *et al.* 2000).

These compounds have been used in a wide variety of applications, including transformer oils, hydraulic fluids, in capacitor dielectrics, heat transfer fluids, and lubricating oils, and in paints and printing inks (ATSDR 1997). PCBs have always been sold as technical mixes rather than individual chemicals, and the Aroclor range manufactured by Monsanto was probably the most widely used. The most important PCB applications in tonnage terms were transformer oils and capacitors (de Voogt & Brinkman 1989).

More detailed information on the uses, environmental behaviour, toxicity and legislation on PCBs is given in Appendix 1.

The sediment sample AM0180 also contained the phthalate ester, DEHP, and the polycyclic synthetic musk, Galaxolide (also known as Musk 50 or HHCB). DEHP has been previously discussed in Section 3.1.2, and more information on phthalate esters is given in Appendix 1. Galaxolide has been previously discussed in Section 3.2.

A sample of river sediment (AG7006) was collected in 1997 from a location very close to that where sample AM0181 was collected for this study. The only organic compound identified in this sample were hydrocarbons, alkyl benzenes, and PAHs.



In addition to the organic pollutants discussed above, the three river sediments also contained a number of toxic metals at significant concentrations, including cadmium, chromium, copper, lead, mercury and zinc. The concentration of all these metals are higher than those found in the corresponding samples collected in 1997 (AG7006 & AG7029).

The concentration of chromium in the sediment collected upstream of the GRD and Americo Gaita tanneries (AM0179) was 170 mg/kg, which is considerably lower than that found in the two downstream river sediment samples (AM0180 and AM0181). This concentration is within the range typically found in freshwater sediments (1-500 mg/kg, ATSDR 1997). The concentration of chromium in the downstream sediments was 1648 and 1099 mg/kg for AM0180 and AM0181 respectively, 3-1648 times typical background values.

The concentrations of chromium in river sediment samples collected in 1997 from this part on the river were somewhat lower; 54 mg/kg in the upstream sample AG7006 (200 metres downstream of Noria bridge), and 837 mg/kg in the furthest downstream sample AG7029 (at the Avellaneda bridge).

While the concentrations of chromium in both the previous and current sets of samples exhibit a similar profile down the river, the concentrations at each location are clearly increasing. The inputs of wastewaters containing high concentrations of chromium from the GRD and Americo Gaita tanneries are a major contributor to the increasing concentrations of this toxic metal in the Riachuelo river. Addition sources of chromium to the river may also be contributing to this increase, as demonstrated by the increase in the concentration of chromium in the river sediment at La Noria bridge, upstream of the GRD and Americo Gaita tanneries.

The concentrations of copper and zinc in all three samples (AM0179-181) were relatively constant, in the range 229-325 mg/kg for copper, and 927-938 mg/kg for zinc. The concentrations of zinc found in river sediments collected in 1997 from similar locations (AG7006 & AG7029) were in the range 410-550 mg/kg. The concentration of copper found in river sediments collected in 1997 from similar locations were 305 mg/kg for the upstream sample AG7029 (corresponding to AM0179) and 153 mg/kg for the downstream sample AG7006 (corresponding to AM0181).

The concentrations of cadmium, lead and mercury in the river sediment samples AM0179-AM0181 are in the range 1-5 mg/kg, 201-407 mg/kg and 0.89-2.30 mg/kg respectively, the highest value in each case being for the sediment collected near the Pompeya bridge (AM0180). These concentrations are significantly higher than the concentrations found in the 1997 samples (AG0029 & AG7006), which contained cadmium, lead and mercury in the range 0-1 mg/kg, 102-159 mg/kg and 0.4-1.4 mg/kg respectively.

As the concentrations of cadmium, copper, lead, mercury and zinc in the river sediments have increased since samples were collected in 1997, significant inputs of these metals to



the Riachuelo river are clearly ongoing, presumably from a number of sources. One example of this is demonstrated by the high concentrations of all these metals found in the sediment sample collected from the Octagon in 2000 (AM0178), as discussed in Section 3.2. The increase in the concentration of copper at the most downstream location (AG7006 & AM0181) suggest the transport of copper from upstream inputs, most likely adsorbed onto suspended particles or bottom sediments (ATSDR 1997, Mance *et al.* 1984). It is likely that additional inputs of copper to the river are also contributing to this increase.

For comparison, the typical concentration of cadmium, copper, lead, mercury and zinc in freshwater sediments are 1 mg/kg for cadmium, 45-50 mg/kg for copper, 20-30 mg/kg for lead, 0.2-0.35 mg/kg for mercury, and less than 100 mg/kg for zinc (Salomons & Forstner 1984, ATSDR 1997). The concentrations these metals in the sediments collected for this study (AM0179-181) are higher than these typical values by 1-5 times for cadmium, 5-7 times for copper, 7-20 times for lead, 3-12 times for mercury, and 9 times for zinc.

The concentrations of cobalt in the river sediments have also increased since 1997, from 5.1-6 mg/kg (AG7029 & AG7006) to 8-10 mg/kg (AM0179-AM0181). While these concentrations are all within the range typically found for uncontaminated freshwater sediments (6-22 mg/kg, Hamilton 1994), the increase in the concentrations over times suggest that inputs of this toxic metal to the Riachuelo are ongoing.

Despite the clearly deteriorating situation in the river relating to metal pollution, none of the wastewaters sampled in 2000 contained exceptionally high concentrations of metals other than chromium. The sources of much of the metal pollution, therefore, remain to be identified.

4 CONCLUSIONS

The wide range of contamination of this area with anthropogenically derived chemicals described in the previous report has clearly not improved, and in many cases the situation has become worse. This is true for both organic compounds and a number of heavy metals. Many of these chemicals are toxic at low concentrations, and some have the potential to bioaccumulate. Some of the chemicals discussed in this and the previous reports are highly persistent and therefore have the potential to damage human and environmental health even if further releases are prevented.

The river sediments at the locations revisited contain many of the organic pollutants previously detected, as well as a number of additional persistent and toxic compounds, including a number of PCBs. The levels of many toxic metals, that were present at high level in the samples collected in 1997, have increased at all three locations, indicating the ongoing discharge of these metals to the Riachuelo river.

The point discharge locations of the two tanneries sampled, GRD and Americo Gaita, remain contaminated with a range of organic pollutants. While the concentrations of



chromium found at the Americo Gaita tannery are lower than those found in 1997, both tanneries continue to discharge high concentrations of this toxic metal, a well known tannery pollutant. The sediments at both locations also remain contaminated with chromium, especially at the GRD tanneries discharge point.

In addition to the inputs of hazardous substances from industrial effluents, discharges of combined urban runoff water and sewage, are contributing to the inputs of pollutants to the Riachuelo. The situation in the sediment at the location sampled has deteriorated since 1997, with additional persistent toxic organic compounds being identified and the levels of many heavy metals increasing, although this cannot be conclusively attributed to the discharge sampled.

Recommendations made in the previous report regarding long-term solutions based on clean production alternatives, renewable resources and pollution prevention clearly remain unaddressed, and this is resulting in increasing decay of the Riachuelo river.

