



R  
E  
P  
O  
R  
T

## Identification and environmental significance of the organic pollutants and heavy metals in samples associated with Arlei and Meiner tanneries, Las Toscas, Santa Fe Province, Argentina 2000

Labunska, I., Brigden, K., Stringer, R., Johnston, P. Santillo, D. & Ashton, J.

Greenpeace Research Laboratories, Department of Biological Sciences, University of Exeter, Exeter, UK.

Date

Technical Note: 15/00

**GREENPEACE**



## TABLE OF CONTENTS

Executive summary .....	3
1 Introduction .....	4
2 Sampling Program .....	4
2.1 General Sampling Procedures .....	4
2.2 Sample Descriptions.....	4
3 Results and discussion .....	7
3.1 Arlei Tannery (samples AM0046, AM0043, AM0013 and AM0014) .....	7
3.2 Meiner Tannery (samples AM0011 and AM0012) .....	8
3.3 Ground water sample AM0047.....	9
3.4 Arlei Tannery dump site (samples AM0044 and AM0045).....	9
4 Conclusions .....	10
5 References .....	11
Appendix 1 Analytical methodology.....	12
Appendix 2 Toxicological outlines for key compounds.....	16



## EXECUTIVE SUMMARY

The Arlei and Meiner leather tanneries are situated close to Route 11, in the town of Las Toscas, Santa Fe Province, Argentina. Each tannery has a network of treatment lagoons to which they discharge wastewater. Treated wastewater is ultimately discharged into the Las Toscas creek, a tributary of the Parana River.

Greenpeace visited this area in the spring/summer of 2000 and collected nine samples which included industrial wastewater from each tannery, associated sediments, ground water in the area close to the tanneries and solid waste from an old dump site of the Arlei tannery. The analysis of these samples for organic compounds and heavy metals showed the following:

- Tannery wastewater and sediments from the Arlei tannery's treatment lagoon contain a high concentration of chromium. Organic contaminants found in these samples (except of ground water sample AM0047) were predominantly aliphatic hydrocarbons (both linear and cyclic) and alkylated benzenes. Industrial wastewater sample AM0043 also contained phthalate esters, phenolic compounds, phenanthrene and traces of 1,4-dichlorobenzene. None of these substances were detected in the sediment sample AM0013 from the treatment lagoon or in the sediment sample AM0014 at the point of discharge from the treatment lagoon. This might be due to a variation of the wastewater composition in time (samples AM0013 and AM0014 were collected in May 2000 and sample AM0043 was collected in August 2000). However, the sediment from the rain runoff channel running beside the Arlei tannery (AM0046) did contain high levels of chromium and similar pattern of organic contaminants to those detected in the sediment sample AM0014, suggesting that wastes from the tannery are entering this channel either by direct discharge or diffuse inputs.
- Both the wastewater and associated sediment samples from the Meiner tannery (AM0011 and AM0012) did not contain any of the metals considered in this study at significant levels. Only a small number of organic compounds were reliably identified in the wastewater sample AM0011, including alkylbenzenes, naphthalene and trace amounts of 1,4-dichlorobenzene. Traces of PCB-138 and PCB-153 detected in sediment sample AM0012 might reflect historical contamination.
- The only heavy metal detected at elevated levels in the sample of groundwater AM0047 collected near Arlei tannery was lead; the possibility that this results from lead components in the pump system which brings the water to the surface cannot be ruled out. 1,4-dichlorobenzene was also the only organic compound reliably identified in this sample. Presence of 1,4-dichlorobenzene is of concern because consumption of water contaminated by this toxic compound may effect human health.
- The high level of chromium found in the solid waste sample AM0044 from the old Arlei dump site indicates the highly contaminated nature of tannery wastes dumped at this location and illustrates the potential for wider contamination of the environment



surrounding this site. The majority of the organic contaminants detected in this sample were aliphatic hydrocarbons. Additionally, butylated hydroxytoluene (BHT) was also found in this sample. A sample of groundwater AM0045 collected from a hand pump located close to the Arlei tannery old dumpsite did not contain significant levels of chromium. However, zinc was found in this sample at a significant level, which is 21 times typical background levels for freshwater. The source of this elevated level of zinc is not clear. Aliphatic hydrocarbons at low levels were the only organic compounds detected in the groundwater sample AM0045. These compounds in the sample might be of natural origin.

## **1 INTRODUCTION**

Both the Arlei and Meiner tanneries are situated close to Route 11, in the town of Las Toscas, Santa Fe Province, Argentina. Each tannery has a network of treatment lagoons to which they discharge wastewater. Treated wastewater is ultimately discharged into the Las Toscas creek, a tributary of the Parana River.

## **2 SAMPLING PROGRAM**

During the summer of 2000, nine samples were collected in association with the Arlei and Meiner tanneries in Las Toscas town, Santa Fe Province, Argentina. The samples included three sediments, two industrial wastewaters, two groundwaters and one sample of solid waste.

### **2.1 General Sampling Procedures**

All samples were collected and stored in pre-cleaned glass bottles that had been rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metals and organic residues. Sediment and solid waste samples were collected in 100ml bottles, and the water samples were collected in 1-litre bottles. All sediment, solid waste and water samples were immediately sealed and cooled upon collection. The samples were returned to the Greenpeace Research Laboratories for analysis. Detailed description of sample preparation and analytical procedures are presented in Appendix 1.

