

**Identification and environmental significance of organic pollutants and heavy metals  
in samples associated with Rhodia S.A. and Carbocloro Industrias Quimicas S.A.,  
Cubatao and Sao Vicente, Brazil, 1998.**

Technical Note 20/98

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## **Introduction**

In April 1998, a preliminary study was conducted to identify potential sources of organic and heavy metal contaminants to the Rio Cubatao/Rio Pereque river system from enterprises situated close to the confluence of these two rivers. A total of 7 samples were collected, including:

- lagoon sediment (one sample LA8008) and soil (one sample LA8007) from a dumpsite (situated on the banks of the Rio Pereque, immediately upstream from its confluence with the Rio Cubatao) which received wastes from the nearby Rhodia S.A. plant until 1993 when the plant was closed down. It is understood that, while in operation, the factory produced a variety of organochlorines, including pentachlorophenol;
- two samples of wood litter LA8070 and LA8071 from trees on the same dumpsite; and
- three samples of sediment from the Rio Cubatao: one (LA8003) upstream from the confluence of the two rivers, one (LA8002) downstream from the Rhodia dumpsite and opposite the Carbocloro Industrias Quimicas S.A. plant, and one (LA8005) downstream of both industries. This section of the Rio Cubatao has been dredged.

In addition to those described above, three further samples of sediment were collected from the vicinity of an additional landfill site operated by Rhodia, located on the banks of the Rio Branco in the Guarentenarrio district of Sao Vicente city. Two samples (LA8009 and LA8010) were collected from small streams running through the site and one sample (LA8011) from the Rio Branco itself.

A single sample of water LA8001 was collected from a private well in the residential area of Guarentenarrio District, opposite the landfill site operated by Rhodia.

## **Materials and Methods**

All samples were collected and stored in glass bottles that had been rinsed with pentane and nitric acid to remove all organic and heavy metal residues. Aqueous samples were collected in 1-litre bottles, rinsed three times with the sample before filling with sample. Bottles were filled completely, ensuring no air bubbles were present. They were stored cold, kept cold during transit, and refrigerated immediately on arrival at the Greenpeace Research Laboratories.

## **1. Organic Screen Analysis**

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

### **Solid Samples**

Solid samples were analysed separately for volatile and extractable organic compounds.

For volatile organic compound analysis, no sample preparation was required. Approximately 2g of sample were transferred to a 20ml headspace vial for analysis as described below.

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 (d8) naphthalene (an internal standard) at a concentration of 4.7 mg/kg. 15 ml of pentane was added, followed by 5 ml 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 20 ml pentane was added and the extraction procedure repeated. Finally, both extracts obtained for each sample were combined and evaporated to a volume of approximately 3 ml. The concentrated extract was cleaned through Florisil column, eluted with a 95:5 mixture of pentane: toluene, and evaporated down to a volume 2 ml under a stream of analytical grade nitrogen. 1-bromonaphthalene was then added to provide an indication of GC/MS performance.

### **Aqueous Samples**

Aqueous samples were analysed separately for extractable and volatile organic compounds.

10ml of the original sample were transferred to a 20ml headspace vial for volatile organic compound (VOC) analysis. The rest of the sample was extracted with pentane. Prior to the extraction, samples were spiked with deuterated (d8) naphthalene (an internal standard) at a concentration of 150 ug/l. 20 ml 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 20 ml pentane was added and the extraction procedure repeated. The cleanup procedure employed was as described above for solid samples.

### **Chromatographic 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.

Instrumentation for the analysis of volatile organic compounds was a Hewlett Packard (HP) 5890 Series II gas chromatograph with HP 19395-A headspace sampler, interfaced with a HP Chem-Station data system, and linked to a HP 5970 Mass Selective Detector operated in scan mode. Again, the identification of compounds was carried out using a combination of computer matching (against a HP Wiley 138 library of 138 000 mass spectra) and expert interpretation.