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APPENDIX 1

TOXICOLOGICAL OUTLINES FOR KEY POLLUTANTS

A.1.1 Chromium

A.1.1.1 Natural Occurrence

Chromium is the 21st most abundant element in the Earth's crust, with an average concentration of 100 mg/kg. However, in some igneous rocks, clays and shales, higher concentrations can be found (Alloway 1990). The only ore of chromium of any commercial importance is chromite (FeCr_2O_4) which is produced principally in South Africa, Albania, Turkey, India and Zimbabwe. Other less plentiful sources are the ores crocoite (PbCrO_4) and chrome ochre (Cr_2O_3) (Mukherjee 1998, USPHS 1997, Alloway 1990, Greenwood and Earnshaw 1984). The gem stones, emerald and ruby, owe their colours to traces of chromium (Alloway 1990).

Emissions from wind-borne soil particles are the largest natural sources of atmospheric chromium, followed by emissions from volcanic activity, biogenic sources, forest fires and sea salt sprays. It is estimated that the total amount of chromium released to the atmosphere from natural sources is 43,000 tonnes / year, compared with an estimated anthropogenic load of 30,400 tonnes / year (Nriagu 1990).

A.1.1.2 Production, Use and Anthropogenic Sources

Chromium is produced in two forms. Firstly as ferrochrome, formed by the reduction of chromite with coke in an electric arc furnace (a low-carbon ferrochrome can be made using silicon, instead of coke, as the reductant). This iron-chromium alloy is used directly as an additive to produce chromium-steels, which are "stainless" and hard. Alternatively, following aerial oxidation of chromite, leaching, precipitation and reduction, chromium metal can be obtained (USPHS 1997, Greenwood and Earnshaw 1984).

Of the 10 million tonnes of chromium produced annually, about 60-70% is used in alloys, including stainless steel, which contains varying amounts of iron, chromium (10-26%) and nickel, depending on the properties required in the final product. The refractory properties of chromium (resistance to high temperatures) are exploited in production of refractory bricks for lining furnaces and kilns, accounting for approximately 15% of the chromate ore used. About 15% is also used in the general chemical industry, where chromium compounds are commonly used as tanning agents, textile pigments and preservatives, anti-fouling paints, catalysts, corrosion inhibitors, drilling muds, high temperature batteries, fungicides, wood preservatives, and in metal finishing and electroplating (USPHS 1997, Alloway 1990, Greenwood and Earnshaw 1984).

Estimates of anthropogenic emissions of chromium are given in Tables A.1.1a-c (Nriagu 1990, Nriagu and Pacyna 1988):



SOURCE	Emission (thousand tonnes / year)
Steel and iron manufacturing	15.6
Energy production (coal and oil combustion)	12.7
Cement production	1.3
Waste incineration (municipal refuse and sewage sludge)	0.8
TOTAL	30.4

Table A.1.1a World-wide atmospheric emissions of chromium from anthropogenic sources

SOURCE	Emission (thousand tonnes / year)
Manufacturing processes (metal, chemicals, paper, petroleum products)	51
Domestic wastewaters	46
Sewage discharges	19
Base metal mining and smelting	12
Atmospheric fallout	9.1
Electric power plants	5.7
TOTAL	142.8

Table A.1.1b World-wide inputs of chromium into aquatic ecosystems

SOURCE	Emission (thousand tonnes / year)
Discarded manufactured products	458
Coal ashes	298
Agricultural and animal wastes	82
Atmospheric fallout	22
Urban refuse	20
Logging and wood wastes	10
Municipal sewage and organic wastes	6.5
Solid wastes from metal fabrication	1.5
Fertilisers and peat	0.32
TOTAL	898.32

Table A.1.1c World-wide inputs of chromium into soils

A.1.1.3 Environmental Levels, Contamination and Behaviour

Chromium is found in varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see Table A.1.1d). However, in areas associated with anthropogenic emissions, ecosystem levels can far exceed natural, background concentrations (see Table A.1.1e).



Environmental Matrix	Concentration	Reference
Seawater (open ocean)	0.057-0.234 ug/l	Bryan and Langston 1992
Freshwater	1.30 ug/l	USPHS 1997
Drinking water	0.4-8.0 ug/l	USPHS 1997
Marine sediment	30-200 mg/kg	Bryan and Langston 1992,
Freshwater sediment / suspended particulates	1-500 mg/kg	USPHS 1997
Soil	<1-100 mg/kg 4-80 mg/kg	Alloway 1990 Dudka and Adriano 1997

Table A.1.1d Background concentrations of chromium found in water, sediment and soil

Environmental Matrix	Concentration	Reference
Marine sediment, Loughor Estuary (tin plate production) in South Wales	800 mg/kg	Bryan and Langston 1992
Marine sediment, Sawyer's Bay, New Zealand (tannery waste)	3700 mg/kg	Bryan and Langston 1992
Soil, chromium smelting, Japan	30-4560 mg/kg	Dudka and Adriano 1997
Soil, of sewage sludge amended farms, UK	138-2020 mg/kg	Alloway 1990
MSW incinerator ash, UK	44-1328 mg/kg	Mitchell et al. 1992

Table A.1.1e Chromium concentrations associated with anthropogenic contamination and waste

Although many different oxidation states of chromium exist in the environment, only the trivalent (III) and hexavalent (VI) forms are considered to be of biological importance. In aquatic environments, chromium (VI) will be present predominantly in a soluble form. These soluble forms may be stable enough to undergo intra-media transport, however chromium (VI) will eventually be converted to chromium (III), by reducing species such as organic substances, hydrogen sulphide, sulphur, iron sulphide, ammonium and nitrite (USPHS 1997, Kimbrough *et al.* 1999). This trivalent form is generally not expected to migrate significantly in natural systems. Instead, it is rapidly precipitated and adsorbed onto suspended particles and bottom sediments. However changes in the chemical and physical properties of an aquatic environment, can result in changes to the chromium (III)-chromium (VI) equilibrium (Richard and Bourg 1991).

Chromium (III) and (VI) have been shown to accumulate in many aquatic species, especially in bottom-feeding fish, such as the brown bullhead (*Ictalurus nebulosus*); and in bivalves, such as the oyster (*Crassostrea virginica*), the blue mussel (*Mytilus edulis*) and the soft shell clam (*Mya arenaria*) (Kimbrough *et al.* 1999).

In soils, chromium (III) is relatively immobile due to its strong adsorption capacity onto soils. In contrast, chromium (VI) is highly unstable and mobile, since it is poorly adsorbed onto soils under natural conditions (Mukherjee 1998). Redox reactions (oxidation of chromium (III) to chromium (VI) and reduction of chromium (VI) to chromium (III)) are



important processes affecting the speciation and hence the bioavailability and toxicity of chromium in soils. Oxidation can occur in the presence of oxides of manganese and iron, in fresh and moist (anaerobic) soils, and under slightly acidic conditions. Reduction can occur in the presence of sulphide and iron (II) (anaerobic conditions), and is accelerated by the presence of organic matter in the soil (Mukherjee 1998).

