BASTA DE CONTAMINACIÓN

EXPEDICIÓN DE
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Organochlorine and heavy metal contaminants in the environment around Primex, Altamira, Mexico

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1 EXECUTIVE SUMMARY

In September 2000, a series of water and sediment samples were collected from the discharge channels around the Primex facility in Altamira, Mexico. These were analysed for organic pollutants and heavy metals at the Greenpeace Research Laboratories in the UK.

Primex buys in vinyl chloride to polymerise to make the common thermoplastic polyvinyl chloride (PVC). No details were available about the technology used at this site.

Vinyl chloride exerts serious toxic effects after both acute and chronic exposure. It is narcotic at high concentrations and can damage the lungs. It can also cause cancer in workers exposed over a long period of time. Moreover, vinyl chloride is extremely hazardous. It is explosive if mixed with air and a large-scale spill may require evacuation of people from the affected area.

If released to the environment, vinyl chloride will quickly evaporate into the air or move into groundwater. It degrades quite quickly in air or surface water, but can persist for decades in groundwater and could render it unfit for human consumption.

Quantitative analyses of volatile organochlorines indicate that 15 700 ug/l of vinyl chloride were being discharged from the facility via the main effluent. This can be compared with European legislation being phased in for effluents from PVC production using suspension polymerisation (1000 ug/l before secondary treatment). Emissions are in excess of 15 times these regulations. US legislation specifies daily maximum concentrations of 172 to 268 ug/l depending upon the type of discharge. The concentration found in this survey is 58-91 times these limits.

In addition to the large quantities of vinyl chloride, hydrocarbon pollutants were also present in the effluent. However, some hydrocarbon pollution and heavy metal contamination is thought to result from runoff from the nearby road. Similarly, the organochlorine 1,4-dichlorobenzene is thought to be present through sewage discharges from the plant as opposed to the primary industrial processes.

2   INTRODUCTION

PVC is one of the mostly widely used thermoplastics in the world. Global production for 1999 was estimated at almost 25 million tonnes, with capacity in Mexico amounting to 429 000 tonnes (Chemical Week 1999).

PVC polymer is made from vinyl chloride, also called vinyl chloride monomer (VCM). This monomer is produced by chlorinating either acetylene or ethylene, though the latter is by far the most common process. VCM is a highly toxic and hazardous compound, which is explosive if mixed with air. It is usually stored as a pressurised liquid.

VCM may be used at the site of manufacture, or it may be shipped to another facility to be turned into PVC. Emergency workers dealing with a spill of VCM are advised to wear breathing equipment and to evacuate people from the area (HSC 1989).

Primex, in Altamira, Mexico, buys vinyl chloride from manufacturers in the USA, shipping it in via the nearby industrial port. It then polymerises the VCM to produce PVC for sale to manufacturers of plastic products. The polymerisation process inevitably results in the release of VCM to the working environment and the local environment. Since it is both slightly water soluble and highly volatile, the predominant routes of release are in the wastewaters and into the air. The current report describes a sampling programme undertaken to ascertain the extent of releases of vinyl chloride and other chemicals from the Primex facility. Background information on the technologies employed, the pollutants detected and the relevant environmental protection measures are included.

3   SAMPLING PROGRAM

During August 2000, samples of effluent and sediment were collected from the discharge points and effluent channels by which effluents are discharged from the Primex facility.

3.1   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 metal and organic residues. Sediment samples were collected in 100ml bottles. Water samples were collected in 1-litre or 125ml bottles. All samples were kept cool and returned to the Greenpeace Research Laboratories for analysis. The 125ml samples were analysed for volatile organochlorines; the one-litre samples were also screened to identify as many organic contaminants as possible and a quantitative determination of a range of heavy metals was carried out. Sediment samples were analysed for heavy metals and screened

for organic contaminants, but volatile organochlorines were not determined. Detailed description of sample preparation and analytical procedures are presented in Appendix 1.

3.2   Sample Descriptions

The samples were collected from the effluent channels close to the perimeter of the factory. These channels carry wastewaters and drainage emanating from three separate discharges. The primary effluent leaves the factory via a pipe close to the perimeter and flows towards the main road in a dedicated effluent channel. Effluent sample AM0144 was collected directly from the discharge pipe and sediment sample AM0145 from immediately downstream of the discharge point.

A few metres down from the main discharge, the effluent channel is joined by a side channel. This side channel starts close to the road leading to the main entrance of the facility and receives two smaller discharges, which probably consist of site drainage water and other wastewaters. A series of water and sediment samples were collected from this side channel. Some parts of the channel were too shallow to allow the one-litre sample bottles to be filled; in this case either sediments or 125ml water samples were obtained.

Sediment samples AM0138 and AM0139 and water sample AM0140 were collected from the upper section of the channel. AM0138 came from the channel before the first discharge point. AM0139 and effluent sample AM0140 were both collected downstream from the first discharge point.

Sediment and effluent samples AM0141 and AM0142 were collected from a second discharge and sediment AM0143 from the channel between this discharge and the main effluent channel. Samples are described in Table 1 and the layout of the site is sketched in Figure 1.

Sample Number	Sample Description	Sample Location
AM0138	sediment	upstream of effluent discharges
AM0139	sediment	between first and second effluent discharges
AM0140	effluent	from side channel downstream of first discharge channel
AM0141	sediment	from second discharge channel
AM0142	effluent	from second discharge channel
AM0143	effluent	from side channel downstream of first and second effluents
AM0144	effluent	effluent from main discharge pipe (third discharge point)
AM0145	sediment	sediment immediately downstream of AM0144

