

Chemical Stockpiles at Union Carbide India Limited in Bhopal: an investigation

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The front cover shows the flare tower at Union Carbide India Limited. This was one of the safety systems not in operation on the night of the disaster. ©Greenpeace/Stringer

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1.1 Summary

The city of Bhopal, in Madhya Pradesh, central India, suffered the world's worst ever industrial disaster in December 1984, when around 500 000 inhabitants were exposed to toxic gas from the Union Carbide India Ltd (UCIL) pesticides factory. Somewhere around 8 000 people died immediately, with estimates ranging from 3 000 to 20 000. A further 150 000 sustained long-term injuries.

Whereas the components of the gas cloud were comparatively short-lived, the factory, now abandoned, remains heavily contaminated with a range of persistent pollutants, both organic and inorganic in nature. Greenpeace first investigated the contamination in and around the site in 1999, focussing primarily on the contamination of soil and drinking water.

However, there are also significant chemical stockpiles housed in several of the buildings of the former factory. They are investigated in this current study, which also updates the status of contamination in the soil of Union Carbide's former solar evaporation ponds (SEPs), into which process wastewaters were discharged over a period of some seven years.

Twelve "stockpile" samples were collected from six locations inside the site and four soil samples were collected from the SEPs. The stockpile samples were analysed to determine their content of carbaryl (sevin), the main product manufactured in Bhopal, as well as hexachlorocyclohexane (HCH) isomers that were also used as an insecticide under the common name of BHC, and hexachlorobenzene, one of the known contaminants of BHC. They were also screened to identify as many of the other organic constituents as possible. In addition to the stockpiles that were sampled, dumped materials were noticed at several locations and the laboratory building was found to contain many bottles of unused reagents. The soil samples from the SEPs were screened for organic contaminants and concentrations of heavy metals were determined.

Eleven of the twelve stockpile samples were found to contain carbaryl at concentrations in the low part per billion range. Ten contained hexachlorocyclohexanes, with total concentrations varying between tens of parts per million and almost 10%. HCB was detected in five samples and quantified in three. Concentrations ranged from 580 to 5 800 parts per billion.

In addition, the screening analysis was able to isolate between 19 and 214 organic compounds from this set of samples. Of these, between 9 and 102 could be reliably identified. Many of the organic contaminants were toxic and persistent organochlorines, with chlorobenzenes, chlorocyclohexanes and chlorocyclohexenes occurring most frequently. Other aromatic organochlorines present in one or more samples were chlorinated naphthalenes and derivatives thereof, chlorinated toluenes, chlorinated biphenyls, DDT and its degradation products, tetrasul and bis-(3,4-dichlorophenyl)-methane. Further aliphatic organochlorines identified were penta- and hexachloroethane and hexachlorobutadiene. Non-chlorinated organic constituents included both aromatic compounds and aliphatic chemicals. Aliphatic compounds were present in all samples except one, with between three and eighteen specific compounds being identifiable. Amongst the cyclic and polycyclic aromatic hydrocarbons, naphthalene and derivatives were found most frequently, followed by alkylated benzenes. Either naphthalene derivatives or alkylated benzenes were present in ten of the twelve samples. Several samples contained numerous compounds from these two

groups, up to a maximum of eighteen compounds. Fluorene, phenanthrene and indene, along with their derivatives, were also commonly identified.

Fewer organic contaminants were isolated and identified in the four SEP soil samples than in the stockpile samples. Nevertheless, both aliphatic hydrocarbons and chlorobenzenes were found in all four.

On a site-by-site basis, the analytical findings can be summarised as follows:

- The “BHC store” was used to store MIC imported from the USA; later, when Union Carbide began manufacturing MIC in Bhopal it stored coke. Now it contains piles of sacks of materials estimated to total over 100 tonnes. Four samples were collected here. All four samples contained carbaryl, three contained HCH isomers and two hexachlorobenzene. Sample IT02006 contained in excess of 2% of HCH isomers, the second highest in the survey. Sample IT02004 contained more isolatable and identifiable organic contaminants than any other at this location, 168 and 102 compounds respectively. The three samples in which HCHs were found also contained a variety of other organochlorines, chlorobenzenes being the most numerous. All samples contained non-chlorinated hydrocarbons, with IT02004 again containing the most, including 18 polycyclic aromatic hydrocarbons and 17 alkyl benzenes.
- The formulation shed, in the northern corner of the Union Carbide site, is where pesticides were mixed into final products for sale. This stockpile probably comprises fifteen to twenty tonnes. All three samples collected here contained carbaryl and HCH isomers, including the highest recorded concentration of HCH, almost 10%, in sample IT02012. 214 organic pollutants were isolated from sample IT02011, more than any other sample. Of these, 85 were reliably identified, primarily chlorinated benzenes, chlorocyclohexanes and chlorocyclohexenes, naphthalene derivatives and alkyl benzenes. The two other samples from this location show similar organochlorine profiles, though the nonchlorinated compounds identified included fewer naphthalene derivatives and no alkyl benzenes.
- The “small shed”, a short distance northwest of the BHC store, contains around two or three tonnes of unidentified materials in sacks. The single sample from this site contained carbaryl, alkyl benzenes and linear aliphatic hydrocarbons, but no organochlorines were identified.
- The “soapstone shed”, close to the formulation shed, contains a mixture of barrels and sacks of material, probably exceeding twenty tonnes. One sample from a sack at this location contained carbaryl at 1.8 ug/kg, the highest recorded in the current survey. HCHs were present at nearly 40 parts per million and among the 30 other organic contaminants detected were nine different chlorinated benzenes.
- The cycle shed is also in the north of the site, near to the formulation shed and the soapstone shed. It contains in excess of 20 tonnes of sevin residues, a solid black tar in rusting barrels. Further materials are stored in sacks. One sample was taken from the barrels and another from the sacks. The sample from the barrels (IT02008) was the only stockpile sample not to contain detectable concentrations of carbaryl. However, both contained tens of parts per million of HCHs and the sample from the