The importance of this lies in the fact that whilst chromium (III) is an essential trace element in animals, chromium (VI) is non-essential and toxic at low concentrations. Thus, because oxidation processes can result in the formation of chromium (VI), anthropogenic activities that release either chromium (III) or chromium (VI) are equally non-desirable. Even if chromium (III) is discharged into the environment, there is no guarantee that it will remain in this chemical state. For example, the landfilling of chromium (III) tannery waste with other acidic industrial wastes, or domestic sewage, which on decomposition can yield acidic conditions, can result in the oxidation of chromium (III) to chromium (VI) (Mukherjee 1998, Outridge and Sheuhammer 1993, UNEP 1991, Richard and Bourg 1991).

A.1.1.4 Toxicity and Essentiality

Chromium (III) is considered an essential trace nutrient, required for glucose, protein and fat metabolism in mammals. Signs of deficiency in humans include weight loss and the impairment of the body to remove glucose from the blood (USPHS 1997, Goyer 1996). The minimum human daily requirement of chromium (III) for optimal health is not known, but a daily ingestion of 50-200 ug/day has been estimated to be safe and adequate. However, although an essential food nutrient, very large doses may be harmful (USPHS 1997).

Chromium (VI) is non-essential and toxic. Compounds are corrosive, and allergic skin reactions readily occur following exposure, independent of dose. Short-term exposure to high levels can result in ulceration of exposed skin, perforations of respiratory surfaces and irritation of the gastrointestinal tract. Damage to the kidney and liver have also been reported (USPHS 1997). In addition, the International Agency for Research on Cancer (IARC) classifies chromium (VI) compounds as known carcinogens (1998). Long-term occupational exposure to airborne levels of chromium higher than those in the natural environment has been associated with lung cancer. Individuals at most risk include those in chromate-production industries and chromium pigment manufacture and use; and similar risks may exist amongst chromium-alloy workers, stainless steel welders, and chrome-platers (Kimbrough 1999, USPHS 1998).

The aquatic toxicology of chromium is also dependant upon speciation, with chromium (III) far less biologically available and toxic than chromium (VI). This has been observed in barnacles, *Balanus* sp., and in the polychaete *Neanthes arenaceodentata*. Experiments have shown that the number of offspring produced by the *Neanthes arenaceodentata* was reduced by exposure to 39 ug/l of dissolved chromium (VI) (Bryan and Langston 1992).



A.1.1.5 Legislation

Unlike mercury, cadmium and lead, chromium and its compounds are not found on National and International Lists of priority pollutants. However, whilst the reduction of anthropogenic sources of chromium does not require priority action, pollution of terrestrial and aquatic environments by chromium still needs to cease. Chromium is therefore included on the majority of subsidiary and secondary pollutant lists. Examples of guidelines and permissible environmental levels include the following:

European Council Directive 75/440/EEC concerning the quality required of surface water intended for the abstraction of drinking water in the Member States. Water containing more than 50 ug/l must be subjected to physical and chemical treatment prior to use.

European Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Chromium is included in List II, and as such water pollution caused by its presence must be reduced in keeping with National Environmental Quality Standards.

European Community Council Directive 80/778/EEC relating to the quality of water intended for human consumption. A Maximum Permissible Concentration of 50 ug/l is set.

Other drinking water legislation includes that set by the WHO (1993), and the USEPA (USPHS 1997). All of these set a guideline / recommended limit of 50 ug/l

Regarding soil contamination, the UK Department of the Environment (ICRCL) classifies a level of 0-100 mg/kg as being typical of uncontamination. Anything above this is classified as contaminated, and as such, restrictions on recreational and agricultural uses apply (Alloway 1990). In terms of permissible sewage sludge levels, acceptable concentrations for chromium range from 200-1200. However resulting soil concentrations should not exceed 150 mg/kg (EC, France, Germany) (Alloway 1990).

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A.1.2 Phthalate esters

Phthalate esters are used in virtually every major product category, including construction, automotive, household products, apparel, toys, packaging, and medical products, resulting in the widest possible distribution of these materials. However, 90% of the total quantities used is in the production of soft PVC. A study published in 1986 showed that the two most abundantly produced phthalate esters were DEHP and DnBP (Menzert *et al* 1986).



DEHP can exert a number of chronic toxic effects following longer exposures and may be an important reproductive poison, (Life Systems, Inc 1993).

More recently concern has been raised about the ability of DEHP and some other phthalates to interact with hormone receptors in animals. Jobling and coworkers (1995) demonstrated that DEHP was able to bind to the human estrogen receptor, although it showed no significant estrogenic activity. Its potential to interfere with other aspects of the hormone system has not been fully investigated.

A group of phthalate esters including dimethyl phthalate; diethyl phthalate; di-n-butyl phthalate; butyl benzyl phthalate; dihexyl phthalate; butyl 2-ethylhexyl phthalate; di-(n-hexyl, n-octyl, n-decyl) phthalate; di-(2-ethylhexyl) phthalate; diisooctyl phthalate; diisononyl phthalate; di-(heptyl, nonyl, undecyl) phthalate; diisodecyl phthalate; diundecyl phthalate; and ditridecyl phthalate has been found to have both acute (Adams W.J *et al* 1995) and chronic (Rhodes J.E. *et al* 1995) toxicity to the representative freshwater and marine species. There was a general trend for the lower-molecular-weight phthalate esters (C-1 to C-4 alkyl chain lengths) to become more toxic with decreasing water solubility for all species tested. Phthalate esters with alkyl chain lengths of six carbon atoms or more were not acutely toxic at concentrations approaching their respective aqueous solubilities. The lack of toxicity observed for the higher-molecular-weight phthalate esters resulted from their limited water solubility.

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A.1.3 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyls are a group of synthetic organic chemicals that contain 209 individual compounds (known as congeners) with varying harmful effects. There are no known natural sources of polychlorinated biphenyls in the environment. PCBs are either oily liquids or solids, and are colourless to light yellow in colour. They have no known smell or taste. PCBs enter the environment as mixtures containing a variety of individual components and impurities. The chlorinated biphenyls may be substituted by chlorine in a number of ways, and the group is generally referred to as polychlorinated biphenyls (PCBs).

The polychlorinated biphenyls have been used in a wide variety of applications, including transformer oils, hydraulic fluids, plasticisers, 'kiss-proof' lipsticks and carbonless copy papers. They have also been used in capacitor dielectrics, heat transfer fluids, lubricating and cutting oils, and in paints and printing inks (ATSDR 1997).

PCBs have always been sold as technical mixes rather than individual chemicals. de Voogt and Brinkman (1989) list some 46 trade names used for PCBs and PCB containing products. Of these, the Aroclor range manufactured by Monsanto was probably the most widely used. The most important PCB applications in tonnage terms were transformer oils and capacitors (de Voogt & Brinkman 1989). In transformer oils, the PCBs were mixed with chlorobenzenes (mainly trichlorobenzenes and tetrachlorobenzenes) as solvents (Swami et al. 1992, de Voogt and Brinkman 1989). PCBs also appear to be associated with *de novo* synthesis as by-products. These include the PVC industry, where waste EDC tars are contaminated, together with aqueous effluents, by dichlorobiphenyls.

PCBs can be absorbed through the skin as well as through ingestion and inhalation. For the general population today, food is the primary source, though dermal exposure may be dominant amongst those directly handling PCBs or PCB-contaminated materials (Lees et al. 1987).