Table 1. Description of samples collected from the effluent channels around the Primex site.
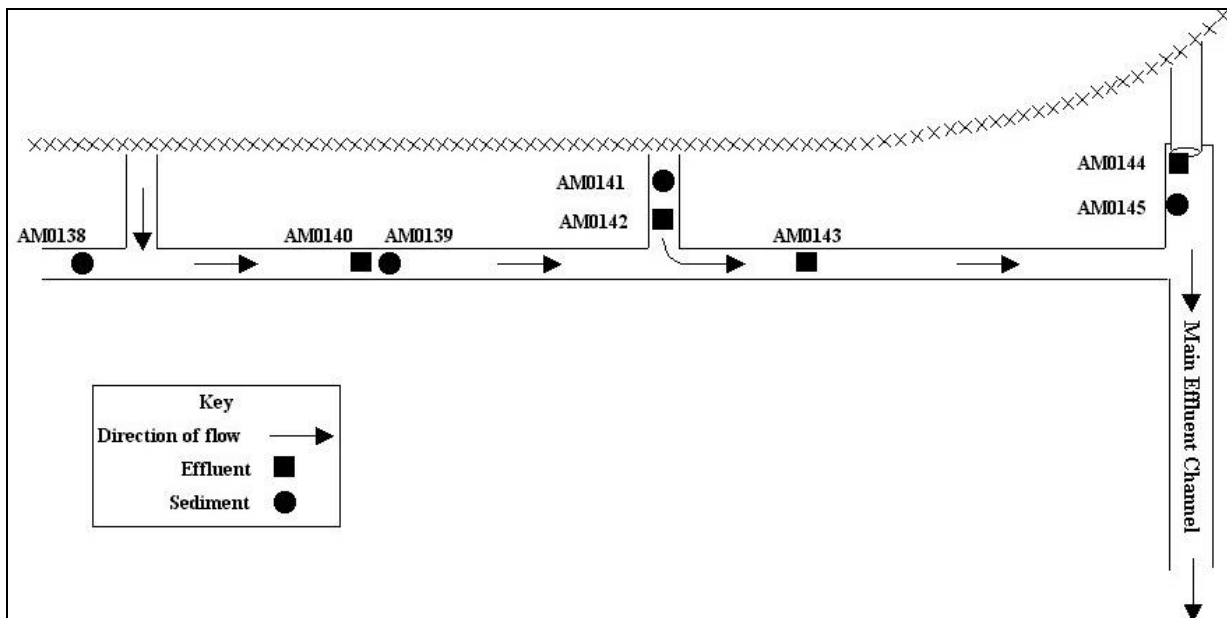
Figure 1. Map of sampling locations

4   RESULTS AND DISCUSSION

The results of the quantitative analyses of heavy metals and volatile organic compounds are given in Table 2. Table 3 shows the results of the qualitative organic screening, and reports compounds identified to a high degree of certainty (>90%).

For more information on the common sources, environmental behaviour and toxicological outlines for key pollutants detected during this study see Appendices 2 and 3.

The processes used to synthesise industrial chemicals always result in the generation of numerous byproducts.   However, a polymerisation facility buying purified VCM as feedstock will release far more vinyl chloride than other pollutants.

This was the case at Primex. The main effluent (sample AM0144) contained a significant concentration of vinyl chloride: 15 700 ug/l. This compound was also detected in two water samples from the other effluent channel; AM0142 and AM0143. These samples came from one of the discharge points into the side channel and the stretch between that discharge and the confluence with the main discharge channel. However, these samples indicated a less significant rate of discharge since the flow was lower and the concentrations (30 and 60 ug/l) were also less than in the main effluent.

Sample Number	AM0138	AM0139	AM0140	AM0141	AM0142	AM0143	AM0144	AM0145
Sample Type	sediment	sediment	effluent	sediment	effluent	effluent	effluent	sediment
METALS	mg/kg	mg/kg	ug/l	mg/kg	ug/l	ug/l	ug/l	mg/kg
Cadmium	1	1	<10	2	<10	<10	<10	2
Chromium	51	49	<20	27	<20	<20	<20	32
Cobalt	7	6	<20	5	<20	<20	<20	7
Copper	47	184	<20	41	<20	<20	<20	24
Lead	125	225	<30	107	<30	42	<30	65
Manganese	207	74	78	146	<10	447	<10	145
Mercury	0.44	0.28	<1	0.51	<1	<1	<1	0.42
Nickel	21	27	<20	14	<20	<20	<20	15
Zinc	800	1717	38	495	362	33	15	726
VOLATILE ORGANIC COMPOUNDS								
Vinyl chloride	N/A	N/A	<10	N/A	30	60	15700	N/A
1,1-Dichloroethene	N/A	N/A	<5	N/A	<5	<5	<5	N/A
Chloroform	N/A	N/A	<5	N/A	<5	<5	70	N/A
Carbon tetrachloride	N/A	N/A	<5	N/A	<5	<5	<5	N/A
Ethylene dichloride	N/A	N/A	<10	N/A	<10	<10	<10	N/A
Tetrachloroethene	N/A	N/A	<5	N/A	<5	<5	<5	N/A

Table 2. Quantitative analyses carried out on the samples collected from the Primex effluent channels. Concentrations of analytes in water samples are reported in ug/l . Concentrations in sediment samples are given in mg/kg on a dry weight basis. N/A: not analysed.

Sample Number	AM0138	AM0139	AM0140	AM0141	AM0142	AM0143	AM0144	AM0145
Sample Type	sediment	sediment	effluent	sediment	effluent	effluent	effluent	sediment
No. of organic compounds isolated	165	152	N/A	70	N/A	40	150	99
No. of organic compounds reliably identified	33(20%)	30(20%)	N/A	21(30%)	N/A	7(18%)	16(11%)	21(21%)
Groups reliably identified			N/A		N/A			
ORGANOHALOGENS								
Benzene, 1,4-dichloro-			N/A	*	N/A	*		
PAHs								
Naphthalene and/or its derivatives			N/A		N/A			1
Anthracene and/or its derivatives	1	1	N/A		N/A			
9H-Fluorene and/or its derivatives	1	1	N/A		N/A			
Chrysene and/or its derivatives		1	N/A		N/A			
Triphenylene and/or its derivatives		1	N/A		N/A			
PHENOLIC COMPOUNDS								
Phenol, 2-(1,1-dimethylethyl)-4-methyl-		1	N/A	1	N/A			
BHT	1	1	N/A	1	N/A	1	1	1
BHT aldehyde			N/A		N/A	1		
PHTHALATE ESTERS								
DEHP			N/A		N/A	1	1	
DBP			N/A		N/A	1		
DiBP			N/A		N/A	1		
OTHER AROMATIC COMPOUNDS								
Ter- and quaterphenyls	3	6	N/A	1	N/A			1
Alkylated benzenes	5	3	N/A	2	N/A		2	6