Results are reported as a list of those compounds reliably and tentatively identified. Match qualities of 90% or greater are assumed to give reliable identifications; tentative identification refers to qualities between 51% and 90%. Analytes yielding match qualities of 50% or less are assumed to be unidentified.

## **2. Metals analysis**

### **Solid samples**

Samples were dried in an oven until weight readings became constant. They were then homogenised using a pestle and mortar and passed through a 2mm sieve to exclude stones and other large debris. A portion of sample (0.5g) was placed in a 120ml Teflon microwave vessel fitted with a screw cap and pressure relief valve. Deionised water (10ml), concentrated hydrochloric acid (7.5ml) and concentrated nitric acid (2.5ml) were then added to the pressure vessel. The vessel was then sealed and the sample digested in a microwave oven (model MDS-2000, CEM Corp.) at full power (630 watts) for 1 hour.

The digests were allowed to cool to room temperature, filtered and diluted to a final volume of 50ml.

Standard reference materials (PACS-1; trace elements in marine sediments) and blank samples were prepared alongside the environmental samples. All samples were analysed by ICP-AES as described below.

### **Aqueous samples**

Water samples were preserved in 5% v/v nitric acid on arrival. 50 ml was transferred to a 120 ml Teflon microwave vessel and digested using the same procedure and programming conditions described above. After cooling to ambient temperature, samples were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed. A quality control standard (internally prepared at a concentration of 8.0 mg/l) and a blank sample were prepared with the batch of samples. Both were prepared in 5% v/v nitric acid.

### **ICP-AES Analysis**

Analysis was carried out using an inductively coupled plasma atomic emission spectrometer (Varian Liberty-100 sequential spectrometer). The following metals were quantified directly:

cadmium (Cd); chromium (Cr); cobalt (Co); copper (Cu); lead (Pb); manganese (Mn); nickel (Ni) and zinc (Zn).

Mercury was determined separately using the same instrumentation operating in cold vapour generation mode. Digests prepared as described above were reacted with sodium borohydride (0.6% w/v); sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar) to reduce the dissolved mercury (II) to mercury (0) vapour. The mercury vapour was drawn through the spectrometer in a stream of argon.

For all metals, calibration was by comparison with matrix matched calibration samples. Concentrations of 10ug/l and 100ug/l were used for mercury analysis; a multi-element standard at 10mg/l was used for all other metals. A quality control sample prepared from different stock standards was also analysed; concentrations were 80ug/l for mercury and 8mg/L for each of the other metals analysed. Any samples falling outside the calibration range were diluted and reanalysed.

## Results and discussion

The results of organic screening analysis are presented in the Table 1. The list of compounds reliably identified in the samples is presented in the Table 2.

Sample code	Number of compounds isolated	Number of reliably identified compounds	Number of reliably identified organohalogen compounds	Number of tentatively identified organohalogen compounds
LA8007	27	17(63%)	10	0
LA8008	45	22(49%)	6	2
LA8070	15	6(40%)	2	0
LA8071	17	8(47%)	4	0
LA8003	32	11(34%)	8	3
LA8002	22	1(5%)	0	2
LA8005	8	3(38%)	0	1
LA8001	5	2(40%)	0	0
LA8009	3	0	0	0
LA8010	32	3(9%)	0	0
LA8011	16	0	0	0

*Table 1. Results of organic screening analysis for the groundwater sample LA8001; soil sample LA8007; lagoon sediment sample LA8008; wood litter samples LA8070 and LA8071; river sediment samples LA8003, LA8005, LA8002, LA8009, LA8010, LA8011; effluents LA8004 and LA8006.*