In a review of PCB toxicity, Safe (1984) lists the following symptoms of PCB toxicity: enzyme induction, decreased vitamin A levels, lymphoid involution, thymic and splenic



atrophy, immunosuppression, chloracne, alopecia, oedema, hyperkeratosis, blepharitis, hyperplasia of the epithelial lining of the extrahepatic bile duct, the gall bladder and urinary tract, hepatomegaly and liver damage including necrosis, haemorrhage, hepatotoxicity (altered porphyrin metabolism), tumour promotion, altered levels of steroid and thyroid hormones, reproductive toxicity including menstrual irregularities, reduced conception, early abortion, excessive menstrual and postconceptual haemorrhage, anovulation, testicular atrophy, decreased spermatogenesis, teratogenesis and developmental toxicity. In addition, low levels of PCBs have caused behavioural impairment in monkeys (Rice 1999).

Aroclor 1254 compromised the immune response of earthworms (Roch & Cooper 1991). Aroclors 1221, 1254 and 1268 all reduced in vitro fertilisation rates in mice. PCB 1254 was the most potent mixture (Kholkute et al. 1994).

Kidney cancer has been reported in workers with known exposure to PCBs although insufficient data are available for statistical analysis and more research is called for (Shalat et al. 1989). In a review of epidemiological PCB research, cancer of the kidney and skin were marginally significant but the reviewers regarded the overall picture as inconclusive (Longnecker et al. 1997). Exposure of “clean” PCBs in an occupational setting exerts effects on the human CNS, with symptoms such as headaches, lassitude and slowed nerve signals (Rogan & Gladen 1992).

Invertebrates display a differential response to individual PCB congeners. In the aquatic snail, *Lymnaea stagnalis*, 2,2'-dichlorobiphenyl was substantially more toxic, being rapidly fatal to over 60% of the test animals (Wilbrink et al., 1990) and also inhibited production of egg masses more rapidly than the other congener under test, 4,4'-dichlorobiphenyl (Wilbrink et al. 1987).

Some congeners, or their metabolites, exhibit endocrine disruption, including both oestrogenicity and anti-oestrogenicity. In general, ortho-substituted PCBs are oestrogenic whereas coplanar PCBs are anti-oestrogenic, as is 2,3,7,8-TCDD (Li et al. 1994). According to a recent review (Brouwer et al. 1999), PCBs may affect not only the oestrogen system, but also the androgen system, the thyroid hormone system, the retinoid system, the corticosteroid system and several other endocrine pathways. In addition, effects on the thyroid system on wild populations of fish-eating birds and captive seals have been correlated with PCB exposure (Brouwer et al. 1999).

Ortho substituted (non-dioxin-like) PCBs have been found to have the greatest effects on neurochemical function. They were found to reduce dopamine synthesis and it was further established that the effects were caused by the congeners rather than their metabolites. 2,2'-dichlorobiphenyl (PCB 4) was the most potent congener (Seegal and Shain 1992).

The dioxin-like PCB 77 (3,3',4,4'-TeCB) also caused long-term changes in behavioural and neurochemical changes in laboratory animals, including alterations in dopamine function. This congener, however, did not accumulate in brain tissue in the same way as



some ortho-substituted congeners, indicating that it operates via a second mechanism, or that it is a metabolite which is the active agent (Seegal & Shain 1992).

The extensive body of information concerning the global cycling of PCBs has been accumulated in response to concerns about the environmental impact of these chemicals. PCBs are highly persistent. Although there is evidence of biodegradation in contaminated sediments (see: Brown & Wagner 1989) and some marine mammals appear to be able to selectively degrade some of the lower chlorinated congeners (Boon *et al.* 1987), the detoxification potential of these processes would appear to be rather limited. Indeed, Cummins (1988) has suggested that unless further escape of PCBs is prevented then the eventual extinction of marine mammals is a very real possibility.

Levels of PCBs in biological material may be several orders of magnitude higher than ambient. PCBs are bioconcentrated to a factor of 6000 for fish and 47000 for invertebrates (Jones *et al.* 1988). Train (1979) reports bioconcentration factors of between 2500 and 100,000.

The effects of chronic exposure to PCBs in marine mammals has been found to include physical deformity and impairment of reproductive success (Reijnders, 1986). More recently, they have been implicated in the outbreaks of disease amongst populations of seals and dolphins (see review by Gilbertson, 1989) suggesting that they may have a disruptive influence on immune capability.

The PCBs are controlled under most of the international legal instruments relating to organochlorines, *inter alia*, the Barcelona, Helsinki, Basel, Bamako, Rotterdam OSPAR and LRTAP Conventions and the International Joint Commission on the Great Lakes. In addition, PCBs are targeted for global production ban under the UNEP POPs Convention currently being drafted. Within the EC, applications for the PCBs were first restricted by directive 76/769/EEC, which deals with the marketing and use of dangerous substances and preparations (EC 1976). This directive, and its amendment (EC 1991) restricted the applications of PCBs and their replacements, the polychlorinated terphenyls (PCTs).

EC regulations on disposal of PCBs, as set out in a 1996 Directive, dictate that PCBs phaseout should be completed by 2010. Further, national enabling legislation should have been enacted by March 1998. Several countries have missed this deadline and in mid 1999, the EC initiated action through the European Court of Justice against Germany, Greece, Spain, Portugal and UK for failing to implement the directive (ENDS 1999).

Within the European Community, PCBs are regarded as "blacklist substances" (Gardiner & Mance 1984) although no regulatory directive has yet been proposed. PCBs are also included in the proposed UK "red list" (Jones *et al.* 1988). The US Toxics Substances Control Act (TOSCA) designates wastes containing greater than 50ppm PCBs as hazardous (Rogan 1995).



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A.1.4 Hexachlorocyclohexanes (HCH)

Mixture of hexachlorocyclohexanes is produced by the photochemical reaction between chlorine and benzene (Safe 1993). Technical grade hexachlorocyclohexane (HCH) is comprised of different isomeric forms. The approximate isomer content is alpha-HCH (60-70%), beta-HCH (7-10%), gamma-HCH (14-15%), delta-HCH (7%), and epsilon-HCH (1-2%). Lindane is the gamma isomer of hexachlorocyclohexane, and it is commercially produced by purification of the technical HCH (Safe 1993). This compound has been produced worldwide for use as an insecticide to control grasshoppers, cotton and rice pests, wireworms, and other soil pests. Lindane has been used for the



protection of seeds, for treatment of poultry and livestock, and for control of household insects. It is also still used as a scabicide and pediculocide, usually as lotions, creams, and shampoos.

Alpha-, beta-, and gamma-HCH are the most important isomers in terms of environmental impact. The relatively high stability and lipophilicity of HCH and its global use pattern has resulted in significant environmental contamination by this chlorinated hydrocarbon. Once introduced into environment HCH may persist for many years (Martijn & Schreuder 1993). The beta-isomer is the more persistent of the isomers (ATSDR 1997).