sacks also contained hexachlorobenzene at 1 900 parts per billion. The presence of HCH in sevin residue is surprising, since these are presumed to be directly from the manufacturing process, but are thought to be a result of contamination on the surface of the barrel with either windblown or spilled HCH. Both samples also contained chlorobenzenes and other chlorinated and non-chlorinated hydrocarbons.

- The sevin structure is the location where MIC was reacted with alpha-nathphol to produce carbaryl. The reaction vessel was full when the plant was abandoned and during 1999 it split, spilling its contents onto the ground. The one sample from this location contained carbaryl and HCH. As with the sevin residue in the cycle shed, the HCH is presumed to be a result of windblown or spilled HCH contaminating the surface of the residue pile. Chlorinated benzenes and aromatic and aliphatic hydrocarbons were also present.
- The solar evaporation ponds, a short distance north of the main factory site, received Union Carbide's liquid effluents between 1977 and 1984. They were closed in the 1990s, but the containment is visibly inadequate with rents in the liner at several locations. Each of the four soil samples from this location contained one or more chlorobenzenes and aliphatic hydrocarbons. Two of the samples also contained phthalate esters, persistent toxic compounds used in many industrial applications. Metals concentrations at the SEPs were not noticeably elevated.

The current survey clearly establishes the presence of significant stockpiles of toxic and persistent chemicals within the Union Carbide India Limited site. They are inadequately contained; indeed the materials from the sevin structure are effectively in the open. Sevin is highly toxic, disrupting transmission of signals from one nerve cell to another. However, it is comparatively easily degraded and after 18 years, concentrations appear to have declined in most stockpiles. Although they were too low to be likely to pose an immediate threat to health, the possibility of higher concentrations amongst the stockpiles cannot be discounted. The HCH isomers, though exhibiting lower acute toxicity, are highly persistent. Consequently they pose a threat to the health of exposed individuals through chronic toxicity. They can also be passed from mother to child. The HCH released from the UCIL site can be expected to remain in the environment for many years. Many of the organochlorines in the stockpiles, including the chlorobenzenes, which were also found in the SEPs, have a similar potential to cause long-term health and environmental impacts.

Local populations are vulnerable to exposure to all the chemicals found in this study through routes such as direct contact with contaminated soil or inhalation of contaminated dust. The HCH and other organochlorines may moreover be passed on in the milk of cattle that the locals graze on the site. Many of the local residents are already suffering the after-effects of exposure to the gas release; a previous Greenpeace study also found the water from several of their wells to be heavily contaminated with organochlorines. Further chemical exposure from the SEPs and the stockpiles is unacceptable.

Cleanup of the UCIL site has been discussed by different agencies over the years since the gas tragedy, but clearly has only been inadequately executed. Greenpeace has recently published standards for the full decontamination of the factory, the solar evaporation ponds and also the groundwater, to be funded by the Dow Chemical Company, who took over Union Carbide in 2001. The current findings, combined with those of previous studies, show a continuing environmental and human health threat, which should be urgently addressed.

1.2 Introduction

On the night of 2nd-3rd December 1984 there was a catastrophic release of toxic gas from the Union Carbide India Limited (UCIL) pesticide factory in Bhopal, India. The gas spread slowly over an estimated 40km² of the city, exposing over 500 000 residents (Subramanian 1985) and causing a disaster of such a scale that it was not even possible to record the number of the dead. Even the lowest estimates acknowledge that over three thousand died in the first few days though the real figure is believed to be around eight thousand and some estimate sixteen to twenty thousand deaths occurred. The gas caused intense irritation of the eyes, nose and throat. Many died because the gas irritated their lungs to such an extent that they filled up with fluid; some suffocated after spasms constricted their bronchial tubes; yet others showed signs indicative of poisoning by cyanide or carbon monoxide (ICMR 1985, Gupta *et al.* 1988, Subramanian 1985). Many of these effects have persisted and in the years since the disaster, with survivors exhibiting severe breathlessness and coughing, eye damage, muscular weakness and fatigue, chest pains, nausea, vomiting and gastrointestinal pain as well as impaired immune function, neurological disturbances such as anxiety, sleep and appetite loss, disorientation and depression; many women suffer severe menstrual disturbances (Subramanian 1985, Gupta *et al.* 1988, Rastogi *et al.* 1988, Saxena *et al.* 1988, Cullinan *et al.* 1996, Cullinan *et al.* 1997). Chronic illnesses resulting from the gas are believed to still affect 150 000 people today.

