Investigation of the distribution of organic compounds and heavy metals in wastes associated with the Bely Island incinerator, St.-Petersburg area, Russia.

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1 EXECUTIVE SUMMARY

Three samples of waste materials associated with the incinerator located on Bely Island, St.-Petersburg, were collected by Greenpeace International during January and February 2001:-

- Wastewater discharged to Finski Bay
- Solid waste collected form the inside surface of the incinerator stack
- Ash, suspected to be fly ash from pollution control filters

All three samples were returned to the Greenpeace Research Laboratories and analysed for the presence of heavy metals and organic contaminants.

Of the three samples, only the ash sample contained heavy metals at levels significantly elevated above background. In the case of chromium (0.59 g/kg), cobalt (0.027 g/kg) and nickel (0.29 g/kg), concentrations were higher in ash from the Bely incinerator than in fly ashes from typical MSW incinerators in USA and Spain. Concentrations of copper (0.71 g/kg) and lead (0.43 g/kg) were also significant in terms of the potential for wider distribution of these toxic metals following disposal of the ashes. The presence of these metals in the ash undoubtedly results from their presence as components or contaminants in the waste feedstock, and indicates the likely levels of contamination associated with fly ash escaping from the stack.

The solid residues from the inside surfaces of the incinerator stack contained the widest range of organic contaminants, including di-, tri-, tetra- and pentachlorobenzene. These organochlorine compounds may have been carried through from incomplete combustion of contaminants in the waste feedstock, or possibly generated through de-novo sysnthesis in the gas cooling phase. The ash sample contained fewer organic compounds, with traces only of 1,4-dichlorobenzene. No organic compounds could be identified in the wastewater sample.

These results confirm the hazardous nature of the ashes generated by the incinerator and highlight the potential for further environmental contamination to result from onward handling or disposal of the ash residues. In addition, the presence of chlorinated benzenes in accretions on the inside of the incinerator stack indicates the presence of a significant chlorine content of the wastes incinerated and suggests that stack emissions result in ongoing release of these and other chlorinated organic pollutants, as well as heavy metals, to the surrounding environment.

2 SAMPLING PROGRAM

During January and February 2001, three samples were collected of waste materials association with the incinerator located on Bely Island, St.-Petersburg area, Russia. The samples included a wastewater, a solid waste and a sample of ash suspected to be fly ash. Full descriptions of the samples are presented in Table 1.

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

Sample Number	Sample Description	Sample Location
Incinerator, Bely Island, St.-Petersburg area, Russia		
BT01013A	Wastewater	Discharge from incinerator into Finski Bay.
BT01013B	Solid waste	Deposits from inside of incinerator stack
BT01021	Ash	Suspected to be fly ash from the filters of the incinerator stack

Table 1. Description of the samples collected on the Island Bely, Russia, 2001

3 RESULTS AND DISCUSSION

The results of the organic screen analysis are presented in Table 2, including a breakdown of the groups of organic compounds identified in the samples. Heavy metals analysis results are presented in Table 3.

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

3.1 Organic analysis

Organic compounds found in the solid waste sample BT01013B collected from inside of the incinerator stack were dominated by linear aliphatic hydrocarbons. Ash sample BT01021 also contained aliphatic hydrocarbons as main constituents. One aromatic hydrocarbon, trimethylbenzene, was also detected in the ash sample BT01021.

The occurrence of alkylbenzenes in the environment is likely largely due to their presence in crude oil and petroleum products. The alkylbenzenes are highly resistant to degradation and may accumulate in sediments (Preston & Raymundo 1993). Alkylbenzenes are useful markers of oil-related pollution (Chalaux *et al.* 1995) and due to their stability, they are very useful in tracing the transport of contaminants from their point sources.

In terms of toxicity, acute exposure to alkylbenzenes can cause central nervous system (CNS) depression. With impaired reaction times and impaired speech the two most commonly noted CNS effects (Klaassen *et al.* 1996). All alkylbenzenes can be irritating to the eyes and mucous membranes and can cause irritation and burning of the skin. All are narcotics at high concentrations (Budavari *et al.* 1989).

