Identification of organic pollutants and heavy metal contaminants in samples collected from the environs of an industrial complex, in the Quilicura district of Santiago, Chile, 2000

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EXECUTIVE SUMMARY

A large and expanding industrial complex is located in the district of Quilicura, on the edge of the city of Santiago, Chile. The ESSA treatment plant, designed to treat sewage waste only, is located with the complex. It is believed that other industrial wastewaters may also pass through this treatment plant. Treated wastewaters from the ESSA plant are discharged into the Estero Las Cruces, a tributary to the Rio Mapocho. A second pipe, located approximately 20 metres downstream of the ESSA discharge pipe, discharges untreated industrial wastewaters directly into the Estero Las Cruces.

Greenpeace visited this industrial area in June and July 2000 and collected a number of samples of treatment plant sludges, discharging wastewaters, river sediments and river and drinking water. These samples were collected to determine the contamination of the local environment from activities within the industrial complex. The analysis of these samples for organic contaminants and heavy metals demonstrated the following:

- A number of organic compounds and elevated levels of a number of potentially toxic metals were found in the Estero Las Cruces in the vicinity of the complex that were not found in the river upstream of the complex. Many of these were also detected in either the ESSA treatment plant sludges or in the wastewater discharges from the downstream outfall pipe.

- Additional organic pollutants were detected in the river that were not found in samples from these two input sources. The presence of these compounds may be as a result of industrial inputs to the river at other locations.

- Two toxic and hormone disrupting chemicals, including nonyl, were found in the river downstream of the complex, suggesting additional inputs to the river downstream of the ESSA treatment facility.

- A sample of drinking water from a well located approximately 2 kilometres south of the complex contained the toxic metal lead at a significant concentration. Elevated levels of lead were also detected in the river sediment in the vicinity of the industrial complex.

The exact sources of many of these chemicals is not clear, and more information as to the processes employed, the chemicals used and wastes produced at plants within the complex must be made available. Procedures need to be put in place to prevent the discharge of pollutants to the environment.

1 INTRODUCTION

A large and expanding industrial complex is located in the district of Quilicura, on the edge of the city of Santiago, Chile. Within the complex is the ESSA treatment plant, designed to treat sewage waste only. It is believed, however, that other industrial wastewaters may also pass through this treatment plant. Treated wastewaters from the ESSA plant are discharged into the Estero Las Cruces, a tributary to the Rio Mapocho, which in turn is a tributary to the Rio Maipo, which ultimately discharges into the Pacific Ocean at San Antonio. Water from the Mapocho river is used to irrigate agricultural land, and therefore pollutants discharged to this river may be transferred to soils and eventually enter the food chain (Schalscha 1998).

A second pipe, located approximately 20 metres downstream of the ESSA discharge pipe, discharges untreated industrial wastewaters directly into the Estero Las Cruces. The following companies were temporarily permitted to discharge via this outlet until April 2000; Gist Brocades S.A. (yeast producer), Cerveceria Chile S.A. (brewery), Tintorerias Industriales P y P (industrial dyeing and dry cleaning), Alvatex S.A. (textile producer and industrial dyeing), and Raul Navarro Chile S.A. (paprika producer). Gist Brocades had a special permission to discharge via this outlet until August 2000, by which time a treatment facility for wastewaters from this plant should have become operative. Members of the local community have reported that the colour and smell of the discharge from this downstream pipe vary greatly over time.

Approximately 60% of the industries within the complex are believed to be operating under temporary licenses.

1.1 ESSA treatment plant

Approximately three months prior to the collection of samples, changes were made at the ESSA treatment plant (see figure 1). The aeration lagoon number 2 was emptied of water into the aeration lagoon number 1, in which a new concrete lining had been installed. In addition, the final settling lagoon number 3 was emptied, a new plastic lining installed and a new discharge pipe installed on the banks of the Estero Las Cruces. At the time of sampling, aeration lagoon number 2 remained empty of wastewaters, but contained large quantities of sludge.

2 SAMPLING PROGRAM

During the period June to August 2000, 14 samples were collected from the area of the industrial complex in the district of Quilicura. The samples included three industrial wastewater samples, two treatment plant sludge samples, seven river sediments, one river water sample, and one well water sample.

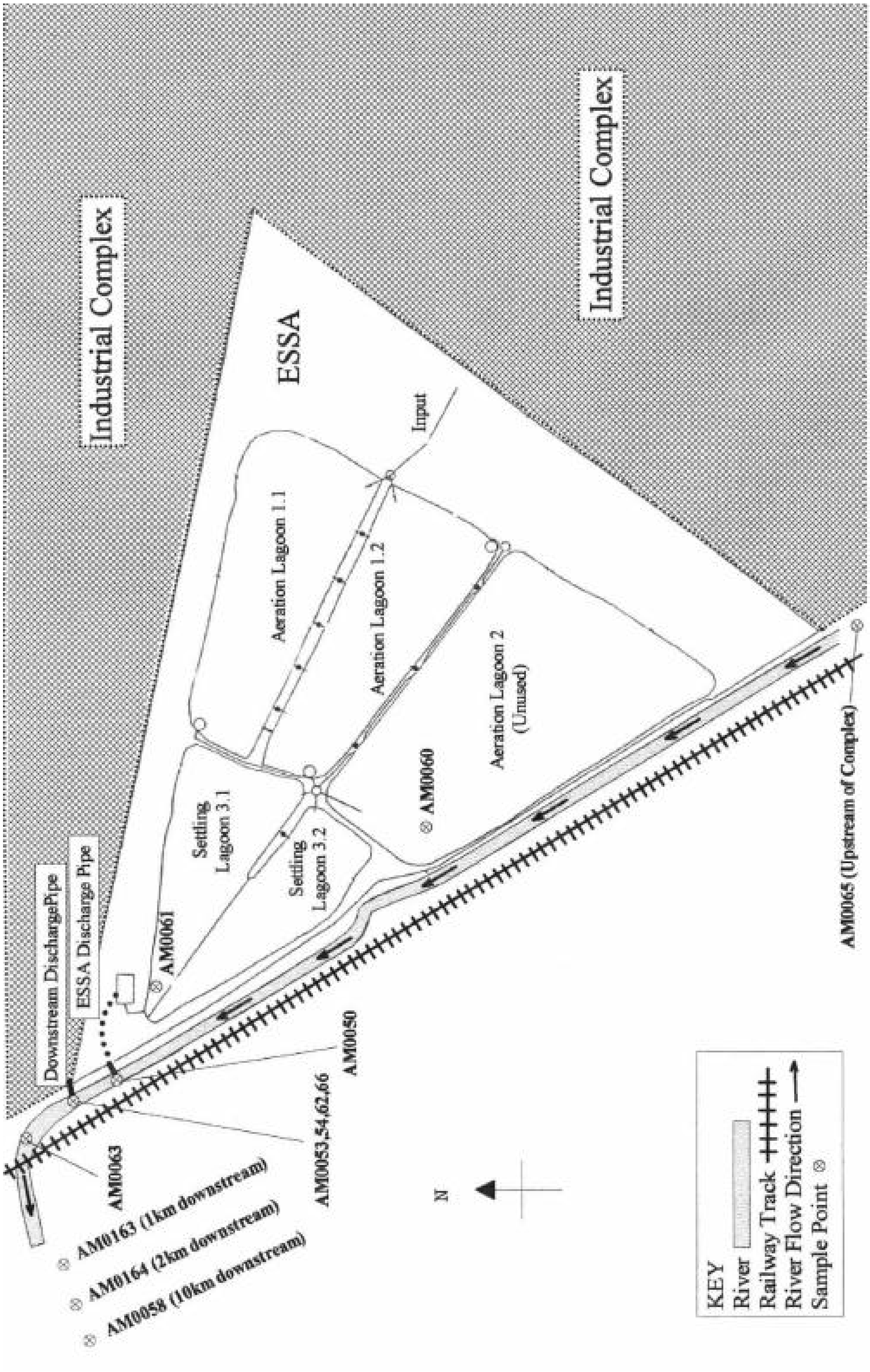

Figure1. Sketch of the ESSA treatment plant and vicinity, the industrial estate in the district of Quilicura, Santiago, Chile 2000.

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/sludge samples were collected in 100ml bottles, and the water samples were collected in 1-litre bottles. All sediment 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.

Sample Number	Sample Description	Sample Location
AM0050	River sediment	The Estero Las Cruces, opposite the ESSA treatment plant discharge pipe
AM0053	River sediment	The Estero Las Cruces, adjacent to the downstream discharge pipe, which bypasses the ESSA treatment plant
AM0055	Industrial wastewater	The downstream discharge pipe, at the point of entry to the Estero Las Cruces, 9th June 2000
AM0058	River sediment	The Estero Las Cruces, at a dairy farm located approximately 10 kilometres downstream of the industrial complex
AM0060	Sludge	The old aeration lagoon (no. 2) of the ESSA treatment plant, unused at the time of sampling
AM0061	Sludge	The new settling lagoon (no. 3.1) of the ESSA treatment plant
AM0062	Industrial wastewater	The downstream discharge pipe, at the point of entry to the Estero Las Cruces, 11th June 2000
AM0063	River sediment	The Estero Las Cruces, approximately 100 metres downstream of the ESSA treatment plant discharge pipe
AM0064	Sediment	A rainwater channel running through the industrial complex
AM0065	River sediment	The Estero Las Cruces, prior to entry to the complex
AM0066	Industrial wastewater	The downstream discharge pipe, at the point of entry to the Estero Las Cruces, July 2000
AM0163	River sediment	The Estero Las Cruces, approximately 1 kilometer downstream of the industrial complex
AM0164	River water	The Estero Las Cruces, approximately 2 kilometres downstream of the industrial complex
AM0165	Well water	A farmyard, approximetely 2 kilometres south of the industrial complex

Table 1. Description of samples collected from the environs of an industrial complex, in the Quilicura district of Santiago, Chile, 2000.

2.2 Sample Descriptions

Two samples of sludge were collected from the ESSA treatment lagoons. One sample (AM0060) was collected from the currently unused aeration lagoon number 2 in order to determine the extent of industrial pollutants that had previously passed through the treatment facility. The second sample (AM0061) was collected from the recently installed settling lagoon number 3.1 to determine the nature of more recent inputs.

Three samples of industrial wastewaters were collected from the downstream discharge pipe on three different days to show the pollutants in the discharge as well as the variation in the composition of the discharges over time. A number of river sediments and one sample of river water were collected from the Estero Las Cruces to show the contamination of the river as a result of the activities at the industrial complex. One sample of river sediment (AM0065) was collected upstream of the industrial complex to distinguish background pollutants in the river from those introduced from the industrial complex.