The disaster was caused by the introduction of water, contaminated with products of corrosion of the plant's steel piping, into storage tank number E610, which contained an estimated 40 tonnes of methyl isocyanate (MIC), a highly volatile, toxic and reactive compound used as a raw product in the manufacture of the carbamate pesticides carbaryl (sevin) and temik. The iron and other contaminants would have catalysed MIC's reaction with the water, leading to a violent exothermic reaction, probably raising the temperature in the storage vessel to over 200°C (UCC 1985, Subramanian 1985). The rupture disk in the tank burst and the safety valve opened at a pressure of 40 psig venting the contents of the tank to the atmosphere; with an average pressure of 180 psig an estimated 54 000 pounds (around 25 tonnes) of MIC and 26 000 pounds (around 12 tonnes) of reaction products were released (UCC 1985, Subramanian 1985). Based on analyses of the residues in this tank by Union Carbide (UCC 1985) and the known thermal degradation products of MIC, the gas cloud is thought to have contained not only MIC but also numerous other toxic chemicals, including hydrogen cyanide, carbon monoxide and dioxide, nitrogen oxides, monomethylamine (MMA), monomethylamine hydrochloride, dimethylamine hydrochloride, trimethylamine hydrochloride, 1,3-dimethyl urea, trimethyl urea, 1,3,5-trimethyl biuret, tetramethyl biuret, 1,3-dimethyl isocyanurate and 1,3,5-trimethyl isocyanurate (UCC 1985, Subramanian 1985). MIC, hydrogen cyanide and monomethylamine (MMA) are believed to have been responsible for many of the immediate deaths and toxic effects (Subramanian 1985).

Union Carbide claimed that the accident had been a result of sabotage by a disgruntled worker, who added the water to the tank deliberately to destroy valuable MIC. The workers themselves, however, refute this entirely, since it was well known how dangerous such an action would be. Instead they blame the management of Union Carbide, both in India and the USA, who presided over a plant where the company's own procedures were not followed, with process and safety equipment poorly maintained and staff often asked to carry out tasks for which they had not been adequately trained. Workers have published a detailed account of operations at the plant and the night of the accident (Chouhan *et al.* 1994). They describe

a history of equipment failures, poor training and safety standards, gas releases and other accidents, with incidents from the commencement of sevin manufacturing in 1977. Workers complained of choking and sickness after exposure to hazardous chemicals resulting from a combination of a lack of protective equipment and the frequent leaks. One worker died in late 1981 after exposure to phosgene, another highly toxic gas that was used at the facility; less than two weeks later, in January 1982, another phosgene leak hospitalised 24 workers. There were further injuries during 1983 and 1984 subsequent to leaks of various process chemicals.

The plant was not a financial success and though it was licensed to produce 5 250 tonnes per annum of sevin and temik, it never achieved this. 1981 saw the maximum production, 2704 tonnes, which dropped to 1 657 tonnes by 1983. With financial losses mounting, Union Carbide decided in 1984 to close the plant and towards the end of the year was making arrangements for the sale of the plant, which was to be dismantled and shipped to a buyer outside India (Chouhan *et al.* 1994).

Consequently, in late 1984, the facility was in a poor state. Cost cutting had reduced the staffing levels and many of the production and safety systems were either in need of maintenance, or, indeed, unserviceable. Even the refrigeration of the highly dangerous and reactive MIC had been switched off, though it should not have been stored above 5°C. At 8.30 pm on the night of the 2nd December, a worker began flushing the pipes of the MIC Unit's Relief Valve Vent Header system to clear a blockage caused by rust and other corrosion products. He left the water running, unaware that a faulty valve was allowing the water to enter tank 610, in which over 40 tonnes of MIC were stored. As the MIC began to react with the water, catalysed by the contaminants it contained, pressure built up and the MIC began to leak from the tank, first being noticed at around 11 pm. MIC leaks were so normal that the only action that the supervisors advised was to spray water over the point of the leakage. By 12.30 am on the 3rd December, the pressure had built up to the point where the safety valve burst and the contents of the tank began to be released far more rapidly, continuing for over an hour. There was no safety system capable of controlling or neutralising the leak, no evacuation plan and no warning was issued to the local residents (Chouhan *et al.* 1994).

The Bhopal plant never operated after the accident, though Union Carbide India Limited continued to exist under the new name of Eveready Industries Limited (NEERI 1995). In 2001, Union Carbide became a wholly owned subsidiary of the Dow Chemical Company (Dow Chemical Company 2001). Although Union Carbide paid US\$470 million in compensation for gas-related deaths and injuries, compensation has been awarded to only half of the estimated 500 000 victims (Kumar 1995), with the highest award being US\$1250 for the loss of a family member. Moreover, this settlement provided no monies for the ongoing healthcare of the survivors, or for the cleanup of the site. Dow Chemical claims that they have no remaining obligations or liabilities regarding the accident or the environmental contamination.

Today the abandoned factory is guarded by a commercial security company, though local people frequently enter it, whether to graze their animals or, in the case of the children, to play. It retains a toxic legacy from its industrial days. Dumping and release to atmosphere of over 1 500 tonnes of chemicals in and around the site between the years of 1969 and 1984 is recorded by a former plant operator (Chouhan 2000).

The Indian National Environmental Engineering Research Institute (NEERI) found sevin, temik, alpha-naphthol and lindane at numerous disposal sites and made recommendations for cleanup (NEERI 1995). Four years later, a Greenpeace investigation in 1999 documented extensive contamination in and around the site. Metallic and organic contaminants remain in the soil of the site, in the drains under the factory buildings and in piles of waste around the site. Solvents used in Union Carbide's processes have leaked into the groundwater over the years and now contaminate the wells that serve thousands of people living nearby. Solar evaporation ponds outside the factory received aqueous wastes after 1977 (Chouhan *et al.* 1994) and though they were filled and sealed in the late 1990s (Cooper 1996) the containment is extremely poor with several large breaches. Consequently they represent another source of pollution to the local environment and its inhabitants.