Both the lagoon sediment LA8008 and soil LA8007 from the Rhodia dumpsite were found to be contaminated with a wide range of organic compounds, including the persistent organochlorines hexachlorobenzene, pentachlorobenzene and hexachloro-1,3-butadiene (HCBd). The soil sample also contained octachlorostyrene, along with a range of di-, tri- and tetrachlorobenzenes. Both hexachlorobenzene and pentachlorobenzene were also detectable in the wood litter

samples collected from the base of the trees on this dumpsite. Hexachlorobenzene was detected in higher concentrations than the other contaminants in each of these samples. Additionally, tetrachloroethene (also known as tetrachloroethylene or perchloroethylene) and hexachloro-1,3-butadiene were identified in one wood litter sample LA8071. It is clear that this dumpsite has been used for the disposal of hazardous chlorinated wastes. The compounds named above have been frequently found as major pollutants in soils, river sediments and aquatic organisms in the vicinity of the industries that produce, use or dispose organochlorine compounds (Amaral *et al.* 1996; Oxyinos *et al.* 1995; Dethlefsen *et al.* 1996; ATSDR 1997). Hexachlorobenzene and octachlorostyrene have been found in blood of aluminium foundry workers (Selden *et al.* 1997) using hexachloroethane for degassing. The characteristics of the wastes from Rhodia dumpsite bear some similarities to those common to wastes from oxychlorination processes (see eg Johnston *et al.* 1996, Stringer & Temuge 1998).

Name of compounds	Sample code
Benzene, hexachloro-	LA8007, LA8008, LA8070, LA8071
Benzene, pentachloro-	LA8007, LA8008, LA8070, LA8071
Benzene, 1,2,3,4-tetrachloro-	LA8007
Benzene, 1,2,4-trichloro-	LA8007
Benzene, 1,2,3-trichloro-	LA8007, LA8003
Benzene, 1,3,5-trichloro-	LA8007, LA8008, LA8003
Benzene, 1,3-dichloro-	LA8007, LA8008, LA8003
Benzene, 1,4-dichloro-	LA8007
Benzene, chloro-	LA8008
1,3-Butadiene, hexachloro-	LA8007, LA8008, LA8071
Benzene, 1-bromo-2,6-dichloro-	LA8003
Benzene, 1-bromo-3,5-dichloro-	LA8003
Benzene, 1-chloro-2-methyl-	LA8003
Styrene, octachloro-	LA8007
Ethene, tetrachloro-	LA8071
Phenol, 4-phenyl-2',4',6'-trichloro-	LA8003
Toluene, 2,4,5-tribromo-	LA8003
Phthalates	LA8001
Benzaldehyde	LA8002
Alkylated benzenes	LA8008, LA8071
1,1'-Biphenyl	LA8008
Terpenes	LA8007, LA8008, LA8005
PAHs	LA8008
tert-Dodecanethiol	LA8008
Straight chain aliphatic hydrocarbons	LA8008, LA8003, LA8070, LA8071

Table 2. List of compounds reliably identified in the groundwater sample LA8001; soil sample LA8007; wood litter samples LA8070 and LA8071; sediment samples LA8008, LA8003, LA8002, LA8005, LA8009, LA8010, and LA8011.

The results for the metals analysis are presented in Table 3 below. This table also includes typical background concentrations for sediments (see eg Salomons and Forstner 1984, Bryan and Langston 1992, Palanques 1993, Palanques *et al.* 1995). Variations in geochemistry will cause some areas to exceed these concentrations naturally. Nevertheless, they remain a useful guideline.

Cadmium was not detected in any of these sediment samples. Concentrations of cobalt, copper, lead, manganese and zinc are well within the range expected in uncontaminated areas. The samples from the Rhodia dumpsite discussed above (LA8007 and LA8008) contained mercury concentrations significantly elevated above “background” levels which may be expected for uncontaminated soils. In the case of the lagoon sediment, mercury was found at a concentration of 21.4 ppm, more than 40 times higher than the maximum which may be expected in typical uncontaminated soils and sediments. The Rhodia site, therefore, contains significant metal and organochlorine contamination.