### **2.2 Sample Descriptions**

Descriptions of the samples are presented in Table 1. Industrial wastewater sample AM0043 was collected from the open concrete channel to which the Arlei tannery is discharging wastewater. This wastewater flows into the treatment lagoons of the Arlei tannery. The sediment sample AM0013 was collected from one of these lagoons. Another sediment sample (AM0014) was collected at the point of discharge of the treated wastewater from the Arlei treatment lagoons into the Las Toscas creek. A single sediment sample AM0046 was collected from the rain runoff channel, which runs beside the Arlei tannery, to the south of this tannery.



Industrial wastewater sample AM0011 was collected from the pipe of the Meiner tannery at the point where it discharges into one of that tannery's treatment lagoons. Sediment sample AM0012 was collected from the treatment lagoon, adjacent to this pipe.

A groundwater sample AM0047 was collected from a pump in a house within block 157 in Las Toscas town. This block is located south of the Arlei tannery, but to the north of the Meiner tannery.

Solid waste sample AM0044 was collected from the Arlei leather tannery old dumpsite located 1500m to the west of Road No.11 (Ruta 11), to the southwest of the Arlei tannery and to the northwest of the Meiner tannery. Groundwater sample AM0045 was collected from a hand pump connected to the well, located close to the Arlei tannery old dumpsite

Sample Number	Sample Type	Sample Description
<b>Arlei Tannery, Las Toscas</b>		
AM0043	Industrial wastewater	Collected from a concrete wastewater channel prior to the treatment lagoons of the Arlei tannery
AM0013	Sediment	Collected from one of the treatment lagoons of the Arlei tannery
AM0014	Sediment	Collected from the point of discharge of the Arlei tannery treated wastewater to Las Toscas creek, a tributary of the Parana River
AM0046	Sediment	Collected from rainwater runoff channel running beside the Arlei tannery, by the road
<b>Meiner Tannery, Las Toscas</b>		
AM0011	Industrial wastewater	Collected from a pipe entering one of the treatment lagoons at the Meiner tannery
AM0012	Sediment	Collected adjacent to a pipe entering one of the treatment lagoons at the Meiner tannery, as AM0011
<b>Las Toscas, between Arlei and Meiner Tanneries</b>		
AM0047	Ground water	Collected from a water pump, to the south of the Arlei tannery and to the north of the Meiner tannery
<b>Arlei Tannery old dump site</b>		
AM0044	Solid waste	Collected from the Arlei leather tannery old dump site, located 1500 m to the west of Route No.11 (Ruta 11).
AM0045	Ground water	Collected from a hand pump, close to the old dump site of the Arlei tannery

*Table 1. Description of samples collected in association with the Arlei and Meiner leather tanneries, Las Toscas, Santa Fe Province, Argentina, 2000.*



Sample number	AM0043	AM0013	AM0014	AM0046	AM0011	AM0012	AM0047	AM0044	AM0045
Description	Industrial wastewater	Sediment	Sediment	Sediment	Industrial wastewater	Sediment	Ground water	Solid waste	Ground water
Location	Concrete channel prior to the treatment lagoons of Arlei tannery	Treatment lagoons, Arlei tannery	Arlei tannery discharge point from treatment lagoons to Las Toscas creek	Rainwater runoff channel, Arlei tannery	Pipe entering treatment lagoons of Meiner tannery	Pipe entering treatment lagoons of Meiner tannery	Water pump, near to Arlei tannery	Arlei leather tannery old dump site	Hand pump close to the old dump site of the Arlei tannery
<b>Metals</b>	(ug/L)	(mg/kg dw)	(mg/kg dw)	(mg/kg dw)	(ug/L)	(mg/kg dw)	(ug/L)	(mg/kg dw)	(ug/L)
Cadmium (Cd)	<20	<2	<2	<2	<20	<2	<20	<2	<20
Chromium (Cr)	1607	1137	205	7946	<20	16	<20	786	<20
Cobalt (Co)	<20	<2	4	5	<20	4	<20	<2	<20
Copper (Cu)	88	6	12	69	40	11	43	<2	70
Lead (Pb)	<30	2	9	69	<30	7	99	6	41
Manganese (Mn)	26	31	122	408	89	252	<10	<10	12
Mercury (Hg)	<1	<0.05	0.13	0.10	<1	0.2	<1	<0.05	<1
Nickel (Ni)	<20	<2	8	17	<20	7	<20	<2	<20
Zinc (Zn)	74	15	21	150	14	37	177	32	1073
No. of organic compounds isolated	154	73	140	120	22	54	5	171	37
No. of organic compounds reliably identified	47(31%)	18(25%)	50(36%)	48(40%)	5(23%)	2(4%)	1(20%)	48(28%)	5(14%)
<b>ORGANOHALOGEN COMPOUNDS</b>									
Benzene, 1,4-dichloro-	*				*		✓		
PCB-138						*			
PCB-153						*			
<b>PAHs</b>									
Naphthalene and/or its derivatives			✓(10)	✓(11)	✓				
Phenanthrene and/or its derivatives	✓								
<b>ORGANOSULPHUR COMPOUNDS</b>									
Sulfur, mol. (S8)			✓		✓				
<b>PHENOLIC COMPOUNDS</b>									
BHT								✓	
Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-	✓								
<b>PHTHALATE ESTERS</b>									
DEHP	✓								
DBP	✓								
<b>OTHER AROMATIC COMPOUNDS</b>									
Indene and/or its derivatives	✓(2)		✓						
Alkylated benzenes	✓(18)	✓	✓(6)	✓(11)	✓(2)				
<b>ALIPHATIC HYDROCARBONS</b>									
Linear	✓(21)	✓(16)	✓(28)	✓(25)				✓(43)	✓(5)
Cyclic		✓	✓(4)	✓				✓(4)	

Table 2. Organic chemicals and heavy metals identified in samples associated with the Meiner and Arlei leather tanneries, Las Toscas, Santa Fe Province, Argentina. 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 levels 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.