In addition, although many of the buildings and other structures of Union Carbide's manufacturing facility have been demolished, others still remain. In these rest stockpiles of chemicals left behind when Union Carbide abandoned the site. Documentation of their precise origin is not available but they are believed to include unsaleable ingredients of the pesticides that were being produced, as well as residues from the sevin production process itself. The current study was therefore undertaken to establish the nature of these stockpiles and residues and to update the status of the former solar evaporation ponds.



Figure 1. Unidentified wastes dumped at the UCIL site. ©Greenpeace/Stringer

1.3 Sampling Program

1.3.1 General Sampling Procedures

During 2002, a total of twelve samples of solid waste were collected from six stockpiles on the territory of former UCIL plant. A further four soil samples were taken from the site of the evaporation ponds, a few hundred metres north of the perimeter wall. All samples were collected and stored in pre-cleaned 100ml glass bottles that had been rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metals and organic residues. The samples were returned to the Greenpeace Research Laboratories for analysis.

All waste samples were screened to identify as many organic constituents as possible. Moreover, a subsample of each was forwarded to a separate laboratory for quantitative analysis of carbaryl, hexachlorobenzene and four isomers of hexachlorocyclohexane (HCH); alpha, beta, gamma and delta-HCH. A fifth isomer, epsilon-HCH, was not determined quantitatively, but its presence or absence was noted.

The soil samples from the solar evaporation ponds were screened for organic contaminants and quantitative determinations of nine metals were made. All these analyses were conducted at the Greenpeace Research Laboratories.

Detailed descriptions of sample preparation and analytical procedures are presented in Appendix 1 and full organic screening and metals results are given in Appendix 3.

1.3.2 Sample Descriptions

Description of the samples and locations of the sampling sites are presented in Table 1 and Figure 2. The stockpile samples were collected from a variety of buildings, all easily accessible.

The “BHC store” was the MIC storage area Union Carbide’s first phase of pesticide manufacturing in Bhopal and later stored coke when Union Carbide began manufacturing their own MIC (Behl *et al.* 1978). It is now the largest single repository identified on the site and is located close to the southern wall, which has partly collapsed, making the shed visible from J.P. Nagar Road, which runs by the factory. It is a large warehouse, containing sacks stacked around the walls of two of its three rooms. Access to these inner rooms was possible through a sliding door secured only by means of a stone wedged in the runner on the floor. Moreover, access is possible directly from the outside via a hole in one of the walls. It is estimated that this store contains in excess of 100 tonnes of materials. Many of the sacks are ripped and some of the material has spilled onto the floor. The materials are not labelled except that there are numbers and letters scrawled on the walls above some of the piles. Some of the sacks were cement sacks, though the contents are clearly not cement. Some of the sacks contain light brown powder; in other cases the contents are of a more crystalline nature and are dark purple in colour.

The formulation shed, where the products of UCIL were once mixed, is in the northern corner of the site. It was established in 1969, when, prior to the establishment of the manufacturing facility, imported pesticides were mixed here. It is of a similar size to the BHC store and is even less secure since not all of the doors to the building remain. One section of the building is fenced off with wire mesh, the lowest part of which is approximately eight feet high.