Sample Number	AM0138	AM0139	AM0140	AM0141	AM0142	AM0143	AM0144	AM0145
Sample Type	sediment	sediment	effluent	sediment	effluent	effluent	effluent	sediment
OTHER AROMATIC COMPOUNDS (Continued)								
Biphenyl and/or its derivatives	1	2	N/A		N/A			1
Diphenyl ether		1	N/A		N/A			1
Benzenemethanol and/or its derivatives			N/A		N/A		2	
Ethanone, 1-phenyl-			N/A		N/A		1	
1H-Indene and/or its derivatives			N/A		N/A			1
ORGANOSULPHUR COMPOUNDS								
Sulfur, mol. (S8)			N/A		N/A		1	
1,2,3,5,6-Pentathiepane			N/A		N/A		1	
1,2,5-Trithiepane			N/A		N/A		1	
ALIPHATIC HYDROCARBONS								
Linear	17	11	N/A	14	N/A	1	2	8
Cyclic	1	1	N/A		N/A		1	
Aliphatic alcohols			N/A		N/A		3	
MISCELLANEOUS								
Terpenoids	3		N/A		N/A			
Phosphonic acid, dioctyl ester			N/A		N/A			1

*Table 3. Screening analysis of the samples collected from the Primex effluent channels. All compounds were identified with 90% certainty or better. Numbers represent the number of compounds within each category identified using general GC/MS screening method; * signifies compounds identified only at trace levels using a selective ion monitoring (SIM) method. N/A: not analysed.*

Vinyl chloride is the monomer used to make PVC. It is highly toxic and extremely hazardous. The hazards derive from its volatility and flammability/explosive nature. Accidents in vinyl chloride plants and during transportation can cause explosions and fires (IPCS 1999). Vinyl chloride travels easily in the air; its volatility also means that people who work with VCM are often exposed to it via the air. Inhalation of high concentrations for even a short time has narcotic effects (ATSDR 1997). Consequently firefighters and others who are expected to deal with large-scale spills of VCM would need to use breathing equipment and evacuation of any local population would be recommended (HSC 1989). Workers with long-term exposure suffer a range of illnesses ranging from cancers to damage to the fingers.

The hazards of VCM have led to it being closely regulated. Domestic sales in Europe and the US have been banned for many years (EEC 1976, USDHHS 2000). Atmospheric concentrations must be kept to a minimum in an attempt to protect workers from its effects and, in Europe, limits on the quantities that can be emitted from the places where it is manufactured are set (OSPAR Decision 98/4).

It is common for VCM to be shipped from the location where it is manufactured to that where it is polymerised to form PVC. For example, in 1994, the USA exported 2.1 billion lbs. (953 400 metric tonnes) of VCM (USDHHS 2000). There are two main polymerisation processes, suspension polymerisation and emulsion polymerisation. European regulations are being brought in to limit the amount of vinyl that can be emitted in the wastewaters from the suspension process: measurements before secondary treatment should only be 1000 ug/l (OSPAR 98/5). The concentrations in the effluent were 15 times this amount. Depending upon the type of discharge, US Title 40 legislation specifies a daily maximum of 172-268 ug/l vinyl chloride in effluents from the plastics sector (USGPO 2000); the discharge analysed contained nearly 58-92 times these amounts.

Clearly the discharges from this plant are well in excess of those which would be acceptable in Europe. They may cause hazards via inhalation, or pollute the watercourse to which the effluent is discharged. Moreover, the vinyl chloride can easily move into the groundwater, where it can remain for decades. The World Health Organisation (WHO) has recommended a guideline figure of 5ug/l of vinyl chloride in drinking water (WHO 1993).

The polymerisation process involves the use of numerous other organic compounds that act as initiators, emulsifying agents, solvents, and so on (Matthews 1996). However, many of these are highly water soluble and as such would not be detectable using the extraction and analysis techniques employed in this survey.

The only other organochlorine detected in the main effluent was trichloromethane (chloroform), present at a level of 70ug/l. Chloroform is a highly narcotic substance that was for many years used as a medical anaesthetic. However, its toxic side-effects mean

that it is now tightly regulated. US Title 40 legislation (USGPO 2000) specifies maximum daily concentrations of 46 or 325 ug/l depending upon the wastewater treatment regime.

All the samples that were subjected to organic screening contained a range of hydrocarbon pollutants.

Two of the effluents (AM0143 and AM0144) contained phthalate esters. AM0143 contained DEHP, DBP and DiBP whereas AM0144 contained DEHP alone. The phthalates are mostly used as plasticisers (softeners) in PVC and their presence in the effluent clearly indicates that they are being released from the factory. However, they are environmentally persistent and accumulate in sediments, so if they were being discharged in significant quantities on a regular basis, they would be detectable in the sediments and this was not the case.

BHT (butylated hydroxytoluene) was present in all samples; this is commonly used as an additive in food products and as an antioxidant in plastics (Jobling *et al.* 1995). It is presumably being used as an antioxidant in this case.

Hydrocarbon contaminants detected in the survey included polycyclic aromatic hydrocarbons (PAHs), phenolic and other monocyclic aromatic hydrocarbons, and linear and cyclic aliphatic hydrocarbons. As with the phthalates, the fact that hydrocarbons are present in the effluent confirms that the factory is releasing them to the environment. Alkyl benzenes may be degradation products of detergents used in the process. However, a greater number of compounds were found in the upper reaches of the side channel, particularly samples AM0138 and AM0139. This is comparatively close to the access road to the factory. Consequently, it is possible that runoff from the road is responsible for some of the hydrocarbon pollution in the effluent channel.

The road is also implicated as a source of metal pollution. The water and effluent samples contained only zinc at detectable concentrations. Most of the sediment samples contained concentrations of metals that are within normal ranges for uncontaminated sites. However, the two sediments closest to the road (AM0138 and AM0139) both contained elevated concentrations of lead and zinc and AM0139 contained elevated concentrations of copper. Lead compounds have been used for many years as an additive to petrol. Zinc is a component of tyres (Doss *et al.* 1995) which is released as they wear. Copper can also be emitted from automobiles (Tong & Lam 2000).

Finally, the screening analysis identified one further organochlorine, 1,4-dichlorobenzene. This was present in samples AM0141 and AM0143. These came from the lower reaches of the side channel. Since 1,4-dichlorobenzene is widely used as a toilet deodorant, this probably indicates that sewage is being discharged via this second discharge point.

5 CONCLUSIONS

The Primex facility is emitting significant quantities of vinyl chloride to the environment. Concentrations of vinyl chloride in the main effluent discharge are over 15 times the concentrations that would be acceptable for a European factory operating according to the regulations proposed by the OSPAR Convention and by the European Community for the suspension process. They are between 58 and 91 times the daily maxima set by the US government for plastics manufacturers.