Human intake of HCH compounds is largely through food consumption (Toppari *et al.* 1995). Alpha-, beta- and gamma-HCH have been recorded in human breast-milk with the beta-isomer being the most ubiquitous (Waliszewski *et al.* 1996; Safe 1993). The generally less widespread nature of the alpha- and gamma-isomers in comparison to beta-HCH is due to the more rapid clearance of these isomers from the body. Like many persistent organochlorines, HCH levels in the body have been found to increase with age (ASTDR 1997).

Hexachlorocyclohexane isomers have been detected in air, surface and ground water, soil and sediments (El-Gendy *et al.* 1991; Safe 1993; Xu 1994; Tan & Vijayaletchumy 1994; Skark & Zullei-Seibert 1995; Ramesh *et al.* 1991), plants (Xu 1994), birds, fish and mammals (Smith 1991; Xu 1994; Abd-Allah 1994; Norstrom & Muir 1994). In humans lindane mostly concentrates in adipose tissue (Safe 1993). It has been reported that lindane and other organochlorine compounds can be transferred through the pathway soil→earthworm→bird/mammal (Hernandez, *et al.* 1992; Romijn *et al.* 1994) thereby causing secondary poisoning.

Lindane, the gamma-isomer of hexachlorocyclohexane, is toxic to animals, humans, and aquatic species. Acute animal poisoning by lindane causes increased respiratory rate, restlessness accompanied by increased frequency of urination, intermittent muscular spasms of the whole body, salivation, grinding of teeth and consequent bleeding from the mouth, backward movement with loss of balance and somersaulting, retraction of the head, convulsions, gasping and biting, and collapse and death usually within a day (Smith 1991).

Chronic health effects can occur at some time after exposure to lindane and can last for months or years. Lindane has been shown to cause liver, lung, endocrine gland and certain other types of cancer in animals (Smith 1991). Repeated overexposure may damage the liver. Chronic toxic effects may also include shortened life span, reproductive problems, lower fertility, and changes in appearance or behaviour. The differential actions of hexachlorocyclohexane isomers may produce variable effects on different regions of the nervous systems and in different species of animals (Nagata *et al.* 1996).

Hexachlorocyclohexane may be introduced to the environment from industrial discharges, insecticide applications or spills, and may cause significant damage. Acute toxic effects may include the death of animals, birds, or fish, and death or low growth rate in plants



(Bunton 1996, Smith 1991). The insecticide load in surface waters does not ordinarily reach concentrations acutely toxic to aquatic fauna. However, lindane has high chronic toxicity to aquatic life. The effects of the low insecticide concentrations often appear only after relatively long exposure times. Chronic exposure to insecticides, such as lindane, (Schulz *et al.* 1995) can be hazardous to freshwater macroinvertebrates even at unexpectedly low concentrations. The low-concentration effects may depend on both species and substance and therefore cannot be predicted from toxicity data at higher concentrations.

Hexachlorocyclohexane, as a toxic, persistent and bioaccumulative chemical, is a subject to the European Community legislation. The limit values and quality objectives for discharges of hexachlorocyclohexane are set by the Council Directive 84/491/EEC (EEC 1984) as amended. The uses of hexachlorocyclohexane (including lindane) were severely restricted under the Persistent Organic Pollutants (POPs) Protocol, which was adopted in 1998 and has 36 contracting parties encompassing not only Europe but also Canada and the United States of America (UNECE 1998). The POPs Protocol is part of the 1979 Convention on Long-Range Transboundary Air Pollution (LRTAP), which is under the auspices of the United Nations Economic Council for Europe. Lindane is also included in the Annex III of the 1998 Rotterdam Convention on the Prior Informed Consent procedure (PIC procedure) among 27 other chemicals (FAO/UNEP 1998). Under the PIC procedure countries should not export any chemical to any other country without first receiving explicit permission. In order to avoid unfair trade barriers arising through the implementation of the Convention, any country that has denied import of any chemical must also stop producing it domestically and may not import it from any country that is not a Party to the Convention.

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APPENDIX 2

LEATHER TANNERIES

A.2.1 Introduction

Tanning is the process by which animal hides are converted into leather. The hides, after removal of flesh and fat, are treated with chemicals that cross-link the microscopical collagen fibres and prevent biological, chemical and thermal degradation. The resulting material is strong, durable, and flexible, and can be further processed according to the intended end use, i.e. trimming, dyeing, buffing and surface coating. Accordingly, there is no single process for producing leather, and many different wastes will be generated from each stage. These will include surplus, spent or washed-out chemicals; volatile sulphide and solvent vapours; animal residues from operations such as cleaning, scraping, splitting and trimming, and sludges resulting from wastewater treatment processes or collection facilities (UNEP 1991, UNEP 1995, Kroschwitz and Howe-Grant 1995).

The composition of a combined tannery effluent that has not been treated is characterised by a high oxygen demand, high salt content, high solids content, high sulphide content, and possibly a high level of chromium. It will also be strongly alkaline, pH 9 or above (Harrison 1996, UNEP 1991, UNEP 1995, Kroschwitz and Howe-Grant 1995, Yamamoto and Win 1990).

A.2.2 The Tanning Process, Chemical inputs, and Wastes

A.2.2.1 Curing of hides and skins

In most developed countries hides and skins are removed and lightly cured with salt in an abattoir or local hide collection centre. Throughput is relatively regular, and technical supervision is available. Preservation by chilling is becoming common, and the hides and skins enter commercial channels and are transported to tanneries for processing (UNEP 1991).

In developing countries it is common for animal slaughter to take place at rural villages sites. The rate of production of hides and skins in these conditions is usually low and erratic, as it is governed partly by seasonal conditions. Under such circumstances, and with high ambient temperatures, curing is not simple. Salt, if available, is applied and the skins are then dried. A major drawback of drying is that the tanner must subsequently reverse this process, and this requires large volumes of water (UNEP 1991, Kroschwitz and Howe-Grant 1995), consequently generating large volumes of contaminated brine.

Curing often incorporates treatment with insecticides to discourage beetle and other insect attack during storage and transport. Insecticides may include pyrethrum, permethrin, p-dichlorobenzene, sodium silico-fluoride and borax. Earlier insecticides such as DDT, benzene hexachloride, dieldrin, and compounds of arsenic and mercury are banned for such use in many industrialised countries because of their persistence and environmental toxicity. However this may not be case in developing countries (UNEP 1991).



A.2.2.2 Beam-house

At this stage the hide is prepared for tanning by cleaning and conditioning, and by ensuring the correct moisture content. Typical steps are:

- a) Soaking / removal of dirt, blood, dung. Chemicals include sodium hydroxide, sodium sulphide, sodium hypochlorite, wetting agents, surfactants, emulsifiers, and enzyme preparations (UNEP 1991, Kroschwitz and Howe-Grant 1995).

Water Pollutants	BOD, COD, suspended and dissolved solids, salts, organic N
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- b) Liming and unhairing. Lime (calcium hydroxide) is blended with sodium sulphide to loosen wool and hair, or dissolve these into a pulp. The duration of this process may vary from a few hours to several days, and is responsible for the major part of the COD (chemical oxygen demand) load from a tannery. Discharges of wastes with a high COD can result in severe oxygen depletion, and in extreme cases, total anoxia, of receiving waters (UNEP 1991, Kroschwitz and Howe-Grant 1995).