### 3 RESULTS AND DISCUSSION

The results of the organic screen analysis and heavy metals analysis are presented in Table 2, including a breakdown of the groups of organic compounds reliably identified in the samples.

For more information on the common sources, environmental behavior and toxicological outlines for key pollutants detected during this study see Appendix 2.

#### 3.1 Arlei Tannery (samples AM0046, AM0043, AM0013 and AM0014)

All four samples (AM0013, AM0014, AM0043 and AM0046) collected in association with the Arlei tannery contained chromium at significantly elevated levels. For comparison, typical background levels of chromium are 1.3ug/l in freshwater and 1-500mg/kg for freshwater sediments (USPHS 1997).

The wastewater sample collected from a channel prior to the treatment lagoons (AM0043) contained chromium at 1607 ug/l, indicative of significant discharges of chromium from the tanning process. Sediment from the lagoon itself (AM0013) contained 1137 mg/kg of chromium. These levels are considerably higher than that found in the sediment at the point of discharge of wastewater from the Arlei tannery treatment lagoons (AM0014) which contained chromium at 205 mg/kg. The level of chromium in sample AM0014, though within the range of typical background level of chromium in freshwater sediments (USPHS 1997), nevertheless appears relatively high. Results from analysis of sediments upstream from the discharge point would be necessary to determine whether the 205 mg/kg reported here was typical of uncontaminated sediments in this river system or if this level represents significant elevation above background as a result of discharge from the tannery. Given the tendency of chromium to adsorb to particulates, some attenuation of chromium levels in the wastewaters during passage through the settling lagoon is to be expected. This inevitably results in a greater degree of contamination of the lagoon sediments, of course.

Organic contaminants found in the samples AM0043, AM0013 and AM0014 were dominated by alkylated benzenes and aliphatic hydrocarbons, both cyclic and linear. These compounds are known as typical pollutants in tannery wastes, resulting from usage of different organic solvents through the technological processes (UNEP 1991).

Wastewater sample AM0043 collected prior to the Arlei treatment lagoons also contained phenanthrene (a PAH), one phenolic compound, two phthalate esters (DEHP and DBP), two indene derivatives and trace amounts of 1,4-dichlorobenzene.

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). The main use of DEHP is 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 these compounds, and taking into account that the sample was collected from an open channel, it is difficult to determine the source of phthalate esters in this sample.

The presence of 1,4-dichlorobenzene in the sample AM0043 might be due to its use as insecticide to discourage beetle and other insect attack during storage and transport of hides and skins (UNEP 1991). However, this compound is very common environmental pollutant mainly due to its use in room deodorants and sanitary deodorant blocks (ATSDR 1997). 1,4-dichlorobenzene is a highly volatile substance that sublimes at room temperature and most of its environmental releases are to the atmosphere. However, this compound may be sorbed to the soil or sediment and adsorption to soil particles may inhibit volatilization by an order of magnitude compared to volatilization from water (ASTDR 1997). Therefore, it is unclear what application caused the presence of 1,4-dichlorobenzene in this sample because, again, this wastewater runs through the open channel and there is a possibility of the 1,4-dichlorobenzene being air transported with soil particles from other locations.

Naphthalene, a polycyclic aromatic hydrocarbon (PAH), and a large number of its derivatives were also found in the sediment AM0014, collected at discharge point from the treatment lagoons. Naphthalene, in addition to other chemicals such as phenolic compounds, may be used alone or in association with chromium and vegetable tannins, for re-tanning or as a principal tanning agent for certain speciality leathers (UNEP 1991; Kroschwitz & Howe-Grant 1995).

A single sample of sediment that was collected from a rainwater runoff channel close to the Arlei tannery (AM0046) contained chromium at 7946 mg/kg, which is greatly in excess of typical background levels.

Organic contaminants found in the samples AM0046 were also represented predominantly by alkylated benzenes and aliphatic hydrocarbons, as was found in all the samples associated with the Arlei tannery (AM0043, AM0013 and AM0014). A similar range of naphthalene derivatives to those detected in the sample AM0014 was also detected in this sediment sample from the rainwater runoff channel. The level of chromium and pattern of organic contaminants found in the sample AM0046 suggests that wastes from the tannery are reaching this rainwater channel, either by direct discharge or by leaching from contaminated areas.

### **3.2 Meiner Tannery (samples AM0011 and AM0012)**

Both the wastewater and associated sediment samples from the Meiner tannery AM0011 and AM0012 did not contain any of the metals considered in this study at significant levels.





Only two organic compounds were reliably identified in the sediment sample AM0012, hexachlorobiphenyl congeners PCB-153 and PCB-138, and then only at trace levels using selective ion monitoring method. As PCBs were always sold as technical mixes containing large number of congeners, the presence of these congeners, and no others, in the sediment may show historical contamination by polychlorobiphenyls rather than recent contamination. Among all the PCB congeners, PCB-153, PCB-138 and PCB-180 are the most persistent. In general, PCBs that have a chlorine in the para-position (in the 4 or the 2 and 5 positions) persist through biotransformation (Ballschmiter *et al* 1989). Both congeners PCB-153 and PCB-138 detected in the sample AM0012 have chlorine in the positions mentioned above.

Industrial wastewater sample AM0011 contained two alkylated benzenes, naphthalene and 1,4-dichlorobenzene (detected only at trace levels) among the organic compounds reliably identified. The presence of these compounds in tannery wastes was discussed in section 1.1.2. Additionally, molecular sulphur was detected in this sample. Sulphur containing chemicals are used on several stages of the tanning process (UNEP 1991) and formation of the molecular sulphur may result from the desulphurisation of the generated wastes.