Vinyl chloride is volatile and can dissolve to a certain extent in water. Consequently, some of the loading in the effluent will escape to the air. A proportion will remain in solution and pollute whichever water body receives the effluent. It could also penetrate into the groundwater. Vinyl chloride is broken down in air or surface water within a matter of days. However, it persists for far longer in ground waters and could render them unfit to drink for many years.

In addition, the volatile organochlorine chloroform, hydrocarbons and phthalate esters appear to be being discharged from the site. Zinc may also be being released though it is one of the least toxic metals and is naturally present in water bodies.

As well as industrial releases, 1,4-dichlorobenzene suggests that sewage effluents are being released to the effluent channel. Finally, runoff is suspected to be a source of hydrocarbon and metal contamination in the samples closest to the road.

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APPENDIX 1 ANALYTICAL METHODOLOGY

A1.1 Organic analysis

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.

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. The samples were then acidified to pH 2 with 10% nitric acid. Following this, a second portion of 15ml of pentane was added, followed by 5ml of acetone and the extraction procedure repeated. Finally, both extracts obtained for each sample were combined and evaporated to a volume of approximately 3ml. 3ml of iso-propanol and 3ml of fresh prepared TBA-reagent (mixture of 3% tetrabutylammonium hydrogen sulfate and 20% sodium sulfite anhydrous in deionised water) were added to concentrated extract and the mixture shaken for 1 min. After shaking, 20ml of deionised water was added to reagent tube and the phases were allowed to separate. Finally, the organic layer was transferred with a Pasteur pipette into a pentane pre-washed Florisil column. The compounds were eluted with a 95:5 mixture of pentane: toluene and the eluent evaporated down to a volume of 2 ml under a stream of analytical grade nitrogen. 1-Bromonaphthalene was then added at a concentration of 10mg/l to provide an indication of GC/MS performance.

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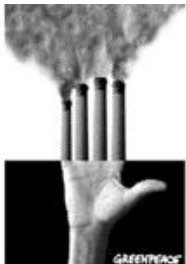
After separation of the phases, the solvent extract was filtered through a hydrophobic phase separator filter and collected in a reagent tube. The aqueous sample was acidified to pH 2 with 10% nitric acid, a second portion of 20ml pentane was added and the extraction procedure repeated. Both extracts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

Chromatographic Analysis

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

List of compounds in the Standard I used for SIM analysis

Organic compounds were identified qualitatively 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. Extracts were also analysed using selective ion monitoring (SIM) method against two standard solutions. The compounds contained in

Standard I and Standard II are listed below. All individual standards were obtained from Sigma Aldrich Co. Ltd., Supelco, UK.
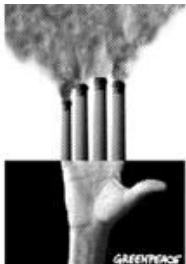
Results are reported as either reliably or tentatively identified. Match qualities of 90% or greater against HP Wiley 275 library or identification confirmed against standard compounds (using retention times and mass-spectra obtained during calibration) are assumed to give reliable identifications. Tentative 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

List of compounds in the Standard II used for SIM analysis

Volatile Organic Compounds (VOCs) analysis

For volatile organic compound analysis, no sample preparation was required. The original sample was sub-sampled immediately after opening. Three portions of 10ml each were transferred into 20ml headspace vials and sealed with Teflon-lined vial caps. One sub-sample was used for the organic screen analysis to evaluate the whole range of volatile compounds in the sample. The second sub-sample was analysed using Selective Ion Monitoring (SIM) method to detect the VOCs listed in the Table below. The third sub-

sample was used for quantification of the detected compounds with an external standard using SIM method. All standard compounds were obtained from Sigma-Aldrich Co. Ltd./Supelco UK.

Name of compound	Target ion	Qualifying ions
1,1,1-Trichloroethane	97	61, 26, 117
1,1-Dichloroethane	63	27, 83, 98
1,1-Dichloroethene	61	96, 26, 35
Carbon tetrachloride	117	35, 47, 82
Chlorobenzene	112	77, 51, 38
Chloroform	83	47, 35, 118
cis-1,2-Dichloroethene	61	96, 26, 35
1,2-Dichloroethane	62	27, 49, 98
Hexachlorobutadiene	225	260, 190, 118
m- & p-Xylene	91	106, 77, 51
o-Xylene	91	106, 77, 51
Tetrachloroethene	166	129, 94, 47
Toluene	91	39, 65, 51
trans-1,2-Dichloroethene	61	96, 26, 37
Trichloroethene	130	95, 60, 35
Vinyl chloride	27	62, 37, 47

List of volatile organic compounds and appropriate ions that were monitored during GC/MS analysis using SIM method.

A1.2. Heavy Metal Analysis

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.

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.

Aqueous samples

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

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

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

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

## APPENDIX 2 TOXICOLOGICAL OUTLINES FOR KEY ORGANIC COMPOUNDS

A2.1 Vinyl chloride

Vinyl chloride (also known as vinyl chloride monomer or VCM) is a colourless, sweet smelling gas under normal conditions. Vinyl chloride manufacture accounts for 36% of global chlorine consumption (Chemical Week 1998). In the US in 1992, 98% of vinyl chloride was used to make PVC (ATSDR 1997). Approximately 95% of the VCM produced globally has an end use in polymer or copolymer applications, of which by far the largest is PVC production. Non-polymeric uses occur in the synthesis of a variety of industrial compounds and in the manufacture of vinylidene chloride and tri- and tetra-chloroethene. Total world capacity of VCM in 1996 was *c.* 25 500 kt y^{-1}, of which about 54% was concentrated in the United States and Western Europe (Cowfer & Gorensek 1997).

In the wider environment, VCM is not persistent. It is degraded in a few hours by the action of light and reactions with the atmospheric OH radical. If released to water, vinyl chloride volatilises rapidly to the air. However, in soil, vinyl chloride migrates rapidly to groundwater. Here it is far more persistent, with a maximum estimated degradation half-life approaching eight years (Howard *et al.* 1991).

Vinyl chloride is an extremely hazardous substance. Mixed with air, it can be explosive and it causes a wide variety of toxic effects in humans and animals. It has been known for other 20 years that it causes cancer in humans. It was classified as known to be a human carcinogen by the US government in 1980. The cancer most strongly associated with vinyl chloride is angiosarcoma of the liver in the occupationally exposed and, although the evidence is less strong, other studies have shown elevated levels of cancers of the brain and nervous system, lung and respiratory tract and the lymphatic/haemapoietic system. There are less well supported indications of cancers at still further sites (ATSDR 1997). Retrospective analysis of histories of individuals with angiosarcomas at different sites suggest that exposure to vinyl chloride, PVC and other polymeric materials may have been a factor (Rhomberg 1998).