Sample Number	**BT01013A**	**BT01013B**	**BT01021**
No. of organic compounds isolated	2	59	22
No. of organic compounds reliably identified	None	24(41%)	12(55%)
Groups of organic compounds reliably identified			
ORGANOHALOGENS			
Benzene, 1,2-dichloro-		*	
Benzene, 1,3-dichloro-		*	
Benzene, 1,4-dichloro-		*	*
Benzene, 1,2,4-trichloro-		*	
Benzene, 1,2,3,5-tetrachloro-		*	
Benzene, 1,2,3,4-tetrachloro-		*	
Benzene, pentachloro-		*	
ALIPHATIC HYDROCARBONS			
Linear		16	8
Cyclic		1	2
AROMATIC HYDROCARBONS			
Alkylated benzene			1

*Table 2. Organic chemical results. For groups of organic compounds, the number given is the number of compounds reliably identified; *(x) signifies the number of compounds identified at trace levels using a selective ion monitoring (SIM) method. Incinerator on Island Bely, Russia, 2000.*

Chlorinated organic compounds were detected in samples BT01013B and BT01021, though only at trace levels (detectable through monitoring for selected ions). Sample BT01013B contained three isomers of dichlorobenzene, one of trichlorobenzene, two of tetrachlorobenzene and pentachlorobenzene. Sample BT01021 contained only one organochlorine compound, p-dichlorobenzene.

Although chlorobenzenes can be produced as products of incomplete combustion in incinerators during processing materials containing chlorine either in organic or inorganic forms (Halonen *et al* 1995), their presence in the particles attached to the inside of the incinerator stack might also arise from their presence in the incinerator feedstock. Chlorobenzenes are the group of compounds which known to be precursors of dioxins (Huang and Buekens 1995).

Dioxins are produced as unintentional by-products of many manufacturing and combustion processes, especially processes that use, produce or dispose of chlorine or chlorine derived chemicals. They are produced by all types of incinerators. Research has shown that while dioxins can be destroyed in the combustion zone of incinerators (under specific conditions), they can be regenerated in the post-combustion zone by processes that are dependent on the temperature profile for gas cooling (Blumenstock *et al.* 2000, Huang and Buekens 1995, Fangmark *et al.* 1994). The predominant formation pathway of dioxins has been reported to be *de novo* synthesis (Johnke and Stelzner 1992), though they are also formed from precursors that are either constituents of the waste or are also formed by chemical recombination of materials in the waste.

None of organic compounds was detected in the wastewater sample BT01013A.

3.2 Heavy metals analysis

Sample Number	**BT01013A**	**BT01013B**	**BT01021**
Concentration	ug/L	mg/kg dry weight	mg/kg dry weight
Cadmium	<10	<1	24
Chromium	<20	27	593
Cobalt	<20	4	27
Copper	<20	16	711
Lead	<30	7	431
Manganese	161	253	1096
Mercury	<1	0.39	1.11
Nickel	<20	6	298
Zinc	19	144	2609

Table 3. Heavy metal analysis results, incinerator on Island Bely, Russia, 2000.

The wastewater sample BT01013A and the solid waste sample BT01013B did not contain any of the metals analysed for at concentrations above those generally found in uncontaminated freshwaters or soils. However, the fly ash sample (BT01021) contained significant concentrations of a number of toxic and potentially toxic heavy metals.

Heavy metals are not destroyed by incineration but are simply concentrated in the remaining ashes, or released to the environment via stack emissions. The concentrations of heavy metals in the ashes are highly dependent on the amounts of these metals in the wastes being incinerated. Table 4 shows the concentrations of heavy metals detected in fly ash from two Spanish MSW incinerators (Alba *et al.* 1997) and in fly ash from a US incinerator (Bucholz and Landsberger 1995). This data clearly demonstrate the high variability in metal concentrations in fly ashes; nevertheless, the concentrations are clearly very high compared to background levels in the environment (Bucholz and Landsberger 1995).

The fly ash sample BT01021 contained copper, lead, mercury and zinc at concentrations within the ranges reported above. The concentration of chromium and cobalt and nickel in this sample were 1.5-3.5 times above the highest values reported in Table 4. Cadmium was the only metal present at a concentration significantly lower than the reported values.

Each metal has its own major source in the raw waste. For example, mercury is present due to the disposal of batteries, fluorescent light bulbs and paints (Carpi 1997). Cadmium is present in paints, PVC plastics and the pigments used to colour plastics. Lead is present in batteries, plastics and pigments (Valerio *et al.* 1995, Korzan and Heck 1990).