### **3.3 Ground water sample AM0047**

A sample of ground water collected from a hand pump in a house near to the Arlei tannery (AM0047) did not contain significant levels of chromium. The only metal in this sample at a significant level was lead at 99 ug/l. The typical concentration of lead in drinking water ranges from below 5 to 30 ug/l (USPHS 1997). The slightly elevated level of lead in this sample may be as a result of the use of lead plumbing, which can result in levels in excess of 100 ug/l (WHO 1995).

Only one organic pollutant was reliably detected in the sample of ground water AM0047 - 1,4-dichlorobenzene. This chemical may leach from hazardous waste sites, be transported through groundwater, and migrate from surface water to groundwater through the soil (ATSDR 1997). However, it is unclear from which facility 1,4-dichlorobenzene has leached into the groundwater and this needs to be further investigated. In laboratory studies, 1,4-dichlorobenzene showed little or no sign of degradation either aerobically or anaerobically (Higgo *et al* 1996). Thus, the presence of 1,4-dichlorobenzene in the sample AM0047 is of concern because consumption of water contaminated by this toxic compound may effect human health. The symptoms include damage to the liver, kidneys and lungs (ATSDR 1997).

### **3.4 Arlei Tannery dump site (samples AM0044 and AM0045)**

A sample of solid waste collected from an old dump site at the Arlei tannery (AM0044) contained chromium at 786 mg/kg, substantially higher than levels typically found in uncontaminated soils (Alloway 1990, Dudka and Adriano 1997). The level of chromium



in this sample is indicative of the highly contaminated nature of the wastes dumped at this location. Combined with the high levels of chromium found in other liquid and solid waste samples associated with this tannery, the potential for this plant to contribute to contamination of the surrounding environment, directly or indirectly (e.g. through leaching from wastes, dumping of contaminated lagoon sediments, etc.), is clear.

Organic compounds found in the sample AM0044 were dominated by aliphatic hydrocarbons and butylated hydroxytoluene (BHT). BHT is used as an antioxidant in food products and in the production of plastics, petrochemicals and some cosmetics (Budavari *et al* 1989).

A sample of ground water collected from a hand pump located close to a waste dump near to the Arlei tannery (AM0045) did not contain significant levels of chromium. The only metal in this sample at a significant level was zinc at 1073 ug/l. The typical concentration of zinc in freshwater is below 50 ug/l (USPHS 1997). The source of this elevated level of zinc, which is 21 times typical background levels, is not clear.

Aliphatic hydrocarbons at low levels were the only compounds detected in the groundwater sample AM0045. These compounds in the sample might be of natural origin.

#### 4 CONCLUSIONS

Elevated levels of chromium were detected in wastewater, treatment lagoon sediment and solid wastes associated with operations at the Arlei tannery, providing strong evidence that this plant is employing chromium tanning processes. These activities are, in turn, undoubtedly resulting in the release of chromium to the surrounding environment, either directly through discharges or indirectly through run-off from the site and/or the disposal of solid wastes and lagoon sediments to land. A more detailed study would be necessary in order to determine the extent of contamination which may be occurring as a result. Nevertheless, the potential is clear.

Wastes associated with the Meiner tannery, in contrast, did not show evidence of elevated chromium concentrations. Information regarding the tanning processes employed at this plant, the waste streams generated and their fate, would be essential if the reasons for the contrasting results were to be further discussed.

Drinking waters collected from groundwater wells in the region did not show evidence of contamination with elevated levels of chromium. Elevated levels were recorded for lead and zinc, although the reasons for this remain unclear. More importantly, these results alone do not provide evidence on which to conclude that the environment in this area has not been contaminated as a result of the activities taking place in the Arlei and Meiner tanneries.



## 5 REFERENCES

- ATSDR (1997) Toxicological Profiles. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service (CD-ROM)
- Ballschmiter, K., Rappe, C. & Buser, H.R. (1989) Chemical properties, analytical methods and environmental levels of PCBs, PCTs, PCNs and PBBS. In: Kimbrough, R.D. & Jensen, A.A. (Eds.) Halogenated biphenyls, terphenyls, naphthalenes, dibenzodioxins and related -products. Publ: Elsevier; p47-69
- Budavari, S.M., O'Neil, J., Smith, A. & Heckleman, P.E. (Eds.) (1989) The Merck Index: an encyclopaedia of chemicals, drugs and biologicals. 11th Edn, Merck and Co, Inc., New Jersey, USA
- Higgo, J.J.W., Nielsen, P.H., Bannon, M.P., Harrison, I., and Christensen, T.H. (1996) Effect of geochemical conditions on fate of organic compounds in groundwater. *Environmental geology* 27: (4) 335-346
- Jobling, S., Reynolds, T., White, R., Parker, M.G. & Sumpter, J.P. (1995) A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic. *Environmental Health Perspectives* 103(6): 582-587.
- Kemi (1994) Phthalic acid esters used as plastic additives. Publ: Swedish National Chemicals Inspectorate; report 12/94, ISSN 0248-1185
- Kroschwitz, I. and Howe-Grant, M. [Eds] (1995). Kirk-Othmer encyclopaedia of chemical technology. Fourth Edition, Volume 14: 208-226. John Wiley and Sons Inc., New York, Chichester, Brisbane, Toronto, Singapore.
- Menzert R.E., Nelson J.O. (1986). Water and soil pollutants. In *Toxicology: the basic science of poisons*. Klaasen C.D., Ambur M.O. and Doull J. [Eds], MacMillan Publishing Co., New York: 825-856.
- UNEP (1991). *Tanneries and the Environment. A Technical Guide to Reducing the Environmental Impact of Tannery Operations*. Technical Report Series No. 4. United Nations Environment Programme Industry and Environment Office.
- World Health Organisation (1995). Inorganic Lead. *Environmental Health Criteria* 165. ISBN 9241571659



## **APPENDIX 1**

## **ANALYTICAL METHODOLOGY**

### **A.1.1 Organic analysis**

#### **A.1.1.1 Preparation of samples for organic screen analysis**

All solvents were of High Purity Grade (PRAG or low haloform). Glassware used in extraction and clean up procedures was cleaned in detergent, rinsed with tap water and deionised water, dried in the oven overnight at 105<sup>0</sup>C, and rinsed three times with low haloform pentane.