In addition, a sample of well water (AM0165) was collected from approximately two kilometres south of the industrial complex to determine whether the activities of the complex are affecting the ground water in the vicinity.

3 RESULTS AND DISCUSSION

The results of the organic screen analysis and heavy metals analysis of the samples of ESSA treatment plant sludges and wastewater discharges are presented in Table 2, including a breakdown of the groups of organic compounds reliably identified in the samples. The results for the samples of river sediments, river water and well water are similarly given in Table 4.

For a full list of organic compounds both reliably and tentatively identified in the samples, see Appendix 2. For more information on the common sources, environmental behavior and toxicological outlines for key pollutants detected during this study see Appendices 3 & 4.

3.1 ESSA treatment plant sludges and wastewater discharges

The two samples of sludge collected from the ESSA treatment plant (AM0060 and AM0061) contain a range of organic pollutants, including two organochlorine compounds. Both samples also contain certain potentially toxic metals at significant levels. The three samples of wastewater collected from the downstream pipe at different times (AM0055, AM0062 and AM0066) also contained a number of organic pollutants, although the concentrations of metals in these samples were not of significant magnitude.

Sample number	AM0060	AM0061	AM0055	AM0062	AM0066
Description	Sludge	Sludge	wastewater	wastewater	wastewater
Location	ESSA lagoon no.2	ESSA lagoon no. 3.1	downstream outfall pipe 9th June	downstream outfall pipe 11th June	downstream outfall pipe July
Metals	mg/kg	mg/kg	ug/l	ug/l	ug/l
Cadmium (Cd)	<1	<1	<10	<10	<10
Chromium (Cr)	48	72	<20	<20	<20
Cobalt (Co)	22	11	<20	<20	<20
Copper (Cu)	442	351	<20	73	<20
Lead (Pb)	83	55	<30	<30	<30
Manganese (Mn)	487	467	<10	12	34
Mercury (Hg)	0.31	0.46	<1	<1	<1
Nickel (Ni)	29	45	<20	<20	<20
Zinc (Zn)	1757	2345	<10	<10	48
No. of organic compounds isolated	60	16	5	8	8
No. of organic compounds reliably identified	24 (40%)	6(37%)	2(40%)	5(62%)	2(25%)
ORGANOHALOGEN COMPOUNDS					
Benzene, 1,2-dichloro-	*				
Benzene, 1,4-dichloro-	✓	*	✓	✓	
Benzene, 1,2,4-trichloro-					
PHENOLIC COMPOUNDS					
Phenol, nonyl-					
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	✓			✓	
Phenol, 2,4-bis(1,1-dimethylethyl)-					
POLYAROMATIC HYDROCARBONS					
Naphthalene				✓	
Alkylated naphthalenes	✓(5)				
Fluoranthene					
Pyrene					
ORGANOSULPHUR COMPOUNDS					
Benzothiazole, 2-(methylthio)-					
Dibenzothiophene, 3-ethyl-					
Trisulfide, dimethyl-			✓	✓	
OTHER AROMATIC COMPOUNDS					
Diethyl phthalate					
Bis(2-ethylhexyl) phthalate					
1H-Indole					
1H-Indole, 7-methyl-					
Alkylated biphenyls					
Alkylated benzenes	✓(2)				✓
Benzaldehyde					
ALIPHATIC HYDROCARBONS					
Linear	✓(14)	✓(5)		✓	✓
Cyclic					

Table 2. Organic chemicals and heavy metals identified in samples from the ESSA treatment plant and a wastewater discharge pipe, the industrial complex in the Quilicura district of Santiago, Chile, 2000. For the groups of organic compounds reliably; ✓(#) 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.*

Of the total number of organic compounds identified in these samples, the majority were linear aliphatic hydrocarbons. In addition, the sample of sludge from the old aeration lagoon (AM0060) contained some alkyl benzene and alkyl naphthalene compounds. One sample of wastewater from the downstream discharge pipe also contained naphthalene. All of these compounds are components of crude oils or petroleum products and as such are very common environmental pollutants (Overton 1994; Mackay 1988; Wang & Fingas 1995).

The organochlorine compounds 1,4-dichlorobenzene was identified in both sludge samples (AM0060 and AM0061), although sample AM0061 contained this compound at trace level and it was only possible to detect it only using a SIM method of GC/MS analysis. Its isomer 1,2-dichlorobenzene was also detected in sample AM0060, though again only at trace level. Of the three samples of wastewater collected from the downstream discharge pipe, 1,4-dichlorobenzene was found in two, AM0055 and AM0062.

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 wastes. It is most likely that this is the source of 1,4-dichlorobenzene in this location, 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 is mainly used in degreasing for the metal and automotive industries (Meek *et al.* 1994). However, in light of occurrence of 1,4-dichlorobenzene in the majority of the samples collected from 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 one of the sludge samples (AM0060) and one of the samples of wastewater from the downstream discharge pipe (AM0062). This compound is used as an antioxidant in different products including rubbers and polymer materials (Jobling *et al.* 1995). It is also used as an antiskinning agent in paints, varnishes and other surface finishes, which may explain its presence in the effluent sample AM0062, as it is known that at least two producers of industrial dyes were among the companies permitted to discharge their wastewaters via this pipe until April 2000 (see Introduction).

There is some evidence that BHT can act as a promoter of liver cancer, in combination with carcinogenic substances, through induction of abnormal liver metabolism (Williams & Weisburger 1986).

The absence of 1,2-dichlorobenzene above detection limits, and the lower level of 1,4-dichlorobenzene in the sludge sample AM0061 are possibly due to the changes that were made to the treatment plant three months prior to the collection of the samples. The settling lagoons from where this sample was collected were totally emptied and a fresh liner installed. Since then, insufficient time might have passed for the level of these chlorinated benzenes to reach the levels found in the sludge collected from the old aeration lagoon no. 2 (AM0060). A similar picture can been seen for BHT, and in the number of linear aliphatic hydrocarbons and alkyl benzene and alkyl naphthalene compounds.

A volatile sulfur-containing compound, dimethyl trisulfide, was detected in two of the combined untreated industrial effluent samples (AM0055 and AM0062). This compound is commonly found as a product of microbial activity in different food products and vegetables, both in the non-inoculated and cultured yeast media (Wilkins 1996). As was mentioned in the Introduction, a yeast producing company Gist Brocades S.A. were discharging wastewaters via this outfall at the time of sampling, and therefore the wastewaters from this company are the probable source of dimethyl trisulfide.

The two samples of sludge (AM0060-61) contained a number of metals at significant levels, including copper, lead, manganese and zinc. For comparison, typical levels of metals in sewage sludges are given in Table 3. It should be noted, however, that the higher values quoted in this table may be due to sludges from treatment facilities that receive both domestic and industrial wastes.

Of the metals analysed for, zinc was present in both sewage sludge samples at the highest concentration; 1757 and 2345 mg/kg for samples AM0060 and AM0061 respectively. While these levels are in the range generally found in sludge from municipal sewage works as outlined in Table 3, they are higher than levels found in sludges from rural sewage works. This would suggest that the ESSA treatment plant may be receiving inputs of zinc from industrial sources.

In the aquatic environment zinc will predominantly bind to suspended material before finally accumulating in the sediment (USPHS 1997, Bryan and Langston 1992, Alloway 1990). Thus the higher level of zinc in the sludge collected from the recently installed settling lagoon 3.1 (AM0061) compared with the sludge from the older lagoon 2 (AM0060) indicates that the ESSA treatment facility is receiving fresh inputs of zinc. As zinc is one of the most extensively utilised “trace” metals (Nriagu 1990), it is not possible to identify the source or sources of zinc to the ESSA plant.

The two sludge samples AM0060 and AM0061 also contained copper and manganese in the ranges 351-442 and 467-487 mg/kg respectively. For both metals, the highest value was found in the sample of sludge form the old aeration lagoon 2 (AM0060). This variation indicates the accumulation of these metals in the sludges over time. The levels found are within the range typically found in sludge from a range of municipal sewage works, including rural locations for copper (see Table 3). Consequently, it seems unlikely that significant industrial inputs of copper and manganese are passing through the ESSA treatment facility.

Metal	Source	Concentration (mg/kg dw)	Reference
Copper	Rural sewage plants (Australia) Compilation of data from a large number of sewage plants	578-1318 50-8000	Lottermoser 1995 Alloway 1991
Manganese	Compilation of data from a large number of sewage plants	60-3900	Alloway 1991
Mercury	Compilation of data from a large number of sewage plants	0.1-55	Alloway 1991
Lead	Rural sewage plants (Australia) Compilation of data from a large number of sewage plants	76-180 29-3600	Lottermoser 1995 Alloway 1991
Zinc	Rural sewage plants (Australia) Compilation of data from a large number of sewage plants	506-1409 91-4900	Lottermoser 1995 Alloway 1991

Table 3. Typical concentrations of heavy metals in sewage sludges.

The sludges also contained lead at 83 and 55 mg/kg for AM0060 and AM0061 respectively. As for copper and manganese, the higher level of lead in AM0060 indicates accumulation over time. While these levels of lead are well within the typical levels found in sewage sludges (see Table 3), a sample of well water collected close to the industrial complex contained lead at a significant level, suggesting that discharges of lead from industrial sources may be affecting the local environment. This is further discussed in Section 4.2.

Copper, manganese and zinc were also detected in two of the samples of wastewater collected from the downstream discharge pipe (AM0062 and AM0066). The highest levels of these metals detected were 73, 34 and 48 ug/l for copper, manganese and zinc respectively. The typical background levels for these metals in freshwater are up to 20ug/l for copper (Mance *et al.* 1984), 12 ug/l for manganese (Bowen, 1966), and up to 50 ug/l zinc (USPHS 1997), though these figures are subject to local variations.

The level of zinc was below that of typical freshwater levels, and while the levels of copper and manganese were above typical freshwater levels this may to be due to regional variations than due to the discharge from industrial sources.

4.2 River water and sediments and well water

The seven samples of river sediments collected from the Estero las Cruces (AM0050, 53, 58, 63, 64, 65 and AM0163) contained a range of organic pollutants, many of which were also identified in the sludge samples from the ESSA treatment facility (AM0060-61). A number of samples also contained certain potentially toxic metals at significant levels.