The most usual route of exposure to vinyl chloride is through inhalation. Vinyl chloride appears to cause emphysema, dyspnea, pulmonary lesions and a number of other lung problems (ATSDR 1997). Exposure to high levels of vinyl chloride can cause Raynaud's phenomenon, where the blood circulation in workers' fingers is damaged so that they become white and painful in cold conditions. This illness is sometimes followed by resorption of the bones in the tips of the fingers or lesions on bones in other parts of the body (ATSDR 1997).
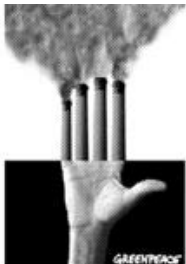
Workers have also been reported to die more frequently from cardiovascular and cerebrovascular disease (e.g. heart attacks and strokes). Vinyl chloride can also reduce the blood's ability to clot normally (ATSDR 1997).

Vinyl chloride is narcotic and inhalation can cause dizziness, headaches, drowsiness or unconsciousness, euphoria, memory loss, visual and/or hearing disturbances, sleep disturbance, nausea, irritability and nervousness. Damage to the nervous system manifests itself in peripheral neuropathy with tingling, pain or numbness in the fingers (ATSDR 1997). Also seen are toxic effects on the immune systems, livers, spleens, thyroid function, eyes and skin of workers. Anorexia (weight loss) has been reported and there are some indications that vinyl chloride can affect the reproductive systems of both men and women (ATSDR 1997).

To protect workers, many countries have set maximum limits for vinyl chloride in air. These range from 1ppm ($2.6mg/m^3$) in the USA to 7ppm ($18.2 mg/m^3$) in Finland, Germany and the UK. These limits are below odour thresholds (IPCS 1999).

The high toxicity of vinyl chloride has lead to it being banned for domestic use in both the USA and the European Community. The US ban dates from 1974 (USDHHS 2000). EC directive 76/769/EEC controls the sales and use of dangerous substances within the European Community. When this directive was brought in in 1976, it banned the use of vinyl chloride as an aerosol propellant on the basis of its hazards to human health (EEC 1976). Vinyl chloride was one of the first three substances controlled under this legislation, a measure of the hazard is represents.

VCM can be produced by the hydrochlorination of ethyne (acetylene), but currently over 90% of world production is carried out by the thermal cracking of 1,2-dichloroethane (EDC) (Cowfer & Gorensek 1997). It is then polymerised to PVC using either the suspension or emulsion process. Emission limits for the ethylene dichloride/vinyl chloride production and PVC polymerisation using the suspension process are given in OSPAR decisions 98/4 and 98/5 respectively. Plants built after February 1999 would have to adhere to these limits immediately, but plants already in existence would have until the beginning of 2006 to meet the EDC/VCM limits and until the beginning of 2006 to meet the polymerisation plant limits. The European Commission has also put forward a proposed Decision which would incorporate these limits into EC law (EC 1999). The OSPAR emission limits are listed in the tables below.

Substance	Emission to:	Limit value
VCM	air	5 mg Nm^{-3}
EDC	air	5 mg Nm^{-3}
dioxins	air	0.1 ng ITEQ Nm^{-3}
chlorinated hydrocarbons	Water (before secondary treatment)	0.7 g per tonne of EDC purification capacity
copper	water (after final treatment)	0.5 g per tonne oxychlorination capacity for plants with fixed bed reactors, 1.0 g per tonne oxychlorination capacity for plants with fluidised bed reactors
dioxins	water (after final treatment)	1 ug TEQ per tonne of oxychlorination capacity
COD	water (after final treatment)	250 mg l^{-1} effluent

Limit values for emissions from plants manufacturing ethylene dichloride and/or vinyl chloride monomer as set by the OSPAR Convention.

Substance	Emission to:	Limit value
VCM	air	80 g per tonne of s-PVC produced
VCM	water (after effluent stripper, before secondary treatment)	1 mg VCM per litre 5 g VCM per tonne s-PVC produced
COD	water (at outlet of effluent water treatment plant)	125 mg per litre for single plants 250 mg per litre for combined plants*
suspended solids	water (at outlet of effluent water treatment plant)	30 mg suspended solids per litre

*Limit values for suspension polymerisation PVC plants as set by the OSPAR Convention. *single plants manufacture only suspension-polymerisation PVC (s-PVC); combined plants are those where s-PVC is produced as part of an industrial site, where other chemical processes are being carried out.*

In the USA, federal legislation has been designed to control the emissions from plastics manufacturers. Title 40, Part 414 specifies a range of limits depending on the type of discharge and measurement period (USGPO 2000). These are summarised below.

Type of discharge	Maximum concentration for any one day	Maximum for any monthly average
Direct discharge point sources that use end-of-pipe biological treatment	268 ug/l	104 ug/l
Direct discharge point sources that do not use end-of-pipe biological treatment	172 ug/l	97 ug/l
Indirect source point discharges	172 ug/l	97 ug/l

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A2.2 Chloroform

Chloroform is a heavy, colourless, non-flammable liquid. It has a characteristic pleasant, sweet, ethereal odour and a sweetish burning taste (CEC 1986).

It has been extensively used in the past as an anaesthetic (Snyder & Andews 1996). Currently the largest use of chloroform is to make HCFC-22, an ozone-depleting refrigerant (Holbrook 1993). The Montreal Protocol, the international legislation which protects the ozone layer, has set targets for reducing the use of HCFC-22, but it will not be totally phased out until 2030 (UNEP 1997).

Chloroform is the most abundant of the trihalomethanes (THMs) which are generated as by-products during water disinfection using chlorine-containing compounds (Oxenford 1996, ATSDR 1997, Health Canada 1996). Additionally it can be formed in washing machines into which chlorinated bleach has been added (Shepherd & Corsi 1996), in the natural waters where chlorine-containing effluents have been discharged (Mills *et al.* 1998). Exposure to chloroform may occur when breathing contaminated air, drinking contaminated water or through skin contact (Weisel & Chen 1994; Weisel & Jo 1996). Water is possibly now the major source of environmental exposure to chloroform.