<b>Sample number</b>	<b>Mn (ppm)</b>	<b>Cr (ppm)</b>	<b>Zn (ppm)</b>	<b>Cu (ppm)</b>	<b>Pb (ppm)</b>	<b>Ni (ppm)</b>	<b>Co (ppm)</b>	<b>Cd (ppm)</b>	<b>Hg (ppm)</b>
LA8002	307.6	38.3	74.5	16.3	15.3	19.9	10.7	n/d	1.8
LA8003	340.7	61.9	100.5	22.7	19.1	29.9	15.5	N/d	2.1
LA8005	932.0	57.5	231.5	41.0	39.5	39.5	15.5	N/d	15.6
LA8007	309.3	54.4	122.5	34.8	33.8	35.8	14.2	0.98	21.4
LA8008	273.8	40.6	93.0	22.4	23.8	26.6	17.3	N/d	3.74
LA8009	190.3	100.0	72.4	17.9	20.4	69.4	9.2	n/d	1.43
LA8011	102.4	22.8	40.8	5.8	14.1	8.7	3.4	n/d	0.97
LA8010	184.5	73.7	63.9	14.9	20.6	77.8	7.73	n/d	1.44
<b>Back-ground</b>	<b>&lt;1000</b>	<b>&lt;50</b>	<b>&lt;100</b>	<b>&lt;50</b>	<b>&lt;50</b>	<b>&lt;50</b>	<b>&lt;50</b>	<b>&lt;0.5</b>	<b>&lt;0.5</b>

*Table 3. Concentrations of metals in soil sample LA8007 and sediment samples LA8002, LA8003, LA8005, LA8008, LA8009, LA8010, and LA8011 and for a typical uncontaminated sediment.*

As described above, three sediment samples were collected from the Rio Cubatao. Sample LA8003 was collected from the river upstream of the confluence with the Rio Pereque and would thus be expected to be relatively unaffected by contamination from the Rhodia site. A number of organohalogen compounds (both chlorinated and brominated) were detected in this sample. Again, elevated mercury levels were detected in this sediment. The organohalogens identified, including bromodichlorobenzenes, tribromotoluene and 4-phenyl-2,4,6-trichlorophenol, do not appear to be associated with the wastes contained within the Rhodia dumpsite, even despite the fact that sample LA8003 contained several chlorinated compounds (chlorinated benzenes) which were also found in the samples from the Rhodia dumpsite. It is possible that they have arisen as a result of contamination from other sources, although it is not possible to speculate further on the basis of existing data. Given the hazardous nature of these compounds, urgent action is required to determine the extent of contamination in the river and, if possible, to locate the sources such that further contamination can be prevented. Moreover, it may be necessary to recover and contain these sediments in order to avoid more widespread contamination of the river over time.

Sediment samples LA8002 and LA8005 that were collected further downstream from the Rhodia dumpsite (adjacent to the Carbochloro plant) did not show significant contamination with the organic compounds, however, organohalogen compounds were detected in trace amounts. Both samples contained a contaminant that was tentatively identified as hexachlorobenzene. Chromatographic retention times were as expected for hexachlorobenzene, but it was present in concentrations too low to allow reliable identification (greater than 90%

certainty on a mass spectral match). The presence of hexachlorobenzene might be expected as a result of contamination leaching from the Rhodia dumpsite.

Additionally, brominated compound was identified in sediment sample LA8002, again with tentative degree of probability due to low concentration of this compound. The source of brominated chemicals in this sample is unknown, however, as it was discussed above, organic compounds containing bromine were also identified (to a high degree of probability) in the sediment sample LA8003 collected from the Rio Cubatao upstream.

The levels of mercury in these samples were again higher than may be expected - 1.8 ppm in the sample LA8002. A more extensive sampling programme would be required in order to determine the extent to which the Rhodia dumpsite was acting as a source of contamination to the river and surrounding environment. The sediment sample LA8005 collected from the bank of the Rio Cubatao directly opposite Carbochloro did show substantial elevation of mercury levels (15.6 ppm) above background. The source of this mercury remains unclear, although the possibility that it has arisen as a result of the manufacture of chlorine at the Carbochloro mercury cell chloralkali facility should be investigated further. It is understood that this section of the river was being dredged at the time of sampling. In this case the dredged material could act as a significant source of volatile mercury to the atmosphere, as well as to the water through resuspension of contaminated sediment. This also applies to the organic contamination discussed above. The final fate of this dredged material should be monitored closely.