Sample number	AM0065	AM0050	AM0053	AM0063	AM0163	AM0058	AM0064	AM0164	AM0165
Description	sediment	sediment	sediment	sediment	sediment	sediment	sediment	riverwater	wellwater
Location	up-stream of the complex	opposite the ESSA outfall pipe	by the down-stream outfall pipe	approx. 100m down-stream of ESSA	approx. 1km down-stream	approx. 10km down-stream	channel running through complex	approx. 2km down-stream	approx. 2km from complex
Metals	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	ug/l	ug/l
Cadmium (Cd)	<1	<1	<1	<1	<1	<1	<1	<10	<10
Chromium (Cr)	15	32	31	36	20	26	20	28	<20
Cobalt (Co)	23	24	25	23	21	24	18	<20	<20
Copper (Cu)	320	412	198	253	201	216	88	48	20
Lead (Pb)	27	62	22	70	24	26	24	<30	50
Manganese (Mn)	925	1024	2280	925	802	893	728	64	22
Mercury (Hg)	0.13	0.97	0.37	0.18	0.10	0.18	<0.10	<1	<1
Nickel (Ni)	13	24	25	26	16	18	13	<20	<20
Zinc (Zn)	136	180	127	231	158	160	188	34	13
No. of organic compounds isolated	16	50	22	11	23	25	26	7	3
No. of organic compounds reliably identified	4(25%)	11(22%)	4(18%)	6(54%)	5(22%)	6(24%)	19(73%)	4(54%)	1(33%)
ORGANOHALOGEN COMPOUNDS									
Benzene, 1,2-dichloro-									
Benzene, 1,4-dichloro-	*	✓	✓	*		*			
Benzene, 1,2,4-trichloro-		*							
PHENOLIC COMPOUNDS									
Phenol, nonyl-					✓				
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-			✓						
Phenol, 2,4-bis(1,1-dimethylethyl)-			✓						
POLYAROMATIC HYDROCARBONS									
Naphtahalene		✓							
Alkylated naphthalenes									
Fluoranthene		✓							
Pyrene		✓							
ORGANOSULPHUR COMPOUNDS									
Benzothiazole,2-(methylthio)-								✓	
Dibenzothiophene, 3-ethyl-					✓				
Trisulfide, dimethyl-								✓	
OTHER AROMATIC COMPOUNDS									
Diethyl phthalate									✓
Bis(2-ethylhexyl) phthalate					✓				
1H-Indole								✓	
1H-Indole, 7-methyl-								✓	
Alkylated biphenyls				✓(2)		✓(2)			
Alkylated benzenes						✓	✓		
Benzaldehyde					✓				
ALIPHATIC HYDROCARBONS									
Linear	✓(3)	✓(6)		✓(3)	✓	✓(2)	✓(16)		
Cyclic			✓				✓(2)		

*Table 4 Organic chemicals and heavy metals identified in samples collected from the Estero las Cruces and a nearby well, the industrial complex in the Quilicura district of Santiago, Chile, 2000. For the groups of organic compounds reliably; ✓(#) 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.*

A sample of river sediment collected from upstream of the complex (AM0065) contained only four organic compounds that could be identified, of which three were linear hydrocarbons. 1,4-dichlorobenzene was also identified, though at trace level only using SIM method of GC/MS analysis. The presence of 1,4-dichlorobenzene and a number of hydrocarbons, both linear and cyclic, were detected in the majority of river sediment samples. Significant levels of hydrocarbons were found only in the sediment sample AM0064 (collected from the rainwater channel running though the industrial complex) and, to a lesser extend, in the river sediment sample AM0050 (collected in the vicinity of untreated effluent discharge). The possible sources of these common pollutants are discussed above, in section 4.1.

The only additional organochlorine compound identified in the river sediments was 1,2,4-trichlorobenzene, which was identified at a trace level in the sediment sample collected opposite the ESSA discharge pipe (AM0050). 1,2,4-trichlorobenzene is used as a solvent, in dielectric fluids and as an intermediate in organic synthesis. In general, chlorinated benzenes are introduced into environment with manufacturing effluents and leachates from chemical waste dumps (Howard 1989). In light of the widespread contamination of the local environment with 1,4-dichlorobenzene, however, the presence of 1,2,4-trichlorobenzene may be due to its presence as a contaminant in 1,4-dichlorobenzene used to prepare sanitary deodorant products.

The sample of river sediment collected upstream of the industrial complex (AM0065) also contained zinc and copper at levels above the typical background levels of up to 100mg/kg for zinc (USPHS 1997, Salomons and Forstner 1984) and 45-50 mg/kg for copper (Salomons and Forstner 1984). The elevated level of these metals may be due to either regional variations in background levels or mining activities in the catchment area for this river (Schalscha 1998). The levels of lead and mercury in this sample were in agreement with average background levels for these metals in freshwater sediments; 20-30mg/kg for lead (USPHS 1997) and 0.2-0.35 mg/kg for mercury (Salomons and Forstner 1984).

The sample of sediment collected from opposite the ESSA discharge pipe (AM0050) contained three polyaromatic hydrocarbons (PAH's); naphthalene, fluoranthene and pyrene. None of these compounds were identified in any of the other samples of river sediment nor in the sewage sludge samples. Naphthalene was identified in one of the samples of wastewater from the downstream discharge pipe (AM0062). As discussed in section 4.1, these compounds are components of crude oils or petroleum products and as such are very common environmental pollutants.

Due to the absence of these PAH compounds in the sewage sludge samples, it is unlikely that the ESSA treatment plant is a source of these compounds. As mentioned in the introduction, three months prior to the collection of the samples a new discharge pipe for the ESSA plant was installed on the banks of the Estero las Cruces, involving considerable disturbance to the river bank at this location. The presence of the PAH compounds in the river sediment at this location may be due to this disturbance.

Of all the river sediment samples collected, AM0050 was the only sample that contained mercury at a significant level, 0.97 mg/kg. This level is slightly elevated over typical background levels for mercury which are generally 0.2-0.35 mg/kg in freshwater sediments (Salomons and Forstner 1984) and 0.02-0.625 mg/kg in soil (Alloway 1990, WHO 1989). The recent disturbance to the river bank is a possible reasons for this local variation.

The sample of sediment collected adjacent to the downstream discharge pipe (AM0053) contained 2,6-bis(1,1-dimethylethyl)-4-methylphenol, also known as butylated hydroxytoluene (BHT). While this compound was not identified in other river sediment samples, it was identified in one of the sludge samples (AM0060) and in one of the wastewater discharge samples from the downstream pipe (AM0062). The presence of BHT in the river sediment AM0053 is clearly a result of these two discharges. The uses and possible sources of BHT are discussed in section 4.1.

A similar compound, 2,6-bis(1,1-dimethylethyl)-phenol, was also identified in the sediment at this location (AM0053). This compound was not identified in any of the other samples collected, and no information is available on the possible sources of this compound.

The levels of zinc in all the river sediment samples collected were in the range 127-231 mg/kg, including a sample collected upstream of the industrial complex (AM0065) with a level of 136 mg/kg. While a slight increase in the level of zinc is found in the river sediments in the vicinity of the two discharge pipes, the highest level of 231 mg/kg in sample AM0063 is less than twice that found in the sediment upstream of the complex, AM0065. In addition, the level of zinc in river water collected approximately two kilometres downstream of the complex (AM0164) was 34 ug/l. Zinc is typically found in uncontaminated freshwater at below 50ug/l (USPHS 1997).

The levels of copper found in the samples of river sediments were in the range 198-412 mg/kg dry weight, with 320 mg/kg in the sample collected upstream of the industrial complex (AM0065). Only one river sediment (AM0050) contained copper at a level above that found in sample AM0065, and then only at a very slightly elevated level of 412 mg/kg. This elevation may be due to the disruption to the riverbank at this location, as described above.

Despite the relatively high levels of zinc and copper in the ESSA sludge samples, there does not appear to be significant contamination by these metals of the Estero las Cruces in the vicinity.

Two of the river sediment samples collected from the vicinity of the two discharge pipes, AM0050 and AM0053, contained manganese at 1024 and 2280 mg/kg respectively. These levels are above those found in other sediment samples from the Estero las Cruces, which contained manganese in 728-925 mg/kg, the highest value being from a sediment collected upstream of the industrial complex (AM0065). The three wastewater samples collected from the downstream discharge pipe (AM0055, 62, 66) did not contain manganese at significant levels. While there are clearly variations in the content of the discharge from this pipe, the levels found would indicate that this is not a significant source of manganese.

The levels of manganese in the two sludge samples AM0060 and AM0061 were below 500 mg/kg, significantly lower than those of all the river sediments. The relatively low levels of manganese in the sludge samples suggests that the ESSA plant does not receive industrial discharges containing significant levels of manganese. It seems unlikely that the elevated levels of manganese in the sediments AM0050 and AM0053 are as a result of discharges from the ESSA plant. This local elevation may be as a result of the recent disruption to the river banks as described above.

A sample of river sediment (AM0163) collected approximately one kilometre downstream of the industrial complex, and a sample of river water (AM0164) collected approximately one kilometre further downstream, contained a number of organic compounds that were not identified in other samples.

In the river sediment AM0163, the persistent chemical nonylphenol (NP) was reliably identified. This compound has been found to affect the estrogenic hormone system and impair sperm production in fish (Jobling *et al.* 1996). Its presence in the freshwater environment results principally from the breakdown of the industrial detergents nonylphenol polyethoxylates (NPEs), and from use as a spreading agent in pesticides. Laboratory experiments have shown that nonyl phenol is toxic to aquatic organisms, particularly to fish (Liber *et al* 1999), and to plant cells (Bokern & Harms 1997).

A phthalate ester, bis(2-ethylhexyl) phthalate (DEHP), was also reliably identified in the river sediment sample AM0163. This chemical is a well known environmental contaminant that has been widely used as a plasticiser (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).

In addition, 3-ethyl dibenzothiphene, an organosulphur compound was identified in this river sediment. This compound is a component of crude oils or petroleum products (Overton 1994; Mackay 1988; Wang & Fingas 1995).

A derivative of benzothiazole, 2-(methylthio)benzothiazole, was detected in the river water sample AM0164. Benzothiazoles are widely used as corrosion inhibitors, especially in petroleum products (Jinturkar *et al.* 1998; Ammeloot *et al.* 1997; Dragun 1988). 2-(methylthio) benzothiazole has also been reported as an important break-down products of the fungicide 2-(thiocyanomethylthio)benzothiazole (Reemtsma *et al.* 1995), widely used in wood-products and in leather production. Alternatively, the benzothiazole derivative identified in this sample may have arisen as a result of discharge from the industries manufacturing or using benzothiazole-based dyes (Archibald and Roy-Arcand 1997). It is unclear as to the source or sources of these compounds to the Estero Las Cruces, and this clearly needs further investigation.