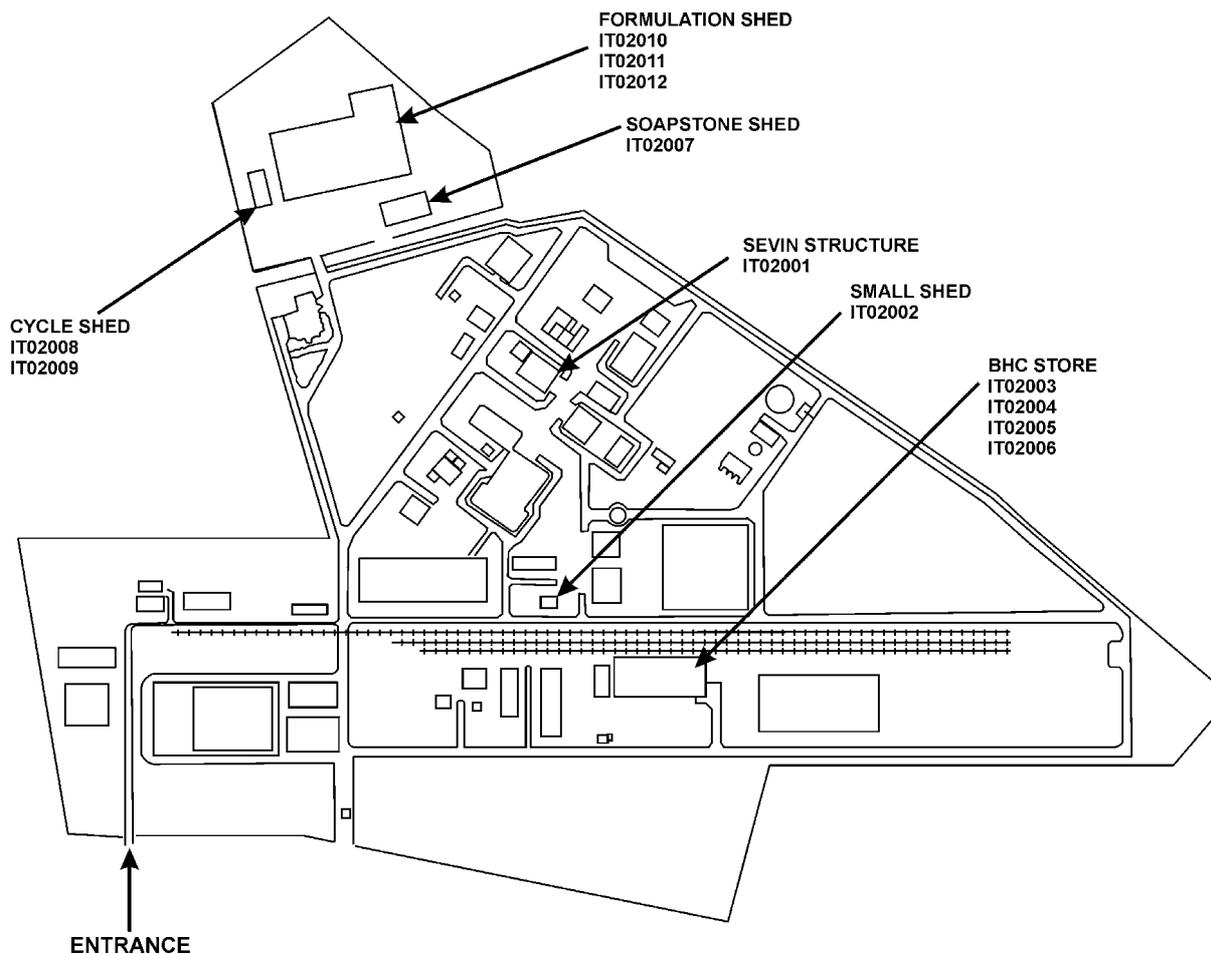


Figure 2. Map of the UCIL plant showing location of the stockpile samples. Adapted from Behl et al. (1978). The solar evaporation ponds, not shown, are approximately 400m to the north of the plant.

Inside this enclosure are several stacks of sacks containing pale brown powder, probably totalling fifteen to twenty tonnes of material. Cardboard signs identify one of these piles as “floor dust”, which was presumably swept up in this building after operations ceased; another was described as “sevidol”, a mixture of sevin and BHC (hexachlorocyclohexane isomers) sold by Union Carbide.

The “small shed” is located slightly north of the BHC store. It too has no doors and sacks containing approximately two to three tonnes of pale powder are piled at one end, with a few more scattered around the floor in the middle of the building. Close to the formulation shed are the “soapstone shed” and the “cycle shed”. Both of these contain a mixture of 40-gallon steel drums and sacks. The drums are in extremely poor condition, rusting and often without lids. The majority contain solid black residues. The sacks again contain unidentified powders. The cycle shed has open sides and a sign on the outside reading “SEVIN - RESIDUE (location - cycleshed) Total Wt 20800 kgs”; this is believed to refer to the solid materials in the drums. The size of the stockpile in the soapstone shed is very difficult to estimate, but is probably greater than that in the cycle shed. Both these areas can be accessed without difficulty.



Figure 3. The second room of the BHC store, showing the extent of the stockpile. ©Greenpeace/Stringer

Sample Number	Sample Description	Sample Location
<i>BHC store</i>		
IT02003	Solid	Sacks on right hand side of first room
IT02004	Solid	Sacks in third pile on left hand side of first room
IT02005	Solid	Sacks in pile D/A 10 in second room
IT02006	Solid	Sacks in pile D/A 4 in second room
<i>Formulation shed</i>		
IT02010	Solid	Sacks
IT02011	Solid	Sacks
IT02012	Solid	Sacks
<i>Small shed</i>		
IT02002	Solid	Sacks
<i>Soapstone shed</i>		
IT02007	Solid	Sacks
<i>Cycle shed</i>		
IT02008	Solid	Barrels
IT02009	Solid	Sacks
<i>Sevin structure</i>		
IT02001	Solid	Reaction vessel
<i>Solar evaporation ponds</i>		
IT02029	Soil	Underneath broken plastic liner
IT02030	Soil	Underneath broken plastic liner
IT02031	Soil	Edge of pond
IT02032	Soil	Underneath broken plastic liner

Table 1. Description of samples collected from the Union Carbide factory site.



Figure 4. The soapstone shed, indicative of the general poor condition of the buildings on the UCIL site. ©Greenpeace/Greig

In addition to these stockpiles, there are also a large amount of chemicals remaining in the sevin production facility. This structure is effectively in the open. At the time of the first Greenpeace visit to the UCIL site in 1999, the reaction vessel at this location was intact, though badly corroded. However, by December 1999 it had split open and spilled hundreds or thousands of kilogrammes of reddish residues onto the ground (Yashwant, pers. comm.)(see Figure 6). By 2002, a black tarry material, presumably resulting from the degradation of the reaction products, was oozing from the bottom of the pile.

In addition to this, there are numerous smaller piles of residues around the site (see Figure 1). NEERI (1995) estimated that 6.4 hectares- 21% of the site- had been used as disposal areas. Moreover, the laboratory still contains hazardous chemicals. Jumbled together in old cupboards are literally dozens of bottles. Some are empty, their contents having evaporated in the years since the site was abandoned, but others still contain laboratory agents ranging from acids to mercury compounds (see Figure 5).