Chloroform has been specified by the International Agency for Research on Cancer in the Group 2B as possibly carcinogenic to humans (IARC 1998). Investigation on animals have shown that the main target organs for carcinogenicity from chloroform are liver, kidney and/or intestine (Dunnick & Melnik 1993; Snyder & Andews 1996; Chiu *et al.* 1996). A guideline value of 200ug/l was calculated to correspond to an excess lifetime cancer risk of 10^{-5} by the World Health Organisation (WHO 1993). There are four contaminants included in this group: chloroform, bromodichloromethane, dibromochloromethane and bromoform (Oxenford 1996).

It is not known whether chloroform causes reproductive effects or birth defects in people, but animal studies have shown that miscarriages occurred in rats and mice that breathed air containing 30–300 ppm chloroform during pregnancy and also in rats that ate chloroform during pregnancy. Offspring of rats and mice that breathed chloroform during pregnancy had birth defects. Abnormal sperm were found in mice that breathed air containing 400 ppm chloroform for a few days (ATSDR 1997).

The levels of chloroform found in treated drinking water depends upon water treatment practice, age of the water, water temperature (Health Canada 1996) and can vary in the range from less than 1ug/l to 200ug/l (Wallace 1997, Health Canada 1996). Levels less than 10ug/l were found in US rural ground water (Wallace 1997). A mean value of 84ug/l was reported for surface waters (if detected) in the same survey.

Chloroform evaporates easily into the air. Most of the chloroform in air breaks down eventually, but it is a slow process. The breakdown products in air include phosgene and hydrogen chloride, which are both toxic (ATSDR 1997). It is poorly absorbed to soil and can travel through soil to groundwater where it can persist for years. Chloroform dissolves easily in water and some of it may break down to other chemicals (ATSDR 1997).

The presence of chloroform (as an organohalogen compound) in groundwater is controlled by European Community Environmental Legislation. Article 3 of EC Council Directive 80/68/EEC of 17 December 1979 on the protection of groundwater against pollution caused by certain dangerous substances (EEC 1979) and amended later (EEC 1991) says that Member States shall take necessary steps to prevent the introduction into groundwater of substances in List I and organohalogen compounds are among the groups of the compounds listed there.

The quality objective of 12ug/l for the aquatic environment (including inland surface waters, estuary waters, internal coastal waters other than estuary waters and territorial waters) is set for chloroform by the EC Council Directive 86/280/EEC (EEC 1986) and amended in 1988 (EEC 1988).

The EC Council Directive 76/769/EEC (EEC 1976) which was last amended in 1996 (EEC 1996) restricts marketing and use of chloroform. Chloroform may not be used in concentrations equal to or greater than 0.1% by weight in substances and preparation placed on the market for sale to the general public and/or in diffusive applications such as in surface cleaning and cleaning of fabrics.

In the USA, federal legislation has been designed to control the emissions from plastics manufacturers. The Environmental Protection Agency Code of Federal Regulations, Title 40, Part 414 specifies a range of limits depending on the type of discharge and measurement period (USGPO 2000). These are summarised below.

Type of discharge	Maximum concentration for any one day	Maximum for any monthly average
Direct discharge point sources that use end-of-pipe biological treatment	46 ug/l	21 ug/l
Direct discharge point sources that do not use end-of-pipe biological treatment	325 ug/l	111 ug/l
Indirect source point discharges	325 ug/l	111 ug/l

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A2.3 BHT

2,6-Bis(1,1-dimethylethyl)-4-methylphenol, also known as butylated hydroxytoluene (BHT), is frequently employed as an antioxidant in food products, rubbers, soaps and in the production of plastics and other petrochemical products (Jobling *et al.* 1995). It is also used as an antiskinning agent in paints, varnishes and other surface finishes and as an antioxidant. The use of BHT as an antioxidant in food has been associated with certain allergic reactions (Dean 1986). 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 *et al.* 1986). Additionally, BHT is one of the main degradation

products of the herbicide terbutol (2,6-di-tert-butyl-4-methylphenyl N-methylcarbamate) (Suzuki *et al.* 1995 & 1996).

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A2.4 Alkylbenzenes

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

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

The acute toxicity of inhaled alkylbenzenes is best described as central nervous system (CNS) depression (Andrews & Snyder, 1986). Acute toxicity does not vary very much within the group. In animal models, relatively similar concentrations of inhaled vapours of different alkyl benzenes were found to be lethal. Impaired reaction times and impaired speech are the two most commonly noted CNS effects (Klaassen *et al.* 1996). All alkylbenzenes mentioned above are irritating to the eyes and mucous membranes, can

cause irritation and burning of the skin and all are narcotics at high concentrations. Benzene itself is a known carcinogen. Chronic exposure can lead to bone marrow depression, which in a few cases, can progress to leukaemia (Budavari *et al.* 1989).

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A2.5 Phthalate esters

Phthalate esters are commonly referred to as phthalates. They are used in every major product category (Kemi 1994). 90% of all plasticisers are used in the production of soft PVC (Cadogan *et al.* 1993) but they are also used in inks and dyes, in cosmetics, as a concrete additive and as a solvent for perfume oils (ATSDR 1997, Jobling *et al.* 1995). Phthalates are persistent and are the most abundant man-made chemicals in the environment (Jobling *et al.* 1995). They can also bioaccumulate to some degree, predominantly from food. The phthalates exhibit a wide range of toxic effects in laboratory animals.

DEHP is the most extensively research phthalate ester. It can cause liver cancer in laboratory animals. It has been classified as possibly carcinogenic to humans by the IARC and US Department of Health and Human Services has determined that DEHP may reasonably be anticipated to be a carcinogen (USDHHS 2000). The European Commission's Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE 1998) noted that the most sensitive effect of DEHP may be damage to the development of the testes, based on tests involving exposure of rats to relatively low concentrations both in the womb and for the first three weeks after birth. The Committee also judged that such testicular toxicity may have greater relevance for humans than carcinogenic effects.

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 oestrogen receptor, although it

showed no significant estrogenic activity. Its potential to interfere with other aspects of the hormone system has not been fully investigated.

DEHP and DnBP (also called DBP) can both damage the male and female reproductive systems (Chan & Meek 1994, ATSDR 1997). Both can damage sperm production (ATSDR 1997, Wine *et al.* 1997), impair reproductive success (Chan & Meek 1994, Ema *et al.* 1995, ATSDR 1997, Wine *et al.* 1997) and cause teratogenicity (malformation of the offspring)(Chan & Meek 1994, Ema *et al.* 1993; Ema *et al.* 1995, ATSDR 1997). The liver and kidneys can also be affected by DnBP (Chan & Meek 1994; ATSDR 1997) and DEHP (ATSDR 1997).