The river water sample AM0164 also contained the volatile sulfur-containing compound, dimethyl trisulfide, which was detected in two of the combined untreated industrial effluent samples (AM0055 and AM0062). The presence of this compound in the river water is clearly as a result of discharges from the downstream pipe. The possible source of this compound is discussed in section 4.1

One samples of river sediment collected approximately 10 kilometres downstream of the complex (AM0058), and a sample of sediment from a rainwater channel running through the complex (AM0064) contains some alkyl benzene compounds. These compounds were not identified in any of the upstream river sediment samples. As discussed in section 4.1, these common environmental pollutants are components of crude oils or petroleum products (Overton 1994; Mackay 1988; Wang & Fingas 1995).

The sample of well water (AM0165) collected approximately 2 kilometres from the industrial complex contained only one organic compound that could be reliably identified, the phthalate ester diethyl phthalate (DEP). Numerous uses of DEP have been reported, including use in cosmetics, as a concrete additive, and as a solvent for perfume oils (ATSDR 1997; Jobling *et al.* 1995). A possible explanation of the presence of DEP in well water may be from its use as an additive to the well concrete.

This sample of well water also contained lead at 50ug/l. The average concentration of lead in freshwater is 3.9 ug/l, although this figure is subject to region variations (USPHS 1997). The World Health Organisation currently recommends a limit of 10 ug/l for drinking water (WHO 1993). The sample of river water collected downstream of the complex (AM0164) did not contain lead above 30ug/l.

Lead has no known, nutrition, biochemical or physiological function (Goyer 1996). The ingestion of lead by humans has been associated with a wide range of adverse effects, including nervous system disorders, anaemia and decreased haemoglobin synthesis, cardiovascular disease, and disorders in bone metabolism, renal function and reproduction. Of particular concern, is the effect of relatively low exposure on cognitive and behavioural development in children (Pirkle *et al.* 1998, USPHS 1997, Bernard *et al.* 1995, Goyer 1993, Nriagu 1988).

Lead is also toxic to all aquatic biota, and even though it is not considered one of the most environmentally mobile of metals, there is still appreciable evidence showing the bioavailability of sediment-bound lead to deposit feeding species (Bryan & Langston 1992). For more information on the behaviour and toxicology of lead, see Appendix 4.

Two samples of river sediment collected in the vicinity of the ESSA treatment plant contained lead at 62 and 70 mg/kg for the samples AM0050 and AM0063 respectively. The level of lead in all other river sediments collected were in the range 24-27 mg/kg including a sediment collected upstream of the complex. Levels of lead in freshwater sediments are generally in the range 20-30mg/kg (USPHS 1997).

While the level of lead in the treatment plant sludge samples AM0060 and AM0061 was not excessively high, the elevated levels in the river sediments in the vicinity and presence of lead at this level in the well water suggests that activities within the industrial complex may be introducing lead to the local environment. It is, however, not possible to rule out other sources of lead to the well water such as the presence of lead piping. The wastewater discharge samples (AM0055, AM0062 & AM0066) did not contain lead above detection limits, and as such this is an unlikely source of the local lead contamination. More information on discharges of lead to the environment from this industrial complex is required.

In all the samples collected, the levels of cadmium, chromium, cobalt, and nickel were below general background levels.

4 CONCLUSIONS

A range of organic pollutants were found in the Estero Las Cruces that were not detected upstream of the industrial complex. It seems likely that the presence of many of these compounds is as a result of activities within the complex. A number of these compounds were also detected in either the sludges of the ESSA treatment facility of in the wastewater discharge from the downstream pipe, such as butylated hydroxytoluene, BHT. The presence of these compounds, and the levels of certain metals in the sludge samples suggests that industrial wastewaters may be passing through the ESSA treatment facility.

The sediment samples from the Estero Las Cruces in the vicinity of the complex show somewhat elevated levels of certain metals, including lead and zinc. While it is not possible to conclusively pinpoint the sources of these metals, the elevated levels may be as a result of activities within the complex.

A number of organic compound of concern were detected in the Estero Las Cruces within the industrial complex that were not detected in either the ESSA treatment plant sludges nor in the wastewaters from the downstream discharge pipe. These include the organochlorine 1,2,4-trichlorobenzene and a number of polyaromatic hydrocarbons. Additional organic compound were found in the Estero Las Cruces downstream of the industrial complex, including the toxic and hormone disrupting chemicals nonyl phenol and bis(2-ethylhexyl) phthalate (DEHP). The exact sources of these chemicals to the local environment is not clear, and more information as to the chemicals used and wastes produced at plants within the complex must be made available.

While the level of pollutants within the three samples collected from the downstream discharge pipe was not significantly high, the composition of the discharge from this pipe has been shown to vary over time. As such, it is possible that addition compound to those detected are discharged via this pipe at other times.

In addition, a sample of well water collected from a farm approximately 2 kilometres from the industrial complex contained lead at a significant level. While the precise source of this contamination to the ground water is not clear, it is possible that it is due to activities within the complex.

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APPENDIX 1 ANALYTICAL METHODOLOGY

A.1 Organic analysis

A.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 105^0C, and rinsed three times with low haloform pentane.

A.1.2 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.1.3 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.1.4 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.

Compound	**Ions to monitor**
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.2 Heavy Metal Analysis

A.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.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.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 thgis 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.

A.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). 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 samples (i.e. in 15% v/v hydrochloric acid and 5% v/v nitric acid). 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

LIST OF COMPOUNDS RELIABLY IDENTIFIED AND GROUPS OF COMPOUNDS TENTATIVELY IDENTIFIED IN THE SAMPLES. * - COMPOUNDS IDENTIFIED ONLY AT TRACE LEVELS USING SELECTIVE ION MONITORING (SIM) METHOD

Sample Number: AM0050	Sample Number: AM0053	Sample Number: AM0055	Sample Number: AM0058	Sample Number: AM0060	Sample Number: AM0061	Sample Number: AM0062
Number of Compounds isolated:50	Number of compounds isolated:22	Number of compounds isolated:5	Number of compounds isolated:25	Number of compounds isolated:60	Number of compounds isolated:16	Number of compounds isolated:8
COMPOUNDS RELIABLY IDENTIFIED: Benzene, 1,2,4-trichloro- * Benzene, 1,4-dichloro- Docosane Eicosane Fluoranthene Hexadecane Naphthalene Pentadecane Pyrene Tricosane Undecane GROUPS OF COMPOUNDS TENTATIVELY IDENTIFIED: Aliphatic hydrocarbons Chlorinated toluene	COMPOUNDS RELIABLY IDENTIFIED: Benzene, 1,4-dichloro- Phenol, 2,4-bis(1,1-dimethylethyl)- Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl- trans-Caryophyllene GROUPS OF COMPOUNDS TENTATIVELY IDENTIFIED : Aliphatic hydrocarbons Alkylated phenol	COMPOUNDS RELIABLY IDENTIFIED: Benzene, 1,4-dichloro- Trisulfide, dimethyl- COMPOUNDS TENTATIVELY IDENTIFIED : Benzaldehyde	COMPOUNDS RELIABLY IDENTIFIED: 1,1'-Biphenyl, 2,2'-diethyl- 1,1'-Biphenyl, 3,4-diethyl- Benzene, 1,2-dimethyl-4-(phenylmethyl)- Benzene, 1,4-dichloro- * Eicosane Heptadecane, 8-methyl- GROUPS OF COMPOUNDS TENTATIVELY IDENTIFIED : Alkylated benzene Alkylated cyclopentadiene Alkylated dibenzothiophenes Aliphatic hydrocarbons	COMPOUNDS RELIABLY IDENTIFIED: Benzene, 1-methyl-2-(4-methylphenoxy)- Benzene, 1-methyl-3-(4-methylphenoxy)- Benzene, 1,2-dichloro- * Benzene, 1,4-dichloro- Decane Docosane Eicosane Hexadecane Hexadecane, 2,6,10,14-tetramethyl- Naphthalene, 1,4,5-trimethyl- Naphthalene, 1,5-dimethyl- Naphthalene, 1-methyl- Naphthalene, 2,6-dimethyl- Naphthalene, 2,7-dimethyl- Nonadecane Octadecane Pentacosane Pentadecane Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl- Tetracosane Tetradecane Tricosane Tridecane Undecane GROUPS OF COMPOUNDS TENTATIVELY IDENTIFIED : Alkylated dibenzothiophenes Aliphatic hydrocarbons Alkylated benzenes	COMPOUNDS RELIABLY IDENTIFIED: Benzene, 1,4-dichloro- * Docosane Octadecane Pentadecane Tetracosane Tetradecane GROUPS OF COMPOUNDS TENTATIVELY IDENTIFIED : Aliphatic hydrocarbons	COMPOUNDS RELIABLY IDENTIFIED: Benzene, 1,4-dichloro- Naphthalene Pentadecane Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl- Trisulfide, dimethyl- COMPOUNDS TENTATIVELY IDENTIFIED : Benzaldehyde