##### **A.1.1.1.1 Solid Samples**

In preparation for analysis of extractable organic compounds, approximately 30g (wet weight) was weighed and transferred to a clean 100 ml glass bottle. Samples were spiked with deuterated naphthalene (an internal standard) at a concentration of 4.7 mg/kg. 15ml of pentane was added, followed by 5ml of acetone. All samples were then sonicated for 2 hours.

Extracts were decanted, filtered through a pre-cleaned hydrophobic phase separator filter and collected in reagent tubes. They were then acidified to pH 2 with 10% nitric acid. Following this, a second portion of 20ml pentane was added and the extraction procedure repeated. Finally, both extracts obtained for each sample were combined and evaporated to a volume of approximately 3ml. The concentrated extract was cleaned through a Florisil column, eluted with a 95:5 mixture of pentane: toluene, and evaporated down to a volume of 2 ml under a stream of analytical grade nitrogen. 1-Bromonaphthalene was then added at concentration 10mg/l to provide an indication of GC/MS performance.

##### **A.1.1.1.2 Aqueous Samples**

Prior to the extraction, samples were spiked with deuterated naphthalene (an internal standard) at a concentration of 10mg/l. 20ml of pentane were added, and the sample agitated for 2 hours on a bottle roller to maximise contact between solvent and sample.

After separation of the phases, the solvent extract was filtered through a hydrophobic phase separator filter and collected in pre-cleaned reagent tube. The aqueous sample was acidified to pH 2 with 10% nitric acid, a second portion of 20ml pentane was added and the extraction procedure repeated. Both extracts were combined and cleaned up as described above for solid samples.

##### **A.1.1.2 Chromatographic Analysis**

Organic compounds were identified qualitatively and quantitatively using Gas Chromatography Mass Spectrometry (GC-MS).

Instrumentation was a Hewlett Packard (HP) 5890 Series II gas chromatograph, interfaced



with a HP Chem-Station data system and linked to a HP 5972 Mass Selective Detector operated in scan mode. The identification of compounds was carried out by computer matching against a HP Wiley 275 library of 275,000 mass spectra combined with expert interpretation. Also all extracts were analysed using selective ion monitoring (SIM) method against two standard solutions. The lists of compounds containing in Standard I and Standard II are presented below. All individual standards were obtained from Sigma Aldrich Co. Ltd., Supelco, UK.

<b>Compound</b>	<b>Ions to monitor</b>
Benzene, 1,3-dichloro-	146, 148, 111, 75
Benzene, 1,4-dichloro-	146, 148, 111, 75
Benzene, 1,2-dichloro-	146, 148, 111, 75
Benzene, 1,3,5-trichloro-	180, 182, 145, 74
Phenol, 2,4-dichloro-	162, 164, 63, 98
Benzene, 1,2,4-trichloro-	180, 182, 145, 109
Benzene, 1,2,3-trichloro-	180, 182, 145, 109
Dichlorvos	109, 185, 79, 47
Benzene, 1,2,3,5-tetrachloro-	216, 214, 218, 179
Benzene, 1,2,4,5-tetrachloro-	216, 214, 218, 179
Benzene, 1,2,3,4-tetrachloro-	216, 214, 218, 179
Benzene, pentachloro-	250, 252, 248, 215
alpha-HCH	181, 183, 219, 217
Benzene, hexachloro-	284, 286, 282, 249
Simazine	200, 215, 202, 173
beta-HCH	181, 183, 219, 217
gamma-HCH	181, 183, 219, 217
delta-HCH	181, 183, 219, 217
o,p'-DDE	246, 248, 318, 176
p,p'-DDE	246, 318, 246, 316
o,p'-DDD	235, 237, 165, 199
p,p'-DDD	235, 237, 165, 199
o,p'-DDT	235, 237, 165, 199
p,p'-DDT	235, 237, 165, 199

***A.1.1 List of compounds in the Standard I used for SIM analysis***

Results are reported as a list of those compounds reliably and tentatively identified. Match qualities of 90% or greater against HP Wiley 275 library or identification confirmed against standard compounds (using retention times and mass-spectra obtained during calibration) are assumed to give reliable identifications. Tentative identification refers to qualities between 51% and 90% against HP Wiley 275 library only. Analytes yielding match qualities of 50% or less are assumed to be unidentified.