Between 1977 and 1984 Union Carbide discharged aqueous effluents to a series of solar evaporation ponds located a few hundred metres north of the factory (Chouhan *et al.* 1994). In 1996 a newspaper report (Cooper 1996) describes the ponds being filled and sealed, though the tractor being used tore through the plastic liner and locals were scavenging scraps of the liner to seal the roofs of their homes. In 2002, the site remains openly accessible, with its perimeter fence completely missing in several areas and dwellings within metres. In some places, the soil is piled up in mounds, but in the southern part there is a pond and children and domestic animal can be observed bathing there. At several locations, the plastic liner has been exposed and breached. Residents have been collecting soil from the mounds to

provide flooring for the porches to their houses, often digging in the holes rent in the liner. Soil samples were collected beneath tears in the liner at three locations and also from the edge of the pond.



Figure 5. The abandoned laboratory, cupboards still full of unwanted reagents. ©Greenpeace/Stringer

1.4 Results

The results of the quantitative analysis for carbaryl, hexachlorobenzene (HCB) and isomers of hexachlorocyclohexane (HCH) are summarised in Table 2. In addition to the four isomers of HCH quantified (alpha, beta, gamma and delta-isomers), epsilon HCH was determined qualitatively and reported as present or absent in Table 2.

Sample no.	carbaryl	alpha-HCH	beta-HCH	gamma-HCH	delta-HCH	epsilon-HCH	HCB
IT02001	0.083	2 130 000	500 000	1 440 000	940 000	present	<10 000
IT02002	0.026	<160	<100	<100	<500	absent	<100
IT02003	0.013	<160	<100	<100	<500	absent	<100
IT02004	0.078	86 000	23 000	41 000	12 000	present	5 800
IT02005	0.962	12 000	108 000	7 500	1 700	present	580
IT02006	0.088	17 600 000	2 100 000	1 500 000	900 000	present	<100 000
IT02007	1.839	20 000	4 900	7 700	5 900	present	<100
IT02008	<100	39 000	1 700	4 000	2 600	present	<100
IT02009	0.096	20 000	8 700	13 400	4 100	present	1 900
IT02010	0.728	183 000	41 000	107 000	61 000	present	<1 000
IT02011	0.695	70 000	45 000	42 000	30 000	present	<1 000
IT02012	1.122	84 000 000	2 500 000	8 500 000	4 700 000	present	<100 000

Table 2. Concentrations (in ug/kg dry weight) of carbaryl, hexachlorobenzene (HCB) and isomers of hexachlorocyclohexane (HCH) found in samples IT02001-IT02012 from the UCIL factory.

The results of the organic screen qualitative analysis for the stockpile samples are presented in Table 3, including a breakdown of the groups of organic compounds reliably identified in the samples. The screening analysis resulted in the isolation of between nineteen and 214 different organic chemicals. The mass spectra of these were matched with those in a computerised library to identify the chemicals isolated. On average, half of those chemicals isolated could be identified to better than 90% certainty and these, which are regarded as “reliably identified” are discussed in the following sections.

The screening analysis for the SEP samples are presented in Table 4, with reporting on the same basis as for the stockpile samples. Quantitative metals data for these samples are given in Table 5.

Details of all analytical methods are given in Appendix 1 and full screening results and metals data are given in Appendix 3, including organic compounds that were identified with a computer matching certainty of 51-90%. These are classified as “tentatively identified” and are not discussed here.



Figure 6. Reaction products spilling from the corroded vessel at the sevin structure. Sample IT02001 was collected from this location. ©Greenpeace/Greig

Sample no.	IT02001	IT02002	IT02003	IT02004	IT02005	IT02006	IT02007	IT02008	IT02009	IT02010	IT02011	IT02012
Location	Sevin structure	Small shed	BHC store	BHC store	BHC store	BHC Store	Soapstone shed	Cycle shed	Cycle shed	Formulation shed	Formulation shed	Formulation shed
Description	from reaction vessel	from sacks	from sacks on right hand side of first room	from sacks in third pile on left hand side of first room	from sacks in pile D/A 10 in second room	from sacks in pile D/A 4 in second room	from sacks	from barrels	from sacks	from sacks	from sacks	from sacks
Number of organic compounds isolated from sample	83	26	19	168	60	25	53	66	101	66	214	57
Number of organic compounds reliably identified (% of total isolated)	44 (53%)	10 (38%)	9 (47%)	102 (61%)	30 (50%)	11 (44%)	30 (57%)	41 (62%)	57 (56%)	36 (55%)	85 (40%)	21 (37%)
Chlorinated organic compounds												
Benzenes, dichloro-	(2)			3	(2)	2, (1)	(2)	(2)	2, (1)	2, (1)	3	3
Benzenes, trichloro-	(2)			3	1, (1)	1	1, (1)	(1)	1	1,(2)	1, (1)	2
Benzenes, tetrachloro-	(3)			1	1, (2)	1	(3)	(1)	(2)	1,(2)	(3)	2
Benzene, pentachloro-	(1)			1	(1)		(1)			(1)	(1)	1
Benzene, hexachloro-	(1)			(1)	(1)		(1)					
Benzene, chlorophenoxy-				1								
Cyclohexenes, tetrachloro-												2
Cyclohexenes, pentachloro-						2				3	1	6
Cyclohexanes, hexachloro-	(3)			4	3	4	4	2, (1)	2, (1)	4	4	4
Cyclohexanes, heptachloro-										2		4
Ethane, pentachloro-											1	
Ethane, hexachloro-	1			1					1		1	
Naphthalene, chloro-	1							1				
Naphthalenes, dichloro-				2								
Naphthalene, dichloromethoxy-							1					
Naphthalenol, dichloro-											1	
Toluenes, dichloro-				3								
Toluenes, trichloro-				4								
Butadiene, hexachloro-				1					1		1	
Biphenyls, chloro-				2								
Biphenyls, dichloro-				1								
Biphenyls, trichloro-											1	
Tetrasul					1							
DDT and its degradation products							4, (1)			(4)		
Methane, bis-(3,4-dichlorophenyl)-					1						1	