A group of phthalate esters including DnBP and DEHP has been found to have both acute (Adams *et al.* 1995) and chronic (Rhodes *et al.* 1995) toxicity to freshwater and marine species, although toxicity may have been limited to some degree by the poor water solubility of these compounds. 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.

PVC plasticised with dibutyl phthalate (DBP) and used in the glazing systems of glasshouses, can be seriously phytotoxic. DBP is released at concentrations far below those regarded as potentially harmful to human health, but is toxic enough to young plants to cause significant damage to, or death of, entire crops. The food plants known to be directly affected include brassicas (particularly some cabbage cultivars), tomatoes and peppers. There is unconfirmed evidence that cucumbers, tobacco, begonias and hibiscus are also affected (Cole *et al.* 1984).

Phthalates are semivolatile and are found in the atmosphere of primary PVC processing plants at levels of 0.02 - 0.5mg m^{-3}. This results in a significant exposure of workers (Dirven *et al.* 1993). Exposure to workers recycling soft PVC is likely to occur at similar levels. Another suspected source of harm to people, particularly children, is from inhaling phthalates. Recent research has suggested that atmospheric DEHP from PVC floors and wallcoverings could have a role in asthma in children (Oie *et al.* 1997, Jaakola *et al.* 1999). The migration of DEHP from cling film into foods, especially fatty foods such as dairy produce, has led many manufacturers to offer non-PVC film, or to reduce the content of DEHP (MAFF 1987 & 1990).

Children's toys, many intended to be chewed by young children, are amongst the products softened with phthalates. Some toys can contain as much as 40% phthalates by weight, as well as a range of other compounds such as the alkyl phenols (Stringer *et al.* 2000). The risk to health that these pose has been the subject of some debate over the last few years (CSTEE 1998 & 1999, Janssen *et al.* 1998, MacKenzie 1997) and resulted in an emergency ban being imposed by the EC (EC 1999). This measure covers toys and child-care items which are intended to be placed in the mouths of children under the age of 3 years and

which contain over 0.1% of DINP, DEHP, DnOP, DIDP, BBP or DBP. The EC's move follows restrictions being placed on various categories of phthalate-containing PVC toys by Austria, Denmark, Finland, France, Germany, Greece, Italy, Spain and Sweden. The three-month ban, which has been extended until March 2001 (EC 2000), is intended to allow the European Parliament and Council time to consider a permanent ban which would be implemented through amendment of Directive 76/769/EC on restrictions on the marketing and use of dangerous substances and preparations (EC 1999). Because of their recognised toxicity and widespread distribution, two phthalates (DBP and DEHP) are included on the OSPAR List of Chemicals for Priority Action (Annex 2 to the OSPAR Strategy with Regard to Hazardous Substances, OSPAR 1998).

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APPENDIX 3 TOXICOLOGICAL OUTLINES FOR HEAVY METALS

A3.1 Lead (Pb)

Lead is one of the most ubiquitous toxic metals. It 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 & 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 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, ATSDR 1997).

Lead is present in uncontaminated aquatic and terrestrial ecosystems at relatively low levels. However, as anthropogenic emissions far exceed those from natural sources, elevations above these natural, background concentrations are often found. Lead tends to accumulate in soils and sediments, where it can remain accessible to the food chain and to human metabolism for many years (Sauve *et al.* 1997, ATSDR 1997, Alloway 1990). However, as with all metals, speciation is critical when assessing bioavailability and the potential threat to the environment.

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).

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 (ATSDR 1997).

Lead has no known, nutrition, biochemical or physiological function (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. Health impacts include 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, ATSDR 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 10 ug/dl (for both adults and children) (ATSDR 1997). However, it has been suggested that there may be no level of blood-lead that does not produce a toxic effect, particularly in the developing central nervous system (ATSDR 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, ATSDR 1997, 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. This can result in high kidney, liver and bone concentrations, reduced growth and development, behavioural 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 & 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).

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.

Council Directive 80/778/EEC relating to the quality of water intended for human consumption set a maximum permissible concentration of 50 ug/l. Other drinking water legislation includes that set by the Bureau of Indian Standards (1995), which currently set a maximum permissible concentration for lead of 50 ug/l; the USEPA, which limits the concentration of lead to 15 ug/l (ATSDR 1997); and the WHO, which currently recommends a limit of 10 ug/l (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 consequently is included in Annex 2 of the OSPAR Strategy with regard to Hazardous Substances (OSPAR 1998b).

Denmark has imposed a wide ranging ban on lead. Apart from a limited number of exceptions, such as second-hand products which met Danish standards when they were first sold, the import and marketing of products containing lead was banned on the 1st March 2001 (Danish EPA 2000).

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A3.2 Copper (Cu)

Abundance of copper in the Earth's crust is reported as ranging from 24-55 mg/kg (Alloway 1990), although higher levels are associated with some shales and clays (Thornton 1995). Copper can occur in the elemental state, however it is found more commonly as a sulphide (copper pyrite), oxide (cuprite) or carbonate (malachite). The largest deposits of copper are found in the USA, Chile, Canada, the Commonwealth of Independent States, Zambia and Peru (Dudka & Adriano 1997, Alloway 1990).

Volcanic activity is the major source of copper released to the atmosphere, followed by emissions from wind-borne soil particles, forest fires, sea salt spray and biogenic processes. 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).

After the copper ore has been mined, crushed, enriched and concentrated, it is roasted at temperatures in excess of 1200°C, sintered and smelted. Alternatively copper can be recovered from secondary sources (i.e. scrap). This process is far less energy intensive and therefore is playing an increasingly important role in terms of global copper production (UNEP 1993).

Copper is a highly malleable and ductile metal, as well as being an excellent conductor of heat and electricity. Its principal use 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, (ATSDR 1997, UNEP 1993).

Copper is a relatively abundant "trace" metal, found at varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems. However, as anthropogenic emissions of copper exceed those from natural sources, elevations above these natural, background concentrations are often found.

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 (ATSDR 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 (ATSDR 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 (ATSDR 1997).

Human deficiency is characterised by anaemia, resulting from defective haemoglobin synthesis (Goyer 1996). However at the other extreme, vomiting, hypotension, jaundice, coma and even death, can result from acute poisoning (ATSDR 1997).