Compound	Ions to monitor
Phenol, 2-chloro-	128, 64, 92, 39
Phenol, 2-methyl-	108, 79, 90, 51
Phenol, 3-methyl- and 4-methyl-	108, 107, 79, 77
Phenol, 2,5-dichloro-	162, 164, 63, 99
Phenol, 2,3-dichloro-	162, 126, 63, 99
Phenol, 4-chloro-	128, 65, 130, 100
Phenol, 2,6-dichloro-	162, 164, 63, 98
Butadiene, hexachloro-	225, 190, 260, 118
Phenol, 2,3,5-trichloro-	196, 198, 160, 97
Phenol, 2,4,5-trichloro-	196, 198, 97, 132
Phenol, 3,5-dichloro-	162, 164, 99, 63
Phenol, 2,3,6-trichloro-	196, 198, 97, 132
Phenol, 3,4-dichloro-	162, 164, 99, 63
Atrazine	200, 215, 202, 173
Phenol, pentachloro-	266, 268, 264, 165
Chlordane I	373, 375, 272, 237
Chlordane II	373, 375, 272, 237
PCB-153	360, 362, 290, 218
PCB-138	360, 362, 290, 292
PCB-180	394, 396, 324, 252

*A.1.2 List of compounds in the Standard II used for SIM analysis*

## A.1.2 Heavy Metal Analysis

### A.1.2.1 Preparation of samples for heavy metal analysis

All chemicals were of High Purity Aristar Grade. All glassware was cleaned in detergent, rinsed with tap water and deionised water, soaked in 10% nitric acid overnight, rinsed with deionised water and dried in an oven.

#### A.1.2.1.1 Solid Samples

Samples were air dried until weighing readings became constant (approx. 5 days). They were then crushed using a pestle and mortar until homogenous and sieved through a 2-mm mesh. 0.5 g of sample was weighed into a glass 100 ml boiling tube and to this 10 ml of deionised water was added, followed by 7.5 ml of concentrated hydrochloric acid and 2.5 ml of concentrated nitric acid. The samples were digested at room temperature overnight prior to being placed onto a Gerhardt Kjeldatherm digestion block (40 space) connected to a Gerhardt Turbosog scrubber unit (filled with 10% w/v sodium hydroxide). The samples were then refluxed at 130 °C for four hours.

After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed. A Standard



Reference Material, BCR-143 (trace elements in a sewage sludge amended soil), certified by the Commission of the European Communities, Brussels, and a blank sample, were prepared with the batch of samples. All were prepared in 15% v/v hydrochloric acid and 5% v/v nitric acid.

#### **A.1.2.1.2 Aqueous samples**

On arrival, 100ml of sample was transferred to a clean glass bottle and acidified with nitric acid (10% v/v). 50 ml of this solution was subsequently transferred to a 100ml boiling tube, placed onto the Gerhardt Kjeldatherm digestion block, and refluxed at 130°C for four hours. After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed. . An 8mg/l standard solution of the metals to be analysed for, and a blank sample, were prepared with the batch of samples.

#### **A.1.2.2 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)**

Following preparation, samples were analysed by ICP-AES, using a Varian Liberty-100 Sequential Spectrometer. The following metals were quantified directly: manganese, chromium, zinc, copper, lead, nickel, cobalt and cadmium. A multi-element instrument calibration standard was prepared at a concentration of 10 mg/l, matrix matched to the samples (i.e. in 15% v/v hydrochloric acid and 5% v/v nitric acid for solid samples, and 10% v/v nitric acid for aqueous samples). The calibration was validated using a quality control standard (8 mg/l), prepared internally from different reagent stocks. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Mercury (Hg) was determined using Cold Vapour Generation ICP-AES. Hg (II) was reduced to Hg (0) i.e. a vapour, following reduction of the samples with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The vapour was carried in a stream of argon into the spectrometer. Two calibration standards were prepared, at 10 ug/l and 100 ug/l, matrix matched to the i.e. in 15% v/v hydrochloric acid and 5% v/v nitric acid for solid samples, and 10% v/v nitric acid for aqueous samples). The calibration was validated using a quality control standard (80 ug/l), prepared internally from different reagent stock. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.



## APPENDIX 2

## TOXICOLOGICAL OUTLINES FOR KEY COMPOUNDS

### A.2.1 Chromium

#### A.2.1.1 Natural Occurrence

Chromium is the 21<sup>st</sup> 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 ( $\text{FeCr}_2\text{O}_4$ ) which is produced principally in South Africa, Albania, Turkey, India and Zimbabwe. Other less plentiful sources are the ores crocoite ( $\text{PbCrO}_4$ ) and chrome ochre ( $\text{Cr}_2\text{O}_3$ ) (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.2.1.2 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.2.1a-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
<b>TOTAL</b>	<b>30.4</b>

*Table A.2.1a 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
<b>TOTAL</b>	<b>142.8</b>

*Table A.2.1b 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
<b>TOTAL</b>	<b>898.32</b>

*Table A.2.1c World-wide inputs of chromium into soils*

### A.2.1.3 Environmental Levels, Contamination and Behaviour

Chromium is found in varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see Table A.2.1d). However, in areas associated with anthropogenic emissions, ecosystem levels can far exceed natural, background concentrations (see Table A.2.1e).



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.2.1d 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.2.1e 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.2.1.4 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.2.1.5 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).