Sample no.	IT02001	IT02002	IT02003	IT02004	IT02005	IT02006	IT02007	IT02008	IT02009	IT02010	IT02011	IT02012
Location	Sevin structure	Small shed	BHC store	BHC store	BHC store	BHC Store	Soapstone shed	Cycle shed	Cycle shed	Formulation shed	Formulation shed	Formulation shed
Description	from reaction vessel	from sacks	from sacks on right hand side of first room	from sacks in third pile on left hand side of first room	from sacks in pile D/A 10 in second room	from sacks in pile D/A 4 in second room	from sacks	from barrels	from sacks	from sacks	from sacks	from sacks
PAHs												
Naphthalene and its derivatives	9			18	1	1		5	16	2	18	1
Naphthalenol and its derivatives	2			3			3		1		1	
Fluorene and its derivatives	1			2	1				2		3	
Anthracene and its derivatives					1							
Benz[a]anthracene									1			
Phenanthrene and its derivatives				2					3		2	
Other aromatic hydrocarbons												
Phthalate esters				1								
Biphenyl and its derivatives	1			3					1		2	
Alkylated benzenes	6	7		17				7	1		18	
Benzene, 1,1'-oxybis-	1			1	1			1	1		1	
Benzene, 1-methyl-2-nitro-												1
Indene and its derivatives	2			6					2		6	
Naphtho-furan derivatives	1			1				1	2		1	
Benzeneacetaldehyde derivatives				1								
Dibenzofuran				1					1			
Dibenzothiophene derivatives				1								
o-Terphenyl				1								
Butadiene derivatives											1	
1H-phenalene, dihydro-									1			
Naphth[2,3-a]azulen-5(12h)-one											1	
Aliphatic hydrocarbons												
Linear	7	3	9	13	11		8	18	14	11	10	4

Table 3. Organic chemicals identified in samples collected from Union Carbide factory site. For the groups of organic compounds, numbers signify the number of compounds reliably identified using general GC/MS screening method; numbers in parenthesis signify additional compounds identified only at trace levels using a selective ion monitoring (SIM) method.

Sample no.	IT02029	IT02030	IT02031	IT02032
Description	soil from beneath broken liner	soil from beneath broken liner	soil from edge of pond	soil from beneath broken liner
Number of organic compounds isolated from sample	82	39	68	36
Number of organic compounds reliably identified (% of total isolated)	27 (33%)	8 (20%)	23 (34%)	11 (30%)
Chlorinated hydrocarbons				
Benzenes, dichloro-	(1)	(1)	(1)	(1)
Benzene, pentachloro-	(1)			
Benzene, hexachloro-	(1)			
Aromatic compounds				
Phthalate esters	2		1	
Alkylated benzenes	8			
Phenol, 2,4-bis(1,1-dimethylethyl)-		1		
Aliphatic hydrocarbons				
Linear	14	6	20	10
Other compounds				
Sulphur (S8)			1	

Table 4: Results of screening analysis of the four soil samples from the solar evaporation pond area. For each group of organic compounds, numbers signify the number of compounds reliably identified using the general GC/MS screening method; numbers in parenthesis signifies additional compounds identified only at trace levels using a selective ion monitoring (SIM) method.

Sample no.	IT02029	IT02030	IT02031	IT02032
Description	soil from beneath broken liner	soil from beneath broken liner	soil from edge of pond	soil from beneath broken liner
Cadmium	<1	<1	<1	<1
Chromium	96	93	61	70
Cobalt	37	20	20	21
Copper	57	41	40	40
Lead	8	9	5	12
Manganese	1461	770	1036	997
Mercury	0.1	<0.1	<0.1	<0.1
Nickel	74	71	53	58
Zinc	69	67	61	64

Table 5: Concentrations of metallic elements (in mg/kg dry weight) in the four soil samples collected from the SEP area.

1.4.1 BHC store (Samples IT02003-IT02006, Figure 3)

The BHC store was the largest single stockpile located in the former UCIL site. Two rooms together contained what was estimated to be over 100 tonnes of bagged materials, mostly pale brown powders. Figure 3 shows the second room, believed to contain in excess of 75 tonnes.

Sevin was present in all samples with concentrations ranging from 0.013-0.962 ug/kg dry weight. HCHs were not detectable in IT02003. In the other three samples, total HCH concentrations ranged from 162 000 to 22 100 000 ug/kg dry weight. This highest value is 2.21% and second in concentration only to one sample collected from the formulation shed.

Samples collected from the sacks located in the BHC store exhibit different groups of organic compounds. Sample IT02003 contained only nine representatives of linear aliphatic hydrocarbons at relatively low abundance. In contrast, samples IT02004, IT02005 and IT02006 contained complex mixtures of chlorinated hydrocarbons and various aromatic hydrocarbons including polycyclic aromatic hydrocarbons (PAHs), as well as linear aliphatic hydrocarbons (see Table 3).

168 organic compounds were isolated from sample IT02004, of which 102 were reliably identified. Of these, 28 were chlorinated compounds including nine chlorinated benzenes, four isomers of HCH, hexachloroethane, two chlorinated naphthalenes, seven chlorinated toluenes, hexachlorobutadiene and three chlorinated biphenyls. Other compounds identified in this sample included 22 derivatives of PAHs, bis(2-ethylhexyl) phthalate (DEHP) and a range of different classes of aromatic hydrocarbons including naphthalenol and its derivatives. In addition, 13 linear aliphatic hydrocarbons were also detected.