Water Pollutants	BOD, COD, suspended and dissolved solids, alkalinity, sulphides, organic N, ammonia N
Air Pollutants	Hydrogen sulphide
Solid Pollutants	Hair, lime, fat and organic matter containing sludge

- c) Deliming, the removal of lime is necessary to avoid interference with the subsequent tanning stage. Thorough washing is followed by the application of neutralising chemicals such as sulphuric, hydrochloric, lactic or formic acids. Ammonium chloride may also be used. Washing requires copious amounts of water, and the acidification of liquids containing sulphide may generate toxic hydrogen sulphide gas. Prior treatment with hydrogen peroxide or sodium bisulphite will oxidise the sulphide and prevent this problem (UNEP 1991, UNEP 1995, Kroschwitz and Howe-Grant 1995).

Water Pollutants	BOD, COD, dissolved solids, ammonia N
Air Pollutants	Ammonia

- d) Bating is an enzymatic process, which removes lime, protein fibres and degradation products, thus improving the grain of the pelt, and the general run and stretch of subsequent leathers. The bating material is typically composed of 50% wood flour or other carrier, 30% deliming agent (ammonium chloride), and 1-5% pancreatic enzyme. This combination replacing an age-old process which entailed treatments with dog dung or pigeon droppings (UNEP 1991, UNEP 1995, Kroschwitz and Howe-Grant 1995).



Water Pollutants	BOD, COD, dissolved solids, ammonia N
Air Pollutants	Ammonia

- e) Degreasing of the hides results in improved quality of the final leather. Solvents and/or surfactants are used and both will end up in the wastewater along with dissolved grease. Solvents used include white spirit, kerosene, and monochlorobenzene. Perchloroethylene is used for cleaning sheepskins (UNEP 1991 Kroschwitz and Howe-Grant 1995).

Water Pollutants	Surfactants, solvents, fat, BOD, COD
Air Pollutants	Solvents

- f) Pickling is the final beam-house operation. It involves the adjustment of pH and the sterilisation of the skin. Chemicals include salt, and sulphuric, hydrochloric, acetic or formic acids. Fungicides such as thiobenzothiazol or parachlorometacresol may also be used, as replacements for para-nitrophenol, pentachlorophenol, naphthol, and mercury fungicides, which are now regarded as too toxic for such use (UNEP 1991, Kroschwitz and Howe-Grant 1995).

Water Pollutants	Fungicide residues, BOD, COD, suspended and dissolved solids, acid pH
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A.2.2.3 Tanning

Tanning is the stabilisation of the collagen structure of the hide, using natural or synthetic chemicals. A wide variety of chemical agents are available, with CHROMIUM the most commonly used. For example, over 95% of all leather manufactured in the USA is chromium tanned (Kroschwitz and Howe-Grant 1995). No solid wastes are directly derived, however acidic effluents containing unused chemical agents will be generated. Subsequent washings will release unfixed chemicals from the hide, and the treatment of effluents will result in the production of contaminated sludges.

The majority of leathers today are chromium tanned in drums for 4-24 hours (UNEP 1991). Chromium salts are used because as well as forming the necessary bonds with the carboxylic groups of the collagen fibres, they are also cheap. In addition, the resulting leather is resistant to cracking from flexing, it is strong, durable and of a light colour (blue) which can be dyed easily.

Other chemicals that can be used as primary tanning materials or as complements to chromium include salts of aluminium, zirconium, and titanium. In addition, SYNTANS



(sulphonated products of phenol, cresol and naphthalene, or resins derived from polyurethanes or polyacrylic acids) are being employed alone or in association with chromium and vegetable tannins, either for re-tannage or as principal tanning agents for certain speciality leathers (UNEP 1991, Kroschwitz and Howe-Grant 1995).

Vegetable tanning agents are extracted from the wood/bark of certain trees. The compounds used have the general structure of polyphenolic compounds, and the most commonly used are derivatives of pyrogallol (tri-hydroxybenzene) and derivatives of catechol (Kroschwitz and Howe-Grant 1995).

In general, the same steps are carried out in preparing the hide for vegetable tannage as are carried out in preparation for chromium tannage (see above).

Water Pollutants	Chromium/vegetable tannins/alternatives, BOD, COD, suspended and dissolved solids, acid pH
Solid Pollutants	Chromium containing sludge/organic matter and shavings

A.2.2.4 Post-tanning activity

Following the tanning process, certain mechanical operations may occur in order to level the surface of the irregular natural material (splitting, shaving, trimming). These operations yield a combination of solids, squeezed-out water and unfixed tanning chemicals.

Following these processes the leathers are dried and finished. Surface coatings consist of dyes or pigments dispersed in a binder. Nitrocellulose lacquer or urethane lacquer may then be applied with organic solvents as top-coats. Common chemicals used in leather finishing are: ethyl and butyl acetate, monochlorobenzene, perchloroethylene, toluene, trichloroethylene and xylene (UNEP 1991).

Water Pollutants	BOD, COD, dissolved solids, chromium/alternatives, salts, solvents
Air Pollutants	Solvents
Solid Pollutants	Chromium trimmings, chromium/finishing chemical-containing organic matter

A.2.3 Chemicals, Toxicity and Alternatives

A.2.3.1 Chromium

Chromium salts are the most commonly used tanning agents. Chromium (III) sulphate is most commonly used, produced from the reduction of potassium dichromate or chromic acid (UNEP 1995). However chromium usage is controversial on account of the persistence and potential toxicity of some of its chemical forms. It can occur in oxidation states ranging from II to VI, and the impact on human, aquatic, and terrestrial life is



dependant upon these states. The trivalent (III) and hexavalent (VI) forms are considered to be of greatest biological importance (USPHS 1997, Sadiq 1992, Alloway 1990, Richard and Bourg 1991, Southart *et al.* 1995, Katz 1991, Kimbrough *et al.* 1999).

The trivalent form is the more common and is an essential trace nutrient. However like any trace element, toxic effects can result following exposure to elevated concentrations (USPHS 1997, Katz 1991). An average daily intake of 50-200 ug/day of chromium (III) is recommended for adults (USPHS 1997), and is required for normal energy metabolism. However, the consumption of contaminated water, fish and other foodstuffs could increase daily intakes above recommended levels, and ingestion of elevated levels over long periods of time can result in adverse health effects including gastro-intestinal irritation, stomach ulcers, kidney and liver damage (USPHS 1997). Dermal exposure can result in severe redness and swelling of the skin.

Hexavalent chromium is non-essential and toxic at low concentrations. Compounds are corrosive and can cause chronic ulceration of exposed skin and respiratory surfaces. Allergenic chromium skin reactions readily occur with exposure and are independent of dose. In addition, the International Agency of Research on Cancer (IARC) classifies chromium (VI) compounds as carcinogenic (US Department of Health and Human Services, 1998, USPHS 1997). Trivalent chromium compounds are unclassified due to inadequate evidence in experimental animals.