### References

- Alloway, B.J. (1990). Heavy metals in soils. John Wiley and Sons, Inc. New York, ISBN 0470215984
- Bryan, G.W. and Langston, W.J. (1992). Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. *Environmental Pollution* 76: 89-131
- Dudka, S. and Adriano, D.C. (1997). Environmental impacts of metal ore mining and processing: a review. *J. Environ. Qual.* 26: 590-602
- EEC (1975). Council Directive 75/440/EEC of 16 June 1975 concerning the quality required of surface water intended for the abstraction of drinking water in the Member States (OJ L 194, 25.7.1975, p. 26)
- EEC (1976). Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (OJ L 129, 18.5.1976, p. 23)
- EEC (1980). Council Directive 80/778/EEC of 15 July 1980 relating to the quality of water intended for human consumption (OJ L 229, 30.8.1980, p. 11)



- Goyer, R.A. (1996). Toxic effects of metals. In Casarett & Doull's Toxicology. The Basic Science of Poisons, Fifth Edition, Klaassen, C.D. [Ed]. McGraw-Hill Health Professions Division, ISBN 0071054766
- Greenwood, N.N. and Earnshaw, A. (1984). Chemistry of the Elements. Pergamon Press Ltd. ISBN 0080220576
- IARC (1998). Chromium and certain chromium compounds. In: IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans. Chemicals, industrial processes and industries associated with cancer in humans. IARC monographs, Vol. 1 to 29
- Kimbrough, D.E, Cohen, Y., Winer, A.M., Creelman, L. and Mabuni, C. (1999). A critical assessment of chromium in the Environment. Critical Reviews in Environmental Science and Technology 29, 1: 1-46
- Mitchell, D.J., Wild, S.R. and Jones, K.C. (1992). Arrested municipal solid waste incinerator fly ash as a source of heavy metals to the UK environment. Environmental Pollution 76: 79-84
- Mukherjee, A.B. (1998). Chromium in the environment of Finland. The Science of the Total Environment 217: 9-19
- Nriagu, J.O. (1990). Global metal pollution. Poisoning the biosphere? Environment 32, 7: 7-11; 28-33
- Nriagu, J.O. and Pacyna, J.M. (1988). Quantitative assessment of World-wide contamination of air, water and soils with trace metals. Nature 333: 134-139
- Outridge, P.M. and Schuehammer, A.M. (1993). Bioaccumulation and toxicology of chromium: implications for wildlife. Reviews of Environmental Contamination and Toxicology 130: 31-77
- Richard, F.C. and Bourg, A.C.M. (1991). Aqueous geochemistry of chromium: a review. Wat. Res. 25, 7: 807-816
- UNEP (1991). Tanneries and the environment. A technical guide to reducing the environmental impact of tannery operations. Technical Report Series No. 4. United Nations Environment Programme Industry and Environment Office
- USPHS (1997). Toxicological profile for chromium on CD-ROM. Agency for Toxic Substances and Disease Registry. U.S. Public Health Service
- USPHS (1998). 8<sup>TH</sup> Report on Carcinogens 1998 Summary.
- World Health Organisation (1993). Guidelines for drinking-water quality. Volume 1: Recommendations. ISBN 9241544600

### A.2.2 Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons occur in a variety of environmental products such as soot, coal, tar, tobacco smoke, petroleum, and cutting oil. They are commonly found as product of incomplete combustion. PAHs are found to cause harm to human health. Individuals exposed by breathing or skin contact for long period of time to mixtures of PAHs and other compounds can develop cancer (ATSDR 1997). Many of the carcinogenic polycyclic aromatic hydrocarbons are derived from an angular benz[a]anthracene skeleton. Anthracene itself is not carcinogenic, but benz[a]anthracene appears to have weak carcinogenicity. Addition of another benzene ring in select positions result in agents with powerful carcinogenicity such as dibenz[a,h]anthracene or benzo[a]pyrene. In addition, substitution of methyl groups on specific carbons of the ring also enhances carcinogenicity. Thus, 7,12-dimethylbenz[a]anthracene (DMBA) is one of the most powerful synthetic, polycyclic aromatic hydrocarbon carcinogenes known (Williams, 1986).

PAHs are prevalent pollutants in the aquatic environment that can cause a wide range of toxic effects. PAHs together with alkylbenzenes are considered to be the most toxic and are the highest in concentration in the initial phase of a crude oil spill (Overton, 1994). The toxicity of certain PAHs to aquatic organisms can be greatly increased upon exposure of the organisms to ultraviolet (UV) radiation present in sunlight (Monson *et al.* 1995; Ankley *et al.* 1995; Arfsten *et al.* 1996; McConkey *et al.* 1997). It was found that



phototoxicity clearly was a function both of PAH dose and light intensity (Ankley *et al.* 1995; Huang *et al.* 1997).

Naphthalene and its alkyl derivatives were predominantly found in the current study. The major products made from naphthalene are moth repellents, in the form of mothballs or crystals, and toilet deodorant blocks. It is also used for making dyes, resins, leather-tanning agents, and the insecticide, carbaryl (ATSDR 1997). The simplest alkyl derivatives of naphthalene, 1-methylnaphthalene and 2-methylnaphthalene are used to make other chemicals such as dyes, resins, and, for 2-methylnaphthalene, vitamin K. Along with naphthalene, they are present in cigarette smoke, wood smoke, tar, and asphalt, and at some hazardous waste sites (ATSDR 1997).

Exposure to a large amount of naphthalene may damage or destroy some of human red blood cells. People, particularly children, have developed this problem after eating naphthalene-containing mothballs or deodorant blocks. Anemia has also occurred in infants wearing diapers after storage in mothballs (ATSDR 1997).

Laboratory rabbits, guinea pigs, mice, and rats sometimes develop cataracts (cloudiness) in their eyes after swallowing naphthalene. It is not clear if cataracts also develop in humans exposed to naphthalene, but the possibility exists. The carcinogenicity of naphthalene has not been determined. The Department of Health and Human Services (DHHS) has determined that naphthalene may cause cancer in female mice but not in male mice or rats of either sex. The International Agency for Research on Cancer (IARC) has determined that naphthalene is not classifiable as to its carcinogenicity to humans. The EPA has determined that naphthalene is not classifiable as to its carcinogenicity to humans (ATSDR 1997).