In addition to the Rhodia dumpsite on the banks of the Rio Cubatao, Rhodia also owns a landfill which is located on the banks of the Rio Branco in the Guarentenário district of São Vicente city. Three sediment samples (LA8009, LA8010 and LA8011) collected from the Rhodia landfill contained organic contaminants of particular significance. Nevertheless, all three contained concentrations of chromium, nickel and mercury which were slightly above what would be expected as maximum values in uncontaminated sediments. It is possible, therefore, that wastes contained within this landfill site are acting as significant sources of heavy metal contamination to the Rio Branco.

Finally, a single sample of water LA8001 collected from a private well in the residential area of Guarentenário District was found to contain a number of organic compounds including the phthalate esters diisobutyl phthalate and di-n-butyl phthalate. While the sources of these contaminants (used as plasticisers in PVC products, as a base for printing inks and in numerous other industrial products) cannot be determined, the possibility that they have been introduced to the groundwater as contaminants in leachate from the nearby landfill should be investigated.

## **Summary**

Eleven samples have been collected from the Rio Cubatao/Rio Pereque and Rio Branco systems to determine possible sources and distribution of the persistent environmental pollutants in these regions. The analyses carried indicate contamination of soil, wood litter and river sediments along Rio Cubatao with environmentally harmful organochlorines which could be associated with the Rhodia dumpsite. Elevated levels of mercury have been also determined in the majority of the samples from this site. One sediment sample collected from the Rio Cubatao unlikely to be influenced by the Rhodia dumpsite also contained a range of halogenated organic compounds (as organochlorines and organobromines). It needs further investigation to identify the source of contamination of this part of the Rio Cubatao. One sample collected downstream

of Carbocloro Industrias Quimicas S.A. contained high level of mercury which might be associated with of the manufacture of chlorine at the Carbocloro mercury cell chloralkali facility. Three sediment samples collected from another landfill operated by Rhodia S.A. (the Rio Branco, Guarentenarío district of Sao Vicente city), contained slightly elevated levels of chromium, nickel and mercury. A single groundwater sample collected from this area has shown contamination by phthalate esters that could leachate from the nearby located Rhodia landfill.

*NB: brief summaries of the toxicology and regulatory status of some of the key organic contaminants identified in this study are included as an annex to this report.*

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**ANNEX: BRIEF TOXICOLOGICAL AND REGULATORY PROFILES  
FOR SOME KEY CONTAMINANTS IDENTIFIED**

## 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. This compound is highly persistent and bioaccumulative. Once introduced into environment, HCB strongly adsorb to soil materials and almost no desorption take place (Bahnick & Doucette 1988). HCB can be transported for long distances through the air attached to the soil particles. If HCB has been discharged directly into the river or sea with industrial wastewater, it partitions in to aquatic organisms, particularly fish with high lipid content (Pastor *et al.* 1996; Lee *et al.* 1997). It has been detected in environmental samples and living organisms from around the world, and is recognised as a global pollutant (US EPA, 1989; Mes *et al.* 1990; Kovats *et al.* 1993; Struger *et al.* 1993; Weseloh *et al.* 1995).

HCB is highly 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 (IARC 1987). Hexachlorobenzene may damage the developing foetus, liver, immune system (increasing risk of infection), thyroid, and kidneys. 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; US EPA 1989). Recent research (van Birgelen 1988) 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.

On account of HCB persistence in the environment and its toxicity, this compound is a regulated chemical. It is included in List 1 of EC Council Directive 76/464/EEC (EC 1976), regarding pollution caused by certain dangerous substances discharged into the aquatic environment. It is further included in Annex 2 of EC Council Directive 86/280/EEC (EC 1986), in which special provisions and quality objectives for discharges of certain dangerous substances included in List 1 of the Annex to Directive 76/464/EEC (EC 1976) are laid down. Provisions for HCB are also set out in Directives 83/101/EEC (EC 1983)(Protocol for the Protection of the Mediterranean Sea against pollution from land-based sources) and 78/319/EEC (EC 1978)(on toxic and dangerous waste).