Element	Concentration (mg/kg dry weight)	
	Spain[1]	USA[2]
Cadmium	246-266	92 ± 2
Chromium	146-169	365 ± 18
Cobalt	11.3-13.5	---
Copper	390-530	1322 ± 90
Lead	3200-4320	5461 ± 236
Mercury	59.1-65.0	0.29 ± 0.03
Nickel	---	117 ± 2
Zinc	13360-13490	9382 ± 208

Table 4. Ranges of elemental abundance in MSW incinerator fly ashes.
Source; (1) Buchholz and Landsberger (1995), (2) Source: Alba et al. (1997).

Heavy metals can remain in their original form during incineration or may react to form new compounds such as metal oxides, chlorides or fluorides (Dempsey & Oppelt 1993). These changes are dependent on the composition of the wastes to be incinerated, and the forms that the metals are in.

Because of their contamination, disposal of incinerator ashes presents significant environmental problems. The fly ash from the Bely Island incinerator is believed to be incorporated into bricks intended for use within the construction industry. It is of concern that a study on the use of fly ash for construction material has shown that metals may leach from these composite materials (Fleming et al. 1996). The future releases these metals due to erosion over time could result in the release of substances back to the environment and, therefore, potentially to human exposure.

Globally, the majority of incinerators ashes are disposed to landfill. This can result in contamination of sub-soils over time with toxic compounds in leachate flowing from the wastes. In some cases, the contamination of groundwater by compounds that have leached from the waste, in particularly, heavy metals like lead and cadmium from fly ash has been documented. The process of incineration greatly enhances the mobility and bioavailability of toxic metals compared with raw municipal waste (Schumacher *et al.* 1998). Consequently, there is greater leaching of metals into the environment from ashes dumped in landfill than from unincinerated waste. In an attempt to reduce leaching, fly ash is sometimes stabilised in cement before disposal. Although this method reduces the immediate leaching of heavy metals and other toxic chemicals, weathering and erosion over time will ultimately cause their release back to the environment. In their document on dangerous substances in waste, the European Environment Agency (EEA) stipulate that fly ash cannot be landfilled without pre-treatment (EEA 2000).

Depending on the pH of the soil, rainfall can leach metals from landfilled ash into groundwater used for drinking. Leaching is greatest under acidic conditions. Since the ashes are frequently co-disposed with ordinary municipal waste, the surrounding soils can be acidified through organic acids, which are the breakdown products of landfilled waste. This leads to greater leaching of heavy metals (Marty 1993). Significant releases of cadmium, lead and chromium have been found to leach from ashes under neutral conditions with distilled water (Mangialardi *et al.* 1998). Lead has been deemed the most leachable heavy metal from fly ash (Chandler *et al.* 1997). In terms of very long time periods over hundreds to thousands of years, it has been noted that little is known about the long-term leaching behaviour of incinerator residues (Chandler *et al.* 1997). This is of immense concern given that landfills are unlikely to be managed indefinitely.

In addition to the concentration of toxic metals in ashes, a proportion of these toxic trace metals is emitted in the stack gases of incinerators to atmosphere. The major proportion of metals is generally present in fly ash and bottom ash with the exception of mercury where the greater proportion is vented via the flue stack.

On a global scale, incineration contributes significantly to atmospheric emissions of many heavy metals (EEA 2000). Within the EU, figures for 1990 estimated incineration to be responsible for 8% (16t/yr) of all cadmium emissions and 16% (36t/yr) of mercury emissions. Emissions of chromium and lead amounted to 46 tonnes and over 300 tonnes respectively (EC 1998). A variety of flue gas treatment systems have been devised in order to reduce stack emissions of heavy metals (EEA 2000). Stack gas data for hazardous waste incinerators indicate that the fabric filter removal efficiencies (with the metals retained in the ash) are in the order of 95% for most metals except mercury.