Sample Number: AM0063	Sample Number: AM0064	Sample Number: AM0065	Sample Number: AM0066	Sample Number: AM0163	Sample Number: AM0164	Sample Number: AM0165
Number of Compounds isolated:11	Number of compounds isolated:26	Number of compounds isolated:16	Number of compounds isolated:8	Number of compounds isolated:23	Number of compounds isolated:7	Number of compounds isolated:3
COMPOUNDS RELIABLY IDENTIFIED: 1,1'-Biphenyl, 2,2'-diethyl- Tetracosahexaene, 2,6,10,15,19,23-hexamethyl- Benzene, 1,2-dimethyl-4-(phenylmethyl)- Benzene, 1,4-dichloro-* Eicosane Pentadecane COMPOUNDS TENTATIVELY IDENTIFIED: 1,1'-Biphenyl, 3,4-diethyl-	COMPOUNDS RELIABLY IDENTIFIED: .beta.-Caryophyllene Benzene, 1-methyl-2-(1-methylethyl)- Camphene Docosane Eicosane Heneicosane Heptadecane Heptadecane, 3-methyl- Hexadecane Hexadecane, 2,6,10,14-tetramethyl- Nonadecane Octadecane Pentacosane Pentadecane Pentadecane, 2,6,10,14-tetramethyl- Tetracosane Tetradecane Tricosane Tridecane COMPOUNDS TENTATIVELY IDENTIFIED : Dodecane, 2,6,10-trimethyl- Hexane, 3,3-dimethyl-	COMPOUNDS RELIABLY IDENTIFIED: Benzene, 1,4-dichloro-* Dodecane Pentadecane Undecane COMPOUNDS TENTATIVELY IDENTIFIED : Octane, 5-ethyl-2-methyl- Tridecane, 3-methyl-	COMPOUNDS RELIABLY IDENTIFIED: Pentadecane Styrene COMPOUNDS TENTATIVELY IDENTIFIED : Benzaldehyde Undecane, 4,7-dimethyl- Undecane, 3,9-dimethyl-	COMPOUNDS RELIABLY IDENTIFIED: 1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester 1-Hexadecanol 3-Ethyldibenzothiophene Benzaldehyde Phenol, nonyl- COMPOUNDS TENTATIVELY IDENTIFIED : 1-Ethyldibenzothiophene 2-Ethyldibenzothiophene 7-Hexadecene, (Z)- Eicosane Heptacosane Heptane, 2,4-dimethyl- Hexadecane Octadecane Tetradecane Undecane, 3,9-dimethyl- Undecane, 4,7-dimethyl-	COMPOUNDS RELIABLY IDENTIFIED: 1H-Indole 1H-Indole, 7-methyl- Benzothiazole, 2-(methylthio)- Trisulfide, dimethyl COMPOUNDS TENTATIVELY IDENTIFIED : None	COMPOUNDS RELIABLY IDENTIFIED: 1,2-Benzenedicarboxylic acid, diethyl ester COMPOUNDS TENTATIVELY IDENTIFIED : None

APPENDIX 3 TOXICOLOGICAL OUTLINES FOR KEY ORGANIC COMPOUNDS

A.3.1 Chlorinated benzenes

The production of chlorinated benzenes is a multiple product operation achieved by direct chlorination of benzene in the liquid phase using a ferric chloride catalyst. Only limited control can be exerted over the final product mix. The distillation train used for separating the mixture has a limited resolving power and the distillates are always mixtures of close boiling isomers which can be further separated by crystallisation (see eg Bryant 1993). Distillation also gives rise to chlorinated tars.

12 chlorinated benzenes are possible, with substitution patterns as follows:

1 chlorine	monochlorobenzene,
2 chlorines	1,2-di-, 1,3-di- and 1,4-dichlorobenzenes
3 chlorines	1,2,3-tri-, 1,2,4-tri- and 1,3,5-trichlorobenzenes
4 chlorines	1,2,3,4-tetra-, 1,2,3,5,-tetra- and 1,2,4,5-tetrachlorobenzenes
5 chlorines	Pentachlorobenzene
6 chlorines	hexachlorobenzene.

Both technological changes and environmental concerns have severely affected the production of chlorobenzenes; today only monochlorobenzene and 1,2- and 1,4-dichlorobenzenes are manufactured in large quantities. These are often produced together, with the economically optimised reaction yielding approximately 85% monochlorobenzene, 10% 1,4-dichlorobenzene and 5% 1,2-dichlorobenzene. Monochlorobenzene yield can be increased to 90% by careful monitoring of the reaction mix density and recycling of unreacted benzene, but total elimination of dichlorobenzene formation is not economical. Should the primary interest be in the para- isomer, yield may be increased by use of a selective catalyst, or the mix can be further chlorinated to produce a mixture of 1,4-dichlorobenzene and 1,2,4-trichlorobenzene. These two products can easily be separated by distillation (Bryant 1993, CEC 1986).

A.3.1.1 Mono- and di-chlorobenzenes.

Chlorobenzene, 1,2-dichlorobenzene and 1,3-dichlorobenzene are colourless liquids; 1,4-dichlorobenzene forms colourless crystals at room temperature (Ware 1988a & b).

One of the earliest uses of chlorobenzene was as an intermediate for the explosive picric acid during the first World War (CEC 1986). It is used as a solvent and as an intermediate in chemical synthesis. In the US in the 1980s, the predominant use was for the production of ortho- and para-chlorobenzenes. Theses are used as intermediates for rubber chemicals, antioxidants, dyes and pigments, pharmaceuticals and agricultural chemicals. The fungicide benomyl, and carbofuran and the parathion group of insecticides are all derived from chlorobenzene. One previously important use was in the manufacture of DDT. Chlorobenzene production has fallen due to the development of other routes to aniline and phenol and the restriction of DDT use. By various routes, chlorobenzene is also used for the manufacture of specialty silicones, Grignard reagents and catalysts (Bryant 1993). Release to the environment is expected to derive from its use as a solvent, either through fugitive emissions or volatilisation from pesticides for which it used as a carrier. Thus, inhalation is thought to be a major route of exposure for humans since it is rarely if ever found in food. It bioaccumulates in algae, fish and aquatic invertebrates. Mammalian metabolites are reported to be p-chlorophenol, p-chlorocatechol and p-chlorophenyl mercapturic acid. Human exposure causes CNS depression and respiratory tract irritation and animal studies have reported liver necrosis, renal toxicity and effects on the pancreas, blood and lymph and adrenal glands (Ware 1988a, Meek *et al.* 1994a). Canada has derived a TDI of 8.1ug/kg body weight/day; estimated exposures (0.05-0.14ug/kg/day) are considerably lower than this (Meek *et al.* 1994a).

Ware (1988b) reports human symptoms after exposure to DCBs, but does not distinguish between isomers. Effects reported are anaemia, skin lesions, vomiting, headaches, eye and respiratory tract irritation, anorexia, weight loss, yellow atrophy of the liver, blood dyscrasias, porphyria, and chromosomal breaks in blood samples. Animal experiments recorded liver and kidney damage to be the most frequent effects, though high doses caused CNS perturbation and death through respiratory depression. The dichlorobenzenes are bioaccumulative in algae, aquatic invertebrates and fish (Ware 1988b). All three have also been reportedly found in blood (Ware 1988b).

1,2-Dichlorobenzene is produced unavoidably in the production of monochlorobenzene, but it is also possible to maximise dichlorobenzene production to 98% of the reaction mixture using suitable catalysts or alternative production methods leading to specific isomers. It is used mainly in the production of dyes and pesticides after conversion to 1,2-dichloro- 4-nitrobenzene or dichloroaniline. Other uses include the solvent phase in the production of toluene di-isocyantes, production of deodorants and disinfectants and on a small scale as a heat transfer fluid. According to Meek *et al.* (1994b), the largest use is in degreasing for the metal and automotive industries.

Exposed laboratory animals exhibited hepatic, renal and haematological effects as well as lymphoid depletion of the thymus and spleen and multifocal mineralisation of both muscular and heart muscles (Ware 1988b, Meek *et al.* 1994b). Developmental toxicity was only observed at concentrations which were overtly toxic to the mother. Human toxicity data are sparse, but chromosomal aberrations, anaemia and leukemia have been reported (Meek *et al.* 1994b). Mammals metabolise 1,2-dichlorobenzene to phenols, catechols, most of which are excreted after conjugation with glucoronic or sulphuric acids. Mercapturic acids may also be produced. The primary metabolites in humans are conjugated phenols (Ware 1988b). 1,2-dichlorobenzene is found in air, food, breast milk and drinking water (Meek *et al.* 1994b). It is also toxic to higher plants, inducing abnormal mitosis (cell division) in onions (Ware 1988b).

1,3-Dichlorobenzene is growing in importance as a starting product in the manufacture of dyes, pesticides and pharmaceuticals. However, this has not yet reached commercial importance. There are some other small, specialised uses, but larger markets have not been developed, mainly because 1,3-dichlorobenzene only occurs as a minor constituent (approx 1%) of the technical dichlorobenzene reaction mix, and to produce it by other routes is expensive (Bryant 1993). Mammalian (and human) metabolism is as for 1,2-dichorobenzene above, but generally little is known about this 1,3-dichlorobenzene in comparison to the more commercially important dichlorobenzenes.

1,4-Dichlorobenzene (p-dichlorobenzene) is used largely in the production of deodorant blocks and room deodorants. It is also used as a moth control agent, as an insecticide and an intermediate for production of insecticides and dyes. An emerging market is in the manufacture of poly(phenylene sulphide) resin (PPS), and minor uses are as a germicide, fungicideand extreme pressure lubricant (Bryant 1993, CEC 1986). 1,4-dichlorobenzene is not spontaneously combustible and does not assist fire, but it is flammable nevertheless. It may be absorbed both through the inhalation of vapours, through the skin and though consumption of contaminated food. Human symptoms include damage to the liver, kidneys and lungs. Accidental poisoning of children, presumably who have eaten moth repellant was widespread in the 1970s (CEC 1986). Once absorbed, 1,4-dichlorobenzene is stored in the adipose tissue, and has been detected in human samples (CEC 1986, Ware 1988b). The metabolism of 1,4-dichlorobenzene by mammals varies from that of the other two isomers in that mercapturic acids are not formed. 1,4-dichlorobenzene causes abnormal mitosis in higher plants. 1,4-Dichlorobenzene has been reported in human adipose tissue, as well as in blood (Ware 1988b).

A.3.1.2 Trichlorobenzenes

1,2,3- and 1,2,4-trichlorobenzene have been produced from the dehydrohalogenation of the unwanted isomers of the production of the pesticide 1,2,3,4,5,6-hexachlorocyclohexane. This is of limited application.

Environmental regulations have curbed the use and discharge of trichlorobenzenes to the environment, as least in Europe and the USA (Harper *et al.* 1992, Bryant 1993). Not surprisingly, therefore, little research appears to have been carried out in comparison with some other chlorobenzenes.

The general human population would probably receive their greatest exposure to trichlorobenzenes through inhalation. The toxicity of all three appear similar; they damage the liver, kidney and thyroid. There is some indication of slight fetotoxicity at high doses. There is little evidence of mutagenicity and too few data are available for the trichlorobenzenes to given a carcinogenicity classification (Giddings *et al.* 1994a). All three isomers are toxic to phytoplankton (Sicko-Goad *et al.* 1989a-d, Sicko-Goad & Andresen 1993a & b).

1,2,3-trichlorobenzene has been detected in air, drinking water, food and breast milk (Giddings *et al.* 1994a) as well as industrially polluted surface waters (Harper *et al.* 1992) and sediment (Labunska *et al.* 1998), though it was not found in human adipose tissue from Canada (Hermanson *et al.* 1997). Little is known about its toxicity other than its ability to damage the liver, kidney and thyroid (Giddings *et al.* 1994a).