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 has been selected and is included on the OSPAR 1998 List of Candidate Substances, Annex 3 of the OSPAR Strategy with regard to Hazardous Substances (OSPAR 1998b).

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). As such, European countries will be required to take effective measures to eliminate the production and use of this compound, even as an unintentional by-product.

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## HEXACHLORO-1,3-BUTADIENE

Hexachloro-1,3-butadiene (HCBD) is not found naturally in the environment. HCBD either commercially manufactured or is known to be a by-product of the manufacture of chlorinated hydrocarbons, particularly the production of PVC and the secondary oxychlorination of EDC wastes in the manufacture of solvents (ATSDR, 1992; US EPA, 1986, Johnston *et al.* 1994). It is also reported as a contaminant in technical formulations of pentachlorophenol, used widely as a wood preservative (Goodrichmahoney *et al.* 1993).

It has historically been used as a solvent for elastomers; heat transfer liquid; transformer and hydraulic fluid; to wash liquor for removing C4 and higher hydrocarbons; solvent for natural rubber, synthetic rubber and other polymers; pesticide; insecticide; herbicide; algicide; chemical intermediate; recovery of chlorine fluid for gyroscopes; recovery of chlorine from "sniff" gas in chlorine plants; and intermediate in the manufacture of rubber compounds and lubricants.

Hexachlorobutadiene is toxic compound. Acute toxic effects may include the death of animals, birds, or fish, and death or low growth rate in plants. Acute effects are seen two to four days after animals or plants come in contact with a toxic chemical substance (US EPA 1986). Chronic toxic effects may include shortened lifespan, reproductive problems, lower fertility, and changes in appearance or behavior. Chronic effects can be seen long after first exposure(s) to a toxic chemical. Hexachlorobutadiene has high acute and chronic toxicity to aquatic life (US EPA 1986).

Hexachlorobutadiene (HCBD) is a potent kidney toxicant in rats causing damage to the proximal tubules (Pahler *et al.* 1997; Rosner *et al.* 1998; Werner *et al.* 1995; Nakagawa *et al.* 1998). An animal study found kidney tumors in rats exposed to low levels of hexachlorobutadiene (US EPA, 1986); studies in rabbits found kidney and liver damage from contact with the chemical on the skin for a short time.

It has been determined as a possible human carcinogen (US EPA, 1986; Lewis & Tatken, 1989; Bretherick, 1986; American Conference of Governmental Industrial Hygienists, 1988). If ingested, HCBD concentrates in the kidney, interferes with fundamental processes of cell respiration and can, as a result of conjugation with other compounds in the body, react with DNA resulting in cell death or the development of tumours (ATSDR 1992). Short and longer-term exposure to very low doses via food, induced kidney and liver damage in laboratory animals, with juveniles more at risk than adults.

Symptoms of exposure to high levels of this compound may include irritation of the skin, eyes, mucous membranes and lungs; liver and kidney damage; and central nervous system effects (Dreisbach, 1983). It may cause corrosion (Aldrich Chemical Company, 1988). Other symptoms may include hypotension, cardiac disease, chronic bronchitis, disturbance of nervous function and chronic hepatitis (World Health Organization, 1989).

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## CHLORINATED BENZENES

Dichlorobenzenes are potent liver and, to a lesser extent, kidney toxins (Valentovic *et al.* 1993). Their toxicity depends on their precise isomeric structure, with 1,2-dichlorobenzene (ortho-DCB) generally reported as more toxic to laboratory rats than 1,3- (meta-) and 1,4- (para-) substituted isomers (Valentovic *et al.* 1993, Umemura *et al.* 1996). Toxicity also varies between organisms, with large differences in the extent of liver damage at a given dose even between different strains of rat (Kulkarni *et al.* 1996). 1,4-dichlorobenzene (p-DCB) is a listed animal carcinogen (ATSDR 1989, Umemura *et al.* 1992, Bornatowicz *et al.* 1994). Similarly, 1,2-DCB (o-DCB) has been classified as “possibly carcinogenic to humans” under Canadian Environmental Protection Act (Meek *et al.* 1994). High acute exposure to dichlorobenzenes can cause central nervous system depression (Budavari 1989).