Both hexavalent and trivalent chromates are used in the tanning process, and tannery workers will be exposed to both forms. However, due to the presence of other chemicals, particularly sulphides, most of the hexavalent chromium will be reduced to the trivalent state. The potential for conversion to the more toxic hexavalent state once discharged is considered low, but is dependant on several physical and chemical conditions. For example, conversion is more likely in a slightly acidic environment (pH 5), and in the presence of certain other metals (manganese or iron) or oxygen. Therefore, even though chromium (III) is the major ion present in tannery sludges, if landfilled with other industrial wastes, particularly acidic wastes, or domestic wastes which on decomposition yield acidic conditions, conversion to the more toxic and bioavailable hexavalent state can occur (UNEP 1991, Richard and Bourg 1991, Outridge and Scheuhammer 1993).

It is also likely, due to oxidation processes at the point of emission, that airborne chromium will be found present as various chromate [Cr(VI)] compounds (Outridge and Scheuhammer 1993).

Environmental effects of chromium i.e. the bioaccumulation and toxicity implications for wildlife, can be summarised as follows:

Chromium (III) is an essential trace element in animals, chromium (VI) is not and is considered the most toxic form to aquatic and terrestrial animals. Toxic effects include tissue damage, swelling and discoloration of the gastro-intestinal tract; nasal perforations, altered immune function and reduction in fertility rates (Kimbrough *et al.* 1999, Outridge and Scheuhammer 1993). As mentioned above, the IARC classifies chromium (VI) as



carcinogenic to both humans and animals. With on-going uncertainty regarding the carcinogenic potential of chromium (III) compounds (Outridge and Scheuhammer 1993, US Department of Health and Human Services 1998).

A.2.3.2 Vegetable tanning agents

Vegetable tanning agents are extracted from the wood/bark of certain trees. The compounds used have the general structure of polyphenolic compounds, and the most commonly used are derivatives of pyrogallol (1,2,3-trihydroxybenzene) and derivatives of catechol (Kroschwitz and Howe-Grant 1995). Although effluents from vegetable tanning will not contain persistent levels of chromium, and many of the plant derivatives used will degrade within hours/days, they still require extensive treatment due to a high pH, a high BOD/COD, and high sulphide, salt and ammonia concentrations (UNEP 1991).

In addition, extreme care should be taken when handling these compounds due to their toxicological properties. For example, ingestion of 1,2,3-trihydroxybenzene may cause gastro-intestinal irritations, renal and hepatic damage, and in extreme cases circulatory collapse and death (Budavari *et al* 1989). Poisoning has also occurred through dermal absorption.

In terms of commercial suitability, the quality of vegetable tanned leather is highly desirable. It can be mechanically shaped and is flexible and durable. It is often the leather of choice for handicraft and specialised work. However, as it is not as thermally stable as chromium tanned leather, its uses are considered limited (UNEP 1991).

A.2.3.3 Alternative tanning chemicals

A large number of alternative tanning chemicals are available, which have a lower acute toxicity than chromium. Examples include aluminium, titanium, iron and zirconium salts, with the most suitable being titanium.

Titanium is an abundant element, which produces salts of generally low toxicity. In addition, titanium sulphate can be used with existing conventional tanning equipment. In order to improve the reactivity of the titanium with the hide, a pre-tanning step is employed, whereby the collagen matrix is first fixed with a polysaccharide derivative. Titanium uptake is then close to 100% (UNEP 1991).

Titanium tanned leather is whitish in appearance and is suitable for commercialisation, although the final properties may not correspond to those exactly achieved following chromium tanning. It is this fact that has inhibited market acceptance and widespread adoption to date (UNEP 1991).

A.2.3.4 Solvents



Both the degreasing and finishing processes will involve the use of solvents. Surfactants may be used instead of solvents in the degreasing process. In finishing, non-solvent based products are rapidly increasing in use. However, the following chemicals are still commonly used, and therefore are present in wastewaters and the working atmospheric environment (UNEP 1991):

Butanol	Ethylmercaptan
Ethyl acetate	Ethyleneglycol
Butyl acetate	Methylbutylketone
Isobutyl acetate	Methylethylketone
Formic acid	Perchloroethylene
Monochlorobenzene	Toluene
Cyclohexane	Trichloroethylene
Di-isobutylketone	Xylene
Ethylbenzene	

Briefly, the human toxicological properties of some of these chemicals are as follows:

Butanol: may cause irritation of mucous membranes, contact dermatitis, headache, dizziness, and drowsiness (Budavari 1989).

Butyl acetate: may cause irritation and conjunctivitis. Narcotic in high concentrations (Budavari 1989).

Formic acid: caustic to skin. Chronic absorption has been reported to cause albuminuria and hematuria, i.e. the presence of albumin and blood in the urine, symptoms of kidney disease (Budavari 1989).

Monochlorobenzene: harmful by inhalation. Can induce headaches, nausea and vomiting. It is also irritating to eyes and skin (USPHS 1997).

Cyclohexane: a skin irritant, in high concentrations it may act as a narcotic (Budavari 1989).

Ethylbenzene: irritating to the eyes, skin and mucous membranes. Narcotic in high concentrations (Budavari 1989).

Ethylmercaptan: irritating to mucous membranes. Narcotic in high concentrations (Budavari 1989).

Ethylene glycol: constitutes a hazard when ingested. Transient stimulation of the central nervous system (CNS) followed by depression, vomiting, drowsiness, coma, respiratory failure, convulsions, and renal failure (Budavari 1989).

Perchloroethylene: narcotic in high concentrations. CNS effects include headache, vertigo, tremors, nausea and vomiting, and fatigue. At higher levels; unconsciousness, liver and



kidney injury are reported (Commission of the European Communities 1986, Budavari 1989). Skin contact can also induce dermatitis (Budavari 1989).

Toluene: narcotic in high concentrations (Budavari 1989).

Trichloroethylene: moderate exposures can cause symptoms similar to alcohol inebriation. Inhalation and ingestion can result in dizziness, drowsiness, headaches, nausea and possibly unconsciousness. It is also irritating to the skin and eyes. Higher concentrations have been attributed to ventricular fibrillation, and have been found to induce hepatocellular carcinomas (UNEP 1991, Commission of the European Communities, 1986, Budavari 1989).

Xylene: may be narcotic in high concentrations (Budavari 1989).

A.2.3.5 Fungicides and Insecticides

As mentioned above, curing often incorporates treatment with insecticides to discourage beetle and other insect attack during storage and transport. Insecticides may include pyrethrum, permethrin, p-dichlorobenzene, sodium silico-fluoride and borax (sodium borate). DDT, benzene hexachloride, dieldrin, and compounds of arsenic and mercury are banned for such use in many industrialised countries because of their persistence and environmental toxicity. However, this may not be case in developing countries (UNEP 1991).