More information is available about 1,2,4-trichlorobenzene. According to Giddings et al. (1994a), only 1,2,4-trichlorobenzene has industrial application in Canada. It is imported for solvent and intermediate use. Environmental releases come from industrial discharges and from spillage of dielectric fluids. As mentioned above, it is toxic to the liver, thyroid and kidney. Liver and kidney weights and porphyrin excretion increase. In some studies, more severe liver damage has occurred, including necrotic and non-necrotic degeneration. 1,2,4-trichlorobenzene may be found in all environmental media, though there is insufficient analytical data to tell how widespread contamination is and it was not found in human adipose tissue from Canada (Hermanson et al. 1997).

Giddings et al. (1994a) report 1,3,5-trichlorobenzene air, drinking water, food, breast milk, though it was not found in human adipose tissue from Canada (Hermanson et al. 1997). It can be found in association with industrial operations (Harper et al. 1992).

A.3.1.3 Tetrachlorobenzenes

Giddings et al. (1994b) reviewed toxicity and exposure data for the tetrachlorobenzenes. They are no longer used or produced in Canada and releases come only from dielectric fluid spills and long-range transport. 1,2,4,5-Tetrachlorobenzene used to be used in the production of 2,4,5-trichlorophenol on a large scale, but this use has now been largely discontinued. There are not expected to be large differences between the behaviour of the isomers. Uptake of 1,2,4,5-tetrachlorobenzene was studied in rainbow trout. It is not volatile enough to evaporate from water easily, and is accumulated by the fish, through its gills. Bioaccumulation depended upon the rate of activity and oxygen uptake of the fish, and only the low water solubility prevented significant toxicity occurring (Brauner et al. 1994).

The greatest exposure of the general population is probably through food. All isomers were found to affect the liver, kidney, thyroid and lungs, with 1,2,4,5-tatrachlorobenzene being the most toxic. Not enough information was available to classify tetrachlorobenzenes as to carcinogenicity.

In addition to the effects noted above, 1,2,4,5-tetrachlorobenzene has also caused changes in the spleen, thymus, lymph nodes and haematological parameters in animals (Giddings et al. 1994b). An increase in chromosomal aberrations was seen in workers exposed to 1,2,4,5-tetrachlorphenol at a pesticide manufacturing complex (Giddings et al. 1994b).

In rats, 1,2,3,4- and 1,2,3,5-tetrachlorobenzene caused reduction in the number of live offspring at concentrations too low to adversely affect the mother (Giddings et al. 1994b).

All isomers have been detected in ambient air, drinking water and food and 1,2,3,4- and 1,2,3,5-tetrachlorobenzene have been identified in breast milk (Giddings et al 1994b), though none of the isomers were detected in Canadian human adipose tissue (Hermanson et al. 1997).

A.3.1.4 Pentachlorobenzene

Giddings et al. (1994c) found that though no longer manufactured or used in Canada, pentachlorobenzene could still enter the environment through spillage of dielectric fluids or atmospheric transport. Animal studies demonstrate weight loss and effects on the liver, thymus, kidney, adrenal glands and digestive tract. Anaemia and malformation of sperm also occurred. There is some indication of fetotoxicity and developmental toxicity. The thyroid was impacted, with and thyroid hormone (free and total thyroxin) concentrations reduced. Pentachlorobenzene cannot be assigned a carcinogenicity classification because of lack of data. Pentachlorbenzene accumulates in, and is toxic to algae (Sicko-Goad et al. 1989d).

Pentachlorobenzene has been detected in air, drinking water, food and breast milk (Giddings et al. 1994b), though according to Hermanson et al. (1997) it was found in less than 15% of human adipose samples collected in Ontario, Canada.

A.3.1.5 Hexachlorobenzene

Hexachlorobenzene (HCB) is a manufactured chemical, which was used as a wood preservative, as a fungicide for treating seeds, and as an intermediate in organic syntheses (Budavari et al. 1989). Additionally, hexachlorobenzene may be formed as an unwanted by-product in the synthesis of other organochlorine compounds high-temperature sources (Newhook & Meek 1994, Sala et al. 1999). The UNECE (1998) lists HCB alongside PCDD/Fs and PAHs as being the most important POPs emitted from stationary sources. HCB emissions from waste incineration, metallurgical industries and burning of chlorinated fuels are highlighted (UNECE 1998)(Annex V).

HCB is toxic to aquatic life, land plants, land animals, and humans. It is listed by the IARC as a Group 2B carcinogen, i.e. possible carcinogen to humans and also appears to be a tumour promoter. Hexachlorobenzene may damage the developing foetus, liver, immune system, thyroid and kidneys and CNS. The liver and nervous system are the most sensitive to its effects. Porphyria is a common symptom of HCB toxicity. High or repeated exposure may damage the nervous system, and can cause irritability, difficulty with walking and co-ordination, muscle weakness, tremor and/or a feeling of pins and needles on the skin. Repeated exposure, especially when skin effects occur, can lead to permanent skin changes, such as changes in pigmentation, tight, thickened skin, easy wrinkling, skin scarring, fragile skin, and increased hair growth, especially on the face and forearms (ATSDR 1997, Newhook & Meek 1994). Recent research (van Birgelen 1998) suggests that HCB has dioxin-like toxicity and more epidemiological studies should be undertaken especially concerning infants fed breast milk in countries with HCB exposure levels.

With the exception of occupational settings, almost all human exposure occurs via food. The greatest body of information on HCB toxicity to humans derives from an incident in Turkey between 1955 and 1959, when HCB-treated grain was made into bread. More than 600 people experienced porphyria cutanea tarda. Children of exposed women had skin lesions and 95% of them died at less than one year old. In the long term (20-30 years), some people continued to have abnormal porphyrin biochemistry and neurological, orthopaedic and dermatological symptoms persisted. Hexachlorobenzene is also thought to have caused porphyria cutanea tarda in populations exposed industrially and through food (Newhook & Meek 1994). High concentrations of HCB were found both in workers at an electrochemical plant at Flix in Spain and the local residents. The authors of the study stated that HCB exposure was associated with specific health effects in the most highly exposed subjects (Sala et al. 1999).

Once introduced into environment, HCB strongly absorb to soil materials and almost no desorption take place (Bahnick & Doucette 1988). It is bioaccumulative and biomagnifies. It can be measured in ambient air, drinking water, soil, food and breast milk (Newhook and Meek 1994).

HCB is one of twelve priority POPs intended for global action by the UN Environment Programme (UNEP) Governing Council. It is intended that HCB will be phased out worldwide under a convention currently being drawn up (UNEP 1995, 1997). Furthermore, HCB is included on Annex I of the Draft UNECE POPs Protocol under the Convention on Long-Range Transboundary Air Pollution (LRTAP)(UNECE 1998).
Within the EC, discharges of HCB are controlled as stipulated by EC Council Directive 86/280/EEC, which amends Directive 76/464/EEC, regarding pollution caused by certain dangerous substances discharged into the aquatic environment (EC 1986, 1976).

HCB is also included in the list of priority hazardous substances agreed by the Third and Fourth North Sea Conferences (MINDEC 1990, 1995), where continuous reduction of all hazardous substances was agreed with the ultimate aim of reducing environmental concentrations of hazardous substances to near background levels (synthetic substances to zero) within the next 25 years. The 1998 Ministerial Meeting of the OSPAR Commission (OSPAR 1998a) further reinforced these objectives. HCB is included on the OSPAR 1998 List of Candidate Substances, Annex 3 of the OSPAR Strategy with regard to Hazardous Substances (OSPAR 1998b).

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A.3.2 Nonylphenol (NP)

Nonylphenol (NP) is a persistent chemical that has been found to mimic the hormone estrogen and impair sperm production in fish (Jobling *et al.* 1996). Its presence in the freshwater environment results principally from the breakdown of nonylphenol polyethoxylates (NPEs), still used as industrial detergents and as spreading agents in pesticides. Laboratory experiments have shown that nonyl phenol is toxic to both aquatic organisms, particularly to fish (Liber *et al* 1999), and plant cells (Bokern & Harms 1997). The toxicity of nonylphenol and related compounds led to a recommendation by the Paris Commission to phase out the use of NPEs in household and industrial detergents (PARCOM 1992). Sweden called for a binding decision to phase out all uses of NPEs which result in contamination of the environment (ENDS 1996), citing in particular the known estrogenicity of nonylphenol. Recently European Commission compiled a list of chemicals suspected of disrupting endocrine system in humans and wildlife and nonyl phenol is listed there as medium priority candidate (ENDS 2000).

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A.3.3 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% is used in the production of soft PVC. 10-15 years before 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.3.4 PAHs

PAHs can occur in a variety of environmental products such as soot, coal, tar, tobacco smoke, petroleum, and crude oil. They are commonly found as products of incomplete combustion of wood and other fuels. In most cases PAHs occur as a mixture of several compounds, not as a single chemical.

Once introduced to the aquatic environment, PAHs can cause toxic effects to its living organisms (Monson *et al.* 1995; Ankley *et al.* 1995). Toxicity of certain PAHs increases during exposure of aquatic organisms to sunlight (Arfsten *et al.* 1996; McConkey *et al.* 1997). In terms of human health the biggest concern about PAHs is carcinogenicity of certain representatives from this class of compounds. Individuals exposed for long period of time to mixtures of PAHs and other compounds by breathing or skin contact can develop cancer (ATSDR 1997).

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APPENDIX 4

TOXICOLOGICAL OUTLINES FOR HEAVY METALS

A.4.1 Cadmium (Cd)

A.4.1.1 Environmental Levels

Cadmium is a rare metal, found naturally as very low concentrations. Typical background levels of cadmium are given in Table A.4.1.1.

Environmental matrix	Concentration	Reference
Freshwater, groundwater, drinking water	<1 ug/l	USPHS 1997, WHO 1992
Seawater (open ocean)	0.02-0.12 ug/l	Sadiq 1992, Bryan and Langston 1992
Seawater (coastal)	0.01-0.17 ug/l	Bryan and Langston 1992
Marine sediment	<1 mg/kg	Sadiq 1992, Salomons and Forstner 1984
Estuarine sediment	0.2 mg/kg	Bryan and Langston 1992
River sediment	1 mg/kg	Salomons and Forstner 1984
Soil	0.01-2.0 mg/kg	USPHS 1997, Alloway 1990

Table A.4.1.1 Background concentrations of cadmium found in water, sediment and soil

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

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USPHS (1997). Toxicological profile for cadmium on CD-ROM. Agency for Toxic Substances and Disease Registry

World Health Organisation (1992). Cadmium. Environmental Health Criteria 135. ISBN 9241571357

A.4.2 Chromium (Cr)

A.4.2.1 Environmental Levels

Chromium is found in varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see Table A.4.2.1).