## References

- Ankley G.T., Erickson R.J., Phipps G.L., Mattson V.R., Kosian P.A., Sheedy B.R., Cox J.S. (1995). Effects of light-intensity on the phototoxicity of fluoranthene to a benthic macroinvertebrate. *Environmental Science and Technology*, Vol.29, No.11, pp.2828-2833.
- Arfsten D.P., Schaeffer D.J., Mulveny D.C. (1996). The effects of near-ultraviolet radiation on the toxic effects of polycyclic aromatic-hydrocarbons in animals and plants - a review. *Ecotoxicology and Environmental Safety*, 1996, Vol.33, No.1, pp.1-24.
- ATSDR (1997) Toxicological Profiles. Agency for Toxic Substances and Disease Registry, U.S. Public Health Service (CD-ROM)
- Huang X.D., McConkey B.J., Babu T.S., Greenberg B.M. (1997). Mechanisms of photoinduced toxicity of photomodified anthracene to plants: Inhibition of photosynthesis in the aquatic higher plant *Lemna gibba* (duckweed). *Environmental Toxicology and Chemistry*, 1997, Vol.16, No.8, pp.1707-1715
- McConkey B.J., Duxbury C.L., Dixon D.G., Greenberg B.M. (1997). Toxicity of a PAH photooxidation product to the bacteria *Photobacterium phosphoreum* and the duckweed *Lemna gibba*: Effects of phenanthrene and its primary photoproduct, phenanthrenequinone. *Environmental Toxicology and Chemistry*, 1997, Vol.16, No.5, pp.892-899.
- Monson P.D., Ankley G.T., Kosian P.A. (1995). Phototoxic response of *lumbricus-variegatus* to sediments contaminated by polycyclic aromatic-hydrocarbons. *Environmental Toxicology and Chemistry*, 1995, vol.14, no.5, pp.891-894.
- Overton, 1994. Toxicity of petroleum. In: *Basic Environmental Toxicology*. Cockerham & Shane [Eds], Chapter 5, pp. 133-156.



Williams G.M., Weisburger J.H. (1986). Chemical carcinogens. In *Toxicology: the basic science of poisons*. Klaasen C.D., Ambur M.O. and Doull J. [Eds], MacMillan Publishing Co., New York: 99-173.

### A.2.3 Alkylbenzenes

Alkylbenzenes are single-ring aromatic compounds containing one or more aliphatic side chains. While there are theoretically thousands of alkylbenzenes, the major products of commerce and, therefore, those to which humans are most likely to be exposed included toluene (methylbenzene), ethylbenzene, cumene (isopropylbenzene), and three xylenes (1,2-, 1,3-, and 1,4-dimethylbenzene).

The occurrence of these compounds in the environment is due to their presence in crude oil and petroleum products. Alkylbenzenes are also produced following the degradation of the linear alkylbenzene sulphonate (LAS) detergents. The alkylbenzenes are highly resistant to degradation and may accumulate in sediments (Preston & Raymundo 1993). Alkylbenzenes are useful sewage markers (Chaloux et al. 1995) and due to their stability in sediments, they are very useful in tracing the transport of contaminants from their point sources. Monoaromatic (benzene derivatives) and polyaromatic hydrocarbons (PAHs) are considered to be the most toxic, and are known to be present at the highest concentrations during the initial phase of a crude oil spill (Overton 1994).

The acute toxicity of inhaled alkylbenzenes is best described as central nervous system (CNS) depression (Andrews & Snyder, 1986). Acute toxicity does not vary very much within the group. In animal models, relatively similar concentrations of inhaled alkylbenzene vapours were found to be lethal. Impaired reaction times and impaired speech are the two most commonly noted CNS effects (Casarett & Doull, 1996). All alkylbenzenes mentioned above are irritating to the eyes and mucous membranes, can cause irritation and burning of the skin, and all are narcotics at high concentrations. Benzene itself is a known carcinogen (Fourth Annual Report on Carcinogens 1985). Chronic exposure can lead to bone marrow depression, which in a few cases, can progress to leukemia (Merck, 1989).

### References

- Andrews L.S. and Snyder R. (1986). Toxic effects of solvents and vapors. In *Toxicology: the basic science of poisons*. Klaasen C.D., Ambur M.O. and Doull J. [Eds], MacMillan Publishing Co., New York: 636-668.
- Budavari, S.M., O'Neil, J., Smith, A. & Heckleman, P.E. (Eds.) (1989) *The Merck Index: an encyclopaedia of chemicals, drugs and biologicals*. 11th Edn, Merck and Co, Inc., New Jersey, USA
- Casarett and Doull (1996). *Toxicology: The basic science of poisons* (ed. Curtis D. Klaassen). ISBN 0-07-105476-6. McGraw-Hill Companies Inc. USA.
- Chaloux N., Takada H., Bayona J.M. (1995). Molecular markers in Tokyo Bay sediments – sources and distribution. *Marine Environmental Research*, Vol., 40, No.1, pp.77-92.
- Fourth Annual Report on Carcinogens (1985). Cited in Merck (1989) *The Merck index: an encyclopaedia of chemicals, drugs and biologicals*. 11th Edn. Budavari, S.M.J. O'Neil, A. Smith and P.E. Heckleman [Eds]. Merck and Co, Inc., New Jersey, USA, 1606p.
- Overton, 1994. Toxicity of petroleum. In: *Basic Environmental Toxicology*. Cockerham & Shane [Eds], Chapter 5, pp. 133-156.



Preston, M.R. & Raymundo, C.C. (1993) The associations of linear alkyl benzenes with the bulk properties of sediments from the River Mersey estuary. *Environmental Pollution*, Vol.81, pp. 7-13.