Inhalation of dust and vapours can irritate the nose, mouth and eyes and cause headaches, dizziness, nausea and diarrhoea. Oral exposure to high levels can cause vomiting, diarrhoea, stomach cramps and nausea (ATSDR 1997). Copper homeostasis plays an important role in the prevention of copper toxicity, in humans, terrestrial animals and aquatic organisms. Copper is readily absorbed from the stomach and small intestine; and after requirements are met, there are several mechanisms that prevent copper overload e.g. bile excretion, increased storage in the liver or bone marrow (ATSDR 1997). However, failure of this homeostatic mechanism can occur in humans and animals following exposure to high levels of copper. This rare disease, known as Wilson's disease, is characterised by the excessive retention of copper in the liver and impaired copper excretion in the bile. Resulting in liver and kidney damage and haemolytic anaemia (ATSDR 1997).

In addition to these effects, developmental and reproductive damage, following exposure to high levels of copper, has been seen in animals. However no such effects have been reported in humans (ATSDR 1997).

Copper is not a priority pollutant but is included on the majority of subsidiary and secondary pollutant lists. Examples of guidelines and permissible environmental levels include the following:

European Council Directive 75/440/EEC concerning the quality required of surface water intended for the abstraction of drinking water in the Member States. Water containing more that 50 ug/l must be subjected to physical and chemical treatment prior to use (EEC 1975).

European Council Directive 78/659/EEC on the quality of fresh waters needing protection or improvement in order to support fish life. An Environmental Quality Standard of 40 ug/l is set (EEC 1978).

European Council Directive 80/778/EEC relating to the quality of water intended for human consumption. Guide levels of 100 ug/l (for outlets of pumping and/or treatment works) and 3000 ug/l (after water has been standing for 12 hours in the piping/made available to the customer) are set (EEC 1980). Other drinking water standards include those set by the Bureau of Indian Standards (1995) (50ug/l), the USEPA (1300 ug/l) (ATSDR 1997) and the WHO (2000 ug/l)(1993).

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A3.3 Zinc (Zn)

Zinc is a relatively common metal, 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 & Forstner 1984). It is not found naturally in its pure form (as a lustrous, blue-white metal) but as a mineral (most commonly sphalerite, zinc sulphide), often associated with the ores of other metals (e.g. copper, lead and cadmium) (Kroschwitz & Howe-Grant 1995).

Natural sources of atmospheric zinc include wind-borne soil particles, emissions from forest fires and volcanoes, biogenic emissions and sea-salt sprays. The total amount of Zinc released to the atmosphere from natural sources is estimated at 45,000 tonnes / year, compared with an estimated anthropogenic load of 132,000 tonnes / year (Nriagu 1990).

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 (ATSDR 1997, Annema & Ros 1994, UNEP 1993, Budavari *et al.* 1989).

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

Zinc is a nutritionally essential metal, having enzymatic, structural and regulatory roles in many biological systems (Goyer 1996, Aggett & Comerford 1995). Deficiency in humans can result in severe health consequences including growth retardation, anorexia, dermatitis, depression and neuropsychiatric symptoms (Aggett & Comerford 1995). At the other extreme, excessive dietary exposure, in both humans and animals, can cause gastrointestinal distress and diarrhoea, pancreatic damage and anaemia (ATSDR 1997, Goyer 1996).

Animal studies involving doses 1,000 times higher than the RDA, taken over a period of a month, resulted in anaemia and injury to the pancreas and kidney; and rats that ate very large amounts of zinc became infertile (ATSDR 1997). Humans taking supplements at higher than recommended doses (400-500 mg/day) suffered severe gastro-enteritis (Abernathy & Poirier 1997); and humans who drank water from galvanised pipes, over a prolonged period, suffered irritability, muscular stiffness and pain, loss of appetite and nausea (UNEP 1993).

With regard to industrial exposure, metal fume fever resulting from the inhalation of zinc oxide fumes presents the most significant effect. Attacks usually begin after 4-8 hours of exposure and last between 24-48 hours. Symptoms include chills and fever, profuse sweating and weakness (ATSDR 1997, Goyer 1996).

At slightly higher concentrations, studies investigating the effects of zinc on the hatching of brine shrimp (*Artemia salina*), noted that although increased concentrations of zinc did not affect development before emergence, the hatching stage of development was highly sensitive to and heavily disrupted by, zinc (Bagshaw *et al.* 1986). In addition, the inhibition of larval development was observed in the echinoderm (e.g. sea urchins and starfish) *Paracentrotus lividus* at a zinc concentration of only 30 ug/l (UNEP 1993). Shell growth in the mussel *Mytillus edulis* was effected at a concentration of 200 ug/l. With oxygen uptake, feeding and filtration rates were reduced at concentrations ranging between 750-2000 ug/l. Harmful effects on mollusc larva were seen to occur at levels as low as 40 ug/l (UNEP 1993).

Plant studies have shown that although an essential element for higher plants, in elevated concentrations zinc is considered phytotoxic, directly affecting crop yield and soil fertility. Soil concentrations ranging from 70-400 mg/kg are classified as critical, above which toxicity is considered likely (Alloway 1990).

Zinc is not a priority pollutant, but it is included on the majority of subsidiary and secondary pollutant lists. Examples of guidelines and permissible environmental levels include the following:

European Council Directive 78/659/EEC on the quality of fresh waters needing protection or improvement in order to support fish life. An Environmental Quality Standard of 0.3 mg/l is set (EEC 1978).

European Council Directive 80/778/EEC relating to the quality of water intended for human consumption sets guide levels of 100 ug/l (for outlets of pumping and / or treatment works) and 5000 ug/l (after water has been standing for 12 hours in the piping / made available to the consumer)(EEC 1980). The USEPA recommends a maximum permissible concentration for drinking water of 5 mg/l (ATSDR 1997) as does the Bureau of Indian Standards (1995).

The UK Department of the Environment (ICRCL) classifies a soil level of 0-250 mg/kg as being typical of uncontamination. Anything above this is classified as contaminated and as such, restrictions on recreational and agricultural uses apply (Alloway 1990). In terms of permissible sewage sludge levels, acceptable concentrations for zinc range from 1000-10,000 mg/kg, however resulting soil concentrations should not exceed 560 mg/kg (UK) or 300 mg/kg (EC, France, Germany) (Alloway 1990).

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