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.4.2.1 Background concentrations of chromium found in water, sediment and soil

References

Alloway, B.J. (1990). Heavy metals in soils. John Wiley and Sons, Inc. New York, ISBN 0470215984

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A.4.3 Cobalt (Co)

A.4.3.1 Environmental Levels

Concentrations of cobalt vary widely in the environment (Alloway 1990). Typical background levels of cobalt are given in Table A.4.3.1.

Environmental Matrix	Concentration	Reference
Freshwater	0.9 ug/l	Bowen 1966
Seawater	0.27 ug/l	Bowen 1966
Soil	1-40 mg/kg	Alloway 1990
Freshwater sediment, UK	6-22 mg/kg	Hamilton 1994
Marine sediment, North Sea	4-5 mg/kg	Hamilton 1994
Marine sediment, Atlantic Ocean	3-6 mg/kg	Hamilton 1994

Table A.4.3.1 Background concentrations of cobalt found in water, sediments and soil

References

Alloway, B.J. (1990). Heavy metals in soils. John Wiley and Sons, Inc. New York, ISBN 0470215984.

Bowen, H.J.M. (1966). Trace Elements in Biochemistry. Academic press, London and New York.

Hamilton, E.I. (1998). The geobiochemistry of cobalt. The Science of the Total Environment 150: 7-39.

A.4.4 Copper (Cu)

A.4.4.1 Natural Occurrence

The largest deposits of copper are found in the USA, Chile, Canada, the Commonwealth of Independent States, Zambia and Peru (Dudka and Adriano 1997, Alloway 1990).

It is estimated that the total amount of copper released to the atmosphere from natural sources is 28,000 tonnes / year, compared with an estimated anthropogenic load of 35,000 tonnes / year (Nriagu 1990).

A.4.4.2 Usage

The principal use of copper is as an electrical conductor (copper cables and wires), however it is also widely employed in coinage alloys, in traditional alloys such as bronze (copper and tin), brass (copper and zinc) and Monel (copper and nickel), in corrosive-resistant and decorative plating, in munitions and in dental alloys. Its compounds are used as chemical catalysts, wood preservatives, algicides, fungicides, anti-fouling paints, disinfectants, nutritional supplements in fertilisers and feeds, in petroleum refining and as printing inks and dyes, (USPHS 1997, UNEP 1993).

A.4.4.3 Environmental Levels, Contamination and Behaviour

Copper is a relatively abundant "trace" metal, found at varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see Table A.4.4.1).

Environmental Matrix	Concentration	Reference
Seawater (English Channel, Irish Sea, North Sea)	0.35-4.0 ug/l (coastal) 0.14-0.9 ug/l (open ocean)	Law et al. 1994
Seawater (background)	0.1 ug/l	Sadiq 1992, Bryan and Langston 1992
Freshwater, UK	<20 ug/l	Mance et al. 1984
Soil	20 –30mg/kg	Alloway 1990
Marine sediment	10-30 mg/kg	UNEP 1993, Bryan and Langston 1992
Freshwater sediment	45-50 mg/kg	Salomons and Forstner 1984,

Table A.4.4.1 Background concentrations of copper found in water, sediment and soil

Copper may exist in natural waters either in the dissolved form as the cupric (+2) ion or complexed with inorganic anions or organic ligands (e.g. carbonates, chlorides, humic and fulvic acids). It may also be present as an insoluble precipitate (e.g. a hydroxide, phosphate, or sulphide) or adsorbed onto particulate matter. Alternatively it can be adsorbed to bottom sediments or exist as settled particulates. The relative concentrations of each of these forms is dependant upon a number of chemical parameters, including pH, salinity, alkalinity, and the presence of organic ligands, inorganic anions and other metal ions. However studies have frequently shown that the free +2 ion concentration is low, compared to the levels of copper associated with suspended and bottom sediments (USPHS 1997, Mance et al. 1984).

In soils, copper has a high affinity for sorption by organic and inorganic ligands (e.g. humic and fulvic acids, hydroxides of iron, aluminium and manganese). However it can also exist as soluble ions and complexes. Copper in a soluble form is far more bioavailable and far more likely to migrate through the environment, than if it is bound to organic matter or present as an insoluble precipitate. Therefore, copper sulphate, or chloride, present in MSW incinerator ash or mine tailings, is far more bioavailable and migratory than the organically bound copper found in sewage sludge (USPHS 1997, Alloway 1990, Mance et al. 1984).

Copper is one of the most important, essential elements for plants and animals. However if plants and animals are exposed to elevated concentrations of bioavailable copper, bioaccumulation can result, with possible toxic effects (USPHS 1997).

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A.4.5 Nickel (Ni)

A.4.5.1 Environmental Levels

Nickel is found in varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see Table A.4.5.1).

Environmental Matrix	Concentration	Reference
Seawater	0.1-0.5 ug/l	USPHS 1997, Law et al. 1994
Freshwater	<10-20 ug/l	USPHS 1997, Mance and Yates 1984
Freshwater sediment	45-65 mg/kg	Salomons and Forstner 1984
Soil	5-500 mg/kg (average 50 mg/kg) 40 mg/kg	USPHS 1997 Alloway 1990

Table A.4.5.1 Background concentrations of nickel found in water, sediment and soil

References

Alloway, B.J. (1990). Heavy metals in soils. John Wiley and Sons, Inc. New York, ISBN 0470215984

Law, R.J., Waldock, M.J., Allchin, C.R., Laslett, R.E. and Bailey, K.J. (1994). Contaminants in seawater around England and Wales: results from monitoring surveys, 1990-1992. Marine Pollution Bulletin 28, 11: 668-675

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USPHS (1997). Toxicological profile for cadmium on CD-ROM. Agency for Toxic Substances and Disease Registry

A.4.6 Manganese (Mn)

A.4.6.1 Environmental Levels

Manganese is found in varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems. Typical background levels of manganese are given in Table A.4.6.1.

Environmental Matrix	Concentration	Reference
Freshwater	12 ug/l	Bowen, 1966
Soil, UK	80-7000 mg/kg	Alloway, B.J. 1990, p202
Marine sediment	790 mg/kg	Goldschmidt, 1954

Table 4.6.1 Background concentrations of manganese found in water, sediment and soil

References

Alloway, B.J. (1990). Heavy metals in soils. John Wiley and Sons, Inc. New York, ISBN 0470215984

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A.4.7 Lead (Pb)

A.4.7.1 Occurrence, Production and Use

There is a general agreement that the abundance of lead in the average crustal rock is approximately 16 mg/kg; although black shales, rich in organic matter and sulphide minerals, can have far higher concentrations (Alloway 1990). Lead is chiefly obtained from the sulphide ore galena, by a roasting process; and is currently mined in 47 countries, making it one of the most widespread metals in terms of primary production. In addition to this, secondary smelters, processing lead metal products, are located in 43 countries, reflecting widespread recycling of lead in electric storage batteries (Dudka and Adriano 1997).

Natural sources of atmospheric lead include wind-borne soil particles and volcanic emissions, forest fires, biogenic processes and sea salt sprays. The total amount of lead released to the atmosphere from natural sources is estimated at 12,000 tonnes / year, compared with an estimated anthropogenic load of 332,000 tonnes /year (Nriagu 1990).

Uses of lead and its compounds are extensive. As a metal, it is often used as pipe-work for water distribution, or as containers for storing for corrosive liquids (e.g. sulphuric acid). Its alloys are used in welding, printing and as anti-friction metals; and great quantities, both of the metal and its dioxide, are used in electric storage batteries. Other uses include cable coverings, ammunition, and in the manufacture of lead tetraethyl, used as an anti-knock compound in petrol. Compounds of lead are used as paint pigments, PVC stabilisers, pesticides, varnishes, lubricants, as glazes for pottery and porcelain, and in leaded glass crystal (Budavari et al. 1989, USPHS 1997).

Estimates of anthropogenic emissions of lead are given in Tables A.4.7.1-A.4.7.3 (Nriagu 1990, Nriagu and Pacyna 1988):

SOURCE	Emission (thousand tonnes / year)
Transportation (anti-knock petrol additives)	248
Non ferrous metal production (Pb, Zn, Cu, Ni, Cd)	46.5
Steel and iron manufacturing	15.7
Energy production	12.7
Commercial uses (cement, chemicals, paint, ceramics)	4.5
Mining	2.55
Waste incineration (municipal refuse and sewage sludge)	2.37
TOTAL	332.32

Table A.4.7.1 World-wide atmospheric emissions of lead from anthropogenic sources

SOURCE	Emission (thousand tonnes / year)
Atmospheric fallout	100
Manufacturing processes (metal, chemicals, paper, petroleum products)	14
Sewage discharges	9.4
Base metal mining and smelting	7.0
Domestic wastewaters	6.8
Electric power plants	0.72
TOTAL	137.92

Table A.4.7.2 World-wide inputs of lead into aquatic ecosystems

SOURCE	Emission (thousand tonnes / year)
Discarded manufactured products	292
Atmospheric fallout	232
Coal ashes	144
Urban refuse	40
Agricultural and animal wastes	26
Solid wastes from metal fabrication	7.6
Logging and wood wastes	7.4
Municipal sewage and organic waste	7.1
Fertilisers and peat	2.9
TOTAL	759

Table A.4.7.3 World-wide inputs of lead into soils

A.4.7.2 Environmental Levels, Contamination and Behaviour

Lead is present in uncontaminated aquatic and terrestrial ecosystems at relatively low levels (see Table A.4.7.4).

Environmental Matrix	Concentration	Reference
Seawater (estuarine waters around England and Wales)	24-880 ng/l	Law et al. 1994
Seawater (open ocean)	5 ng/l 1-14 ng/l 20-71 ng/l	UPHS 1997 Bryan and Langston 1992 Law et al. 1994
Freshwater (mean value from 39,490 measurements)	3.9 ug/l	USPHS 1997
Drinking water	<5-30 ug/l	USPHS 1997
Soil	10-30 mg/kg	Alloway 1990
Freshwater / marine sediment	20-30 mg/kg	USPHS 1997

Table A.4.7.4 Background concentrations of lead found in water, sediments and soil

However, as anthropogenic emissions far exceed those from natural sources, elevations above these natural, background concentrations are often found (Table A.4.7.5).

When lead is released into the environment it has a long residence time compared with most pollutants. As a result, it tends to accumulate in soils and sediments. Where, due to low solubility, it can remain accessible to the food chain and to human metabolism far into the future (Sauve *et al.* 1997, USPHS 1997, Alloway 1990). However, as with all metals, speciation is critical when assessing bioavailability and the potential threat to the environment.