Pyrethrum and permethrin are both pyrethroid pesticides. Permethrin is an organochlorine compound and is irritating to the skin and eyes (Budavari 1989, Hartley *et al.* 1987). Skin contact with pyrethrum can cause severe allergic dermatitis, with higher concentrations causing nausea, vomiting, headaches and other CNS disturbances (Budavari 1989). In addition, this pesticide is classified as being highly toxic to fish (Hartley *et al.* 1987 Kidd *et al.* 1986).

p-Dichlorobenzene is reported to cause headaches and dizziness, toxic effects in the liver and kidney, and increases in the rates of cancer among experimental animals (USPHS 1997, Bornatowicz *et al.* 1994). There is no direct evidence that p-DCB can cause cancer, birth defects, or affect reproduction in humans. However, the Department of Health and Human Services (DHHS) in the United States has determined that p-DCB may reasonably be anticipated to be a carcinogen. The International Agency for Research on Cancer (IARC) has determined that p-DCB is possibly carcinogenic to humans. The EPA has also determined that p-DCB is a possible human carcinogen. p-DCB is a listed animal carcinogen (Umemura *et al.* 1992).

Fungicides such as thiobenzothiazol or parachlorometacresol (4-chloro-3-methylphenol) may be used during the pickling process, where the hide is sterilized. p-Nitrophenol, pentachlorophenol, naphthol, and mercury fungicides, are now regarded as too toxic and should no longer be used (UNEP 1991, Kroschwitz and Howe-Grant 1995).



The increasing use of insecticides and biocides for hide preservation presents serious problems for the subsequent tannery operations. The wash-out of pesticides from the hides during tanning can cause wastewaters, and hence rivers, to become contaminated with these chemicals. In addition, handling of the chemicals themselves, as well as the preserved hides, can poison workers (UNEP 1991).

A.2.3.6 Miscellaneous Chemicals

These include surfactants, sulphides, ammonium compounds, dyestuffs, emulsifiers and enzymes preparations. Individual compounds used will enormously vary from one tannery to another. However it is probable that residues of these chemicals will be present in untreated effluents and sludges.

A.2.4 Waste Treatment, Sludge Disposal and Recycling

A.2.4.1 Treatment

Tannery wastes are classified as hazardous and priority wastes due to the presence of chromium (EPA 1981, MINDEC 1990, MINDEC 1995, Kroschwitz and Howe-Grant 1995), and even if effluent quality standards are achieved, and chromium is removed from the wastewater, the tanner still faces the problem of contaminated sludge disposal.

As mentioned above, the composition of a combined tannery effluent that has not been treated is characterised by a high oxygen demand, high salt content, high solids content, high sulphide content, high ammonia-N content and, if chromium has been used, a persistent high load of it will remain. It will also be strongly alkaline, pH 9 or above (Harrison 1996, UNEP 1991, UNEP 1995, Kroschwitz and Howe-Grant 1995, Yamamoto and Win 1990). Untreated wastes discharged to surface waters can bring about rapid deterioration of their physical, chemical and biological qualities (UNEP 1991).

For example, wastes may give rise to noxious odours from the decomposition of organic matter. Their decomposition may deplete the dissolved oxygen in the water that is vital for aquatic life. The water may also become saline and hard due to the presence of inorganic salts, and acquire some toxicity from the chromium, sulphides and ammonia in the wastes. Release of nitrogenous compounds will stimulate plant growth, contributing to eutrophication of the receiving water body. Pathogenic microorganisms such as *B. anthrax* may also be present. Finally, due to turbidity and colour, photosynthesis may be restricted, affecting the primary link in the food chain (UNEP 1991).

Physically, the wastewater will appear very turbid, coloured (usually red), frothy and malodorous. Most of the chromium will be in the form of chromium (III) hydroxide, which will form a green precipitate at high pH levels, i.e. 12 or above (UNEP 1995). Treatment will involve pH adjustment, sulphide oxidation, chemical precipitation and



coagulation, gravity settling and biological (anaerobic digestion and activated sludge) treatment (Kabdasli *et al.* 1993, Tunay *et al.* 1994, Yamamoto and Win 1990, UNEP 1991, UNEP 1995, Harrison 1996).

To remove the chromium specifically, a two-stage process is usually employed. Firstly, hexavalent chromium is reduced to the trivalent form. Sulphur dioxide is commonly used for this process (UNEP 1991, UNEP 1995). This is followed by precipitation of trivalent chromium in the form of an insoluble hydroxide. This is achieved by the addition of lime. However, even though this is an efficient means of treating the chromium containing effluent, it does generate a secondary waste in the form of chromium containing sludge.

“What has been hardest for the industry to accept is that certain measures intended to control pollution can themselves create secondary environmental impacts...these so-called cross-media impacts include groundwater pollution, soil contamination, sludge dumping and chemical poisoning. They commonly occur when a particular problem is “solved” using an end-of-pipe treatment approach in which the eventual fate of residues has not adequately been thought through” (UNEP 1991).

A.2.4.2 Disposal

a) Landfill

There is vigorous debate concerning the environmental hazard of landfilling chromium-containing sludges, with much of this debate concerned with the potential conversion of chromium (III) to chromium (VI). As mentioned above, landfills receiving other industrial wastes, particularly acidic ones, may not be suitable for receiving tannery waste. In addition, the decomposition of domestic waste can lead to the formation of acidic condition, which again are not suitable. Conversion can occur, and chromium sludges can dissolve to liberate soluble chromium, which may escape from the site via leachate seepage to groundwater. Furthermore, acidic industrial wastes can react with sulphide-rich tannery wastes, to liberate hydrogen sulphide gas.

b) Incineration

In response to tightening landfill restrictions, incineration and pyrolysis are being increasingly considered. However, incineration will not destroy or decompose the chromium present in the sludge. Instead, it will be redistributed amongst further waste products i.e. fly and bottom ash, air emissions, and pollution control devices. The incineration of metal-containing sludges leads to problems with both air emissions and with soluble metals e.g. chromium (VI), in the ash (UNEP 1991).

c) Land application

Tannery sludge, if free from chromium and sulphides, can have a certain value as a soil conditioner (Hughes 1988, UNEP 1991). It also has some minor fertiliser effect due to the



nitrogenous components. However, if chromium tanning agents are used, chromium will be present in sludges and solid residues, which will then be classified as hazardous waste (see above). A number of European studies have shown that moderate applications are not immediately harmful to soils or crops, however these same environmental authorities are less and less certain about the long-term effects on soil and plant quality (UNEP 1991). Others note that even initial crop establishment is poor (Hughes, 1988). There are suggested maximum values for trivalent chromium in solids and sludges (ranging from 150-250 in soils, to 1000-1500 in sludges based on a background concentration of 50 mg/kg, UNEP 1991), but as described above, the assumption that all chromium released from a tannery will remain in the (III) state is both naïve and misinformed.

A.2.5 Conclusion

This review has attempted to summarise the tanning process, in light of the chemicals used, the various procedures employed, and the kinds of wastes generated. It has shown that pollution from tanneries is both varied and considerable, involving substantial chemical usage and the copious generation of effluents and solid wastes. Detrimental health and environmental impacts resulting from these processes, can therefore only be removed if cleaner practices, involving the use of non-toxic and/or biodegradable chemicals are used, coupled with efficient and effective treatment technology, and the assurance and practice of worker safety. With the right combination of technology and organisation, with sufficient guidance from the authorities, and with good backup from industry, an environmentally sound basis for tanning operations is achievable. However, a reduced input from any of these sectors will require disproportionate contributions from the others, threatening the attainment of these environmental goals (UNEP 1991).

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