The major source of o-DCB emission to the atmosphere has been reported to be solvent applications, which may emit 25% of annual production to the atmosphere. Use of m-DCB, as a fumigant will release it directly to the atmosphere. The major source of p-DCB emission to the atmosphere is volatilisation from use in toilet bowl deodorants, garbage deodorants, and moth flakes. It is worth noting that the main application of two of these compounds is based on their toxicity. Dichlorobenzenes have also been used as solvents for waxes, gums, resins, tars, rubbers, oils, and asphalts; as fumigants, insecticides, and degreasing agents for metals, leather, and wool; as an ingredient of metal polishes; and as intermediates in dye manufacture.

If released to soil, o-DCB, m-DCB and p-DCB can be moderately to tightly absorbed. Leaching from hazardous waste disposal areas has occurred and the detection of o-, p- and m-DCB in various ground waters indicates that leaching can occur. o-DCB was reported as a useful marker of the extent of contamination for untreated sewage discharges (Chapman *et al.* 1996). Dichlorobenzenes are included on Annex 1D of the Ministerial declaration indicating that they should be considered for prioritization in the future.

Trichlorobenzenes induce similar toxic effects in a range of aquatic and terrestrial organisms. In addition to their environmental persistence, both di- and tri-chlorobenzenes have a high tendency to bioaccumulate, with bioconcentration factors for invertebrates, fish and mammals in the range of 100 to 10000 (IUCLID 1996). Dichlorobenzenes are relatively volatile compounds, a property which has led to their use as moth repellents (Mizutani *et al.* 1994). Inhalation must therefore be considered as a potential route of entry to the body in humans and animals exposed to contaminated effluents and sludges.

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## DIISOBUTYL PHTHALATE AND DI-n-BUTYL PHTHALATE

Phthalate esters, more often referred to as the phthalates, are used as plasticisers or other additives in virtually every major product category, including construction, automotive, household products, apparel, toys, packaging, and medical products (Kemi 1994). Within these sectors, 90% is used in the production of soft PVC. 10-15 years ago the two most abundantly produced phthalate esters were diethylhexyl phthalate (DEHP) and dibutyl phthalate (DBP) (Menzert & Nelson 1986). More recent investigations suggest a significant market shift away from these phthalates to longer chain and isomeric phthalates in a number of product groups (e.g. Stringer *et al.* 1997).

Phthalates are persistent in the environment 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. The summary below illustrates the scope of the toxicological problems associated with these two isomers of dibutyl phthalate.

- Effects on the liver (Chan & Meek 1994; Life Systems, Inc. 1990)
- Effects on the kidney (Chan & Meek 1994; Life Systems, Inc. 1990).
- Damage to the male and female reproductive system (Chan & Meek 1994. Reproductive success can be impaired by DBP (Chan & Meek 1994; Ema *et al.* 1995; Life Systems, Inc. 1990, Wine *et al.* 1997).
- Teratogenicity (malformation of the offspring) (Chan & Meek 1994; Ema *et al.* 1993; Ema *et al.* 1995).
- There is some evidence for impacts of DBP on sperm production (Life Systems, Inc. 1990, Wine *et al.* 1997).
- Some phthalates including DBP (Jobling *et al.* 1995) are known to be capable of binding to the human oestrogen receptor and may demonstrate weak oestrogenic activity.
- A group of phthalate esters including di butyl phthalate has been found to have both acute (Adams *et al.* 1995) and chronic (Rhodes *et al.* 1995) toxicity to the representatives of 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.

Because of their recognised toxicity and widespread distribution, two phthalates, including dibutyl phthalate, 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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