Fewer organic compounds were isolated from sample IT02005 than sample IT02004 (60 compared to 168), but chlorinated compounds and PAHs were nevertheless present. 47% of the compounds reliably identified in this sample were chlorine-containing and comprised nine chlorinated benzenes, three isomers of HCH, the sulphur-bridged acaricide Tetrasul and bis-(3,4-dichlorophenyl)methane. Furthermore, this sample contained four groups of isomeric compounds that it was not possible to identify using the HP Wiley7N library of organic compound mass-spectra. However, these compounds clearly had a pattern of fragmentation typical for chlorine-containing compounds. Also, sample IT02005 contained three PAHs, oxybis-benzene and eleven linear aliphatic hydrocarbons.

A comparatively small number of compounds (25) were isolated from the last sample from BHC store (IT02006) and of these only 11 were reliably identified. However, over 90% of those reliably identified were chlorinated: five chlorinated benzenes, four HCHs and two pentachlorocyclohexenes. Only one non-chlorinated chemical, a naphthalene derivative, was reliably identified.

1.4.2 Formulation shed (samples IT02010-IT02012, Figure 7)

Samples IT02010, IT02011 and IT02012 from the formulation shed were each collected from the sacks stacked behind the mesh fence in the southwest corner of the building. Cardboard signs describe some of the piles of sacks here as “sevidol” (a mixture of sevin and BHC) or “floor dust”. Sevin was present in all three samples, with a concentration range of 0.695-1.122 ug/kg dry weight and a mean of 0.848 ug/kg dry weight. The maximum concentration was exceeded only by sample IT02007 from the soapstone shed; the mean concentration was considerably higher than that for the sample set as a whole.

The concentrations of HCHs were also considerably above the mean for this survey. The highest concentrations of HCH isomers were recorded in sample IT02012, which contained a total of 99 700 000 ug/kg dry weight; i.e. just under 10% total HCH.

The greatest number of organic compounds was isolated from sample IT02011 (214 compounds) followed by IT02010 (66 compounds) and IT02012 (57 compounds).

All three contained a range of chlorinated benzenes (from di- to hexachlorinated), chlorinated cyclohexanes and cyclohexenes. In addition, sample IT02011, in which the greatest number of contaminants was identified, also contained penta- and hexachloroethane, a chlorinated derivative of naphthalenol, hexachlorobutadiene, trichlorobiphenyl and bis-(3,4-dichlorophenyl)methane. Residues of DDT and two of its degradation products, p,p'-DDE and o,p'-DDD, were detected at trace levels in sample IT02010.

Other organic compounds detected in samples IT02010-IT02012 included PAHs, aliphatic hydrocarbons and miscellaneous compounds belonging to various classes of aromatic hydrocarbons. Again, sample IT02011 had the most numerous identifiable constituents, with over 60 recorded (see Table 3).



Figure 7. Close-up of the stockpile in the formulation shed. ©Greenpeace/Greig

1.4.3 Small shed (Sample IT02002)

Carbaryl was present at 0.26 ug/kg dry weight in the single sample collected from the small shed. However, HCH isomers were not detected. Only 26 compounds were isolated from sample IT02002 and ten of them were reliably identified as alkyl benzenes and aliphatic hydrocarbons. However, given that there was only a single sample from a stockpile estimated to total two to three tonnes, the presence of more toxic compounds cannot be discounted.

1.4.4 Soapstone shed (sample IT02007, Figures 4 & 8)

The single sample (IT02007) that was collected from a sack in the soapstone shed contained sevin at a concentration of 1.839 ug/kg dry weight, the highest recorded in

this survey. The total HCH concentration, at 38 500 ug/kg, was, however, the third lowest of the stockpile samples.

The profile of other organic compounds was similar to that found in one of the samples collected from the formulation shed (IT02010). Thirty organic compounds were reliably identified in IT02007 out of a total of 53 compounds isolated from this sample. The group of chlorinated organic compounds included nine chlorinated benzenes (some of them detected at trace levels – see Table 3), four isomers of HCH, dichloromethoxynaphthalene and DDT together with its degradation products DDE and DDD. Other compounds identified in this sample were derivatives of naphthalene and aliphatic hydrocarbons.



Figure 8. Mixed waste in the soapstone shed. Note the poor condition of the barrels. ©Greenpeace/Stringer

1.4.5 Cycle shed (Samples IT02008-IT02009, Figure 9)

Of the two samples collected from the cycle shed, one (IT02008) came from a barrel of solid black material and the other from a sack (IT02009). Sample IT02008 was the only sample from the stockpiles in which carbaryl was not detectable; IT02009 contained 0.096 ug/kg.

HCH isomers were present in both samples. At 47 300 ug/kg (IT02008) and 46 200 ug/kg (IT02009), concentrations were at the lower end of those from the stockpiles, but significant nevertheless.

IT02008 and IT02009 contained 66 and 101 isolatable organic compounds respectively. A relatively high proportion of compounds were reliably identified: 62% in sample IT02008 and 56% in sample IT02009. In addition to the HCH isomers, both samples contained di-, tri- and tetrachlorinated benzenes. Other chloroorganic compounds included chloronaphthalene (sample IT02008), hexachloroethane and hexachlorobutadiene (sample IT02009). PAHs were also

present in these samples: naphthalene and its derivatives (both samples