Site Description	Concentration	Reference
River water, Donana National Park, Spain (close to mining site)	<5-2500 ug/l	Pain et al. 1998
Drinking water, USA (contaminated from lead pipes / lead solder).	500 ug/l	USPHS 1997
Soil, Socorro, New Mexico (USA). Close to an abandoned lead smelter	25-10,000 mg/kg	Brandvoid et al. 1996
Paddy soil, Taiwan. Close to plastic stabiliser manufacturing plant	6.3-12,740 mg/kg	Chen 1991
Soil close to lead smelting sites, Montreal, Canada	40-14,860 mg/kg	Sauve et al. 1997
Gannel estuary sediments, UK. Received waste from old lead mines	2700 mg/kg	Bryan and Langston 1992
Oiartzun river sediments, Spain. Close to lead-zinc mining sites	68-5540 mg/kg	Sanchez et al. 1994

Table A.4.7.5 lead concentrations associated with anthropogenic contamination

Two oxidation states of lead, +2 and +4, are stable, but the environmental chemistry is dominated by the Pb^{+2} ion, its compounds, and complexes. In general the free +2 ion is more toxic than inorganic complexes, and therefore any factor which increases complexation and decreases the concentration of the free ion is bound to affect lead toxicity adversely. Toxic organic forms of lead are also present in the environment. From direct inputs (manufacture, transport and storage of leaded petrol and consequent car exhaust emissions) and the possible chemical / biological methylation of inorganic lead in anaerobic sediments (Sadiq 1992, Forsyth *et al.* 1991).

As mentioned, lead has a tendency to form compounds with anions having low solubility, such as hydroxides, carbonates, and phosphates. Thus the amount of lead remaining in solution in surface waters (also dependent upon pH and salinity) is often low. In addition to this, a significant fraction of insoluble lead may be incorporated in surface particulate matter from runoff, or as sorbed ions or surface coatings on sediment, or may be carried as a part of suspended living or nonliving organic matter (USPHS 1997).

In soils and sediments, the fate of lead is affected by similar processes, which often lead to the formation of relatively stable organic-metal complexes. Most of the lead is retained strongly, and very little is transported into surface water or groundwater. However re-entry to surface waters as a result of erosion of lead-containing soil particulates; or through the conversion to the relatively soluble lead sulphate at the soil / sediment surface, can occur (USPHS 1997, Sadiq 1992, Alloway 1990). As can the downward movement of lead from soil to groundwater by leaching (USPHS 1997).

Plants and animals can accumulate lead from water, soil and sediment, with organic forms being more easily absorbed than inorganic. In general, the highest lead concentrations are found in aquatic and terrestrial organisms that live near to lead mining, smelting, and refining facilities; storage battery recycling plants; areas affected by high automobile and truck traffic; sewage sludge and spoil disposal areas; sites where dredging has occurred; areas of heavy hunting (spent lead shot); and in urban and industrialised areas (USPHS 1997).

A.4.7.3 Toxicity

Lead is one of the most ubiquitous toxic metals. It has no known, nutrition, biochemical or physiological function, and because there is no demonstrated biological need, and because it is toxic to most living things, the major concern of the moment is at what dose does lead become toxic (Goyer 1996)? The toxic effects of lead are the same, irrespective of whether it is ingested or inhaled, and blood levels as low as <10-100 ug/dl in children, and 10-100 ug/dl in adults have been associated with a wide range of adverse effects. Including nervous system disorders, anaemia and decreased haemoglobin synthesis, cardiovascular disease, and disorders in bone metabolism, renal function and reproduction. Of particular concern, is the effect of relatively low exposure on cognitive and behavioural development in children (Pirkle *et al.* 1998, USPHS 1997, Bernard *et al.* 1995, Goyer 1993, Nriagu 1988).

In 1975 the Centre for Disease control (CDC) in Atlanta recommended that the maximum permissible level of blood-lead be 30 ug/dl (for both adults and children). This levels was revised downward in 1985 to 25 ug/dl, and again in 1991, defining a blood-lead of 10 ug/l as an action or intervention level (USPHS 1997). Perhaps even more importantly is the now suggested recommendation that there may be no level of blood-lead that does not produce a toxic effect, particularly in the developing central nervous system (USPHS 1997, Goyer 1993).

Animals studies have reproduced many of the toxic effects listed above, and animals feeding close to smelting, mining and recycling facilities, have often ingested levels of lead that have resulted in poisoning and death (Henny *et al.* 1991, Blus *et al.* 1991, USPHS 1997, WHO 1989, Collivignarelli *et al.* 1986). In addition, birds feeding on contaminated prey or ingesting lead shot into their gizzards, can be exposed to severe levels of lead. Resulting in high kidney, liver and bone concentrations, reduced growth and development, behavioral abnormalities, and sometimes death (Mateo *et al.* 1997, WHO 1989).

Lead is also toxic to all aquatic biota, and even though it is not considered one of the most environmentally mobile of metals, there is still appreciable evidence showing the bioavailability of sediment-bound lead to deposit feeding species (Bryan and Langston 1992). In addition, lead can be accumulated directly from sea and fresh waters, especially in organisms that utilise gill tissue as the major nutrient uptake route (Sadiq 1992). Toxicological studies have reported sub-lethal effects in fish including changes in morphology, metabolism and enzymatic activity. Avoidance behaviour has also been observed in adult fish exposed to levels ranging from 10-100 mg/l (WHO 1989). Studies involving invertebrates (oysters, sea urchins, snails, copepods and water fleas) often report a reduction in growth, fertility and reproduction suppression, and mortality, at ug/l (parts per billion) concentrations (WHO 1989).

A.4.7.4 Legislation

European legislation concerned with water quality and permissible environmental levels, does not generally treat lead as a priority pollutant. However, anthropogenic discharges of lead into the aquatic environment still need to cease, and therefore lead is included on the majority of subsidiary and secondary lists. Examples include:

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 intensive physical and chemical treatment prior to use.

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

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 USEPA, which limits the concentration of lead to 15 ug/l (USPHS 1997); and the WHO, which currently recommends a limit of 10 ug (WHO 1993).

The Water Research Centre in the UK recommends the following Environmental Quality Standards for lead: protection of freshwater salmonid fish 4-20 ug/l; protection of freshwater coarse fish 50-250 ug/l; protection of other freshwater life and associated non-aquatic organisms 5-60 ug/l; protection of saltwater fish, shellfish, other salt water life and associated non-aquatic organisms 25 ug/l (Brown *et al.* 1984).

Regarding soil contamination, the UK Department of the Environment (ICRCL) regards a level of 0-500 mg/kg as being typical of uncontamination. Anything above this is regarded as being contaminated, and as such, restrictions on recreational and agricultural uses apply (Alloway 1990). In terms of permissible sewage sludge levels, acceptable concentrations for lead range from 300-1200 mg/kg. However resulting soil concentrations should not exceed 50-100 mg/kg (recommended EC, UK, France, Germany) (Alloway 1990).

Finally, lead is included in the list of priority hazardous substances agreed by the Third North Sea Conference (MINDEC 1990), Annex 1A to the Hague Declaration, and confirmed at the Fourth Conference in Esjberg, Denmark, in 1995 (MINDEC 1995). Here it was agreed that environmental concentrations of hazardous substances should be reduced to near background level within the next 25 years. An objective further reinforced in the Sintra Statement at the 1998 Ministerial Meeting of the OSPAR Commission (OSPAR 1998a). Lead and organic lead compounds were selected for priority action, and as such as included in Annex 2 of the OSPAR Strategy with regard to Hazardous Substances (OSPAR 1998b).

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A.4.8 Zinc (Zn)

A.4.8.1 Natural Occurrence

Zinc is a relatively common metal, being 23rd in order of chemical abundance. It is found in the Earth's crust at an average concentration of 80 mg/kg, although some clay sediments and shales may contain higher concentrations (Alloway 1990, Salomons and Forstner 1984).

A.4.8.2 Usage

Zinc is one of the most extensively utilised "trace" metals (Nriagu 1990). It is most commonly employed as a protective coating for other metals e.g. galvanised steel, or as a component of bronze, brass and die-casting alloys. In addition, zinc salts are widely employed as wood preservatives, herbicides, catalysts, analytical reagents, vulcanisation accelerators for rubber, and stabilisers in PVC. They can also be found in ceramics, textiles, fertilisers, paints, pigments, batteries and dental, medical, and household products (USPHS 1997, Annema and Ros 1994, UNEP 1993, Budavari *et al.* 1989).

A.4.8.3 Environmental Levels, Contamination and Behaviour

Zinc is a relatively abundant "trace" metal, found at varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see Table A.4.8.1).

Environmental Matrix	Concentration	Reference
Seawater	<1 ug/l (open ocean) 0.3-70 ug/l (coastal and estuarine)	Bryan and Langston 1992. UNEP 1993
Freshwater	<50 ug/l	USPHS 1997
Drinking water	0.02-1.2 mg/l	USPHS 1997
Soil	10-300 mg/kg (50 mg/kg average)	Alloway 1990
Freshwater sediment	<100 mg/kg	USPHS 1997, Salomons and Forstner 1984
Marine Sediment	<100 mg/kg	Bryan and Langston 1992, UNEP 1993

Table A.4.8.1 Background concentrations of zinc found in water, sediments and soil

Zinc occurs in the environment primarily in the +2 oxidation state, either as the free (hydrated) zinc ion, or as dissolved and insoluble complexes and compounds (USPHS 1997). In soils, it often remains strongly sorbed, and in the aquatic environment it will predominantly bind to suspended material before finally accumulating in the sediment (USPHS 1997, Bryan and Langston 1992, Alloway 1990). However re-solubilisation back into an aqueous, more bioavailable phase is possible under certain physical-chemical conditions, e.g. the presence of soluble anions, the absence of organic matter, clay minerals and hydrous oxides of iron and manganese, low pH and increased salinity (USPHS 1997). Zinc in a soluble form (e.g. sulphate or chloride, present in incinerator ash, or mine tailings) is far more likely to migrate through the environment than if it is bound to organic matter or present as an insoluble precipitate (e.g. as in sewage sludge) (USPHS 1997).

Zinc is an essential element, present in the tissues of animals and plants even at normal, ambient concentrations. However if plants and animals are exposed to high concentrations of bioavailable zinc, significant bioaccumulation can results, with possible toxic effects (USPHS 1997).

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