The EEA (2000) notes that control of mercury emissions constitutes a special problem in incineration. Almost 100% of the elemental mercury present in waste is emitted *via* the stack gases because it does not adsorb to filter dusts or ashes. Elemental mercury comprises about 20-50% of the total mercury emitted. The remainder is in the form of divalent mercury, which may be predominantly mercury chloride ($HgCl_2$). After emission to the atmosphere, divalent mercury, which is water soluble, may be deposited close to the incinerator. On the other hand, elemental mercury may be transported for long distances by atmospheric currents before it is eventually converted to the divalent form. This can then become deposited on the ground (Carpi 1997). A number of reported cases exist of the contamination of areas surrounding municipal waste incinerators (including those fitted with pollution control equipment such as electostatic precipitators) with metals including cadmium and lead and mercury (Collett *et al.* 1998, Bache *et al.* 1992, Carpi & Weinstein 1994).

Many heavy metals are known to exert a broad range of toxic effects on humans, terrestrial and aquatic life and plants, even at low concentrations. A number of metals also have the potential to bioaccumulate, including cadmium, chromium, lead, mercury and zinc (USPHS 1997, Kimbrough *et al.* 1999, MINDEC 1995). In addition, certain forms of cadmium and chromium have carcinogenic properties (USPHS 1998).

A study on exposure to heavy metals in individuals residing near to incinerators investigated changes in the level of mercury between 1984 and 1994 in the hair of individuals who lived near to a hazardous waste incinerator in Finland (Kurttio *et al.* 1998). Mercury concentrations were found to increase in workers at the plant and in residents such that levels increased with decreasing distance from the incinerator. The result indicated that the incinerator was the likely source of exposure among residents.

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APPENDIX 1 ANALYTICAL METHODOLOGY

A1.1 Organic analysis

A1.1.1 Preparation of samples for organic screen analysis

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

A1.1.1.1 Solid Samples

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

Extracts were decanted, filtered through a pre-cleaned hydrophobic phase separator filter and collected in reagent tubes. 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 elluent 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.

A1.1.1.2 Aqueous Samples

Prior to the extraction, samples were spiked with deuterated naphthalene (an internal standard) at a concentration of 10mg/l. 20ml of pentane was 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 pre-cleaned hydrophobic phase separator filter and collected in a pre-cleaned reagent tube. The aqueous sample was acidified to pH 2 with 10% nitric acid, a second portion of 20ml pentane was added and the extraction procedure repeated. Both extracts were combined and cleaned up as described above for solid samples.

A1.1.2 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. Also, all extracts were analysed using selective ion monitoring (SIM) method against two standard solutions. The lists of compounds contained in Standard I and Standard II are presented below. All individual standards were obtained from Sigma Aldrich Co. Ltd., Supelco, UK.

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

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

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

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

A1.2. Heavy Metal Analysis

A1.2.1. Preparation of samples for heavy metal analysis

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

A1.2.1.1. Solid Samples

Samples were air dried until weighing readings became constant (approx. 5 days). They were then crushed using a pestle and mortar until homogenous and sieved through a 2-mm mesh.

0.5 g of sample was weighed into a glass 100 ml boiling tube and to this 10 ml of deionised water was added, followed by 7.5 ml of concentrated hydrochloric acid and 2.5 ml of concentrated nitric acid. The samples were digested at room temperature overnight prior to being placed onto a Gerhardt Kjeldatherm digestion block (40 space) connected to a Gerhardt Turbosog scrubber unit (filled with 10% w/v sodium hydroxide). The samples were then refluxed at 130°C for four hours.

After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed. A Standard Reference Material, BCR-143 (trace elements in a sewage sludge amended soil), certified by the Commission of the European Communities, Brussels, and a blank sample, were prepared with the batch of samples. All were prepared in 15% v/v hydrochloric acid and 5% v/v nitric acid.

A1.2.1.2. Aqueous samples

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

A1.2.2. Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

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

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

APPENDIX 2 TOXICOLOGICAL OUTLINES FOR KEY COMPOUNDS

Chlorinated benzenes

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

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

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

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

1.1 Mono- and di-chlorobenzenes

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

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

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

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

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

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

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

1.2 Trichlorobenzenes

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

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

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

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

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

Giddings *et al* (1994a) report 1,3,5-trichlorobenzene air, drinking water, food, breast milk, though it was not found in human adipose tissue from Canada (Hermanson *et al* 1997). It can be found in association with industrial operations (Harper *et al* 1992) including PVC industry (Johnston *et al* 1993).

1.3 Tetrachlorobenzenes

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

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

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

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

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

1.4 Pentachlorobenzene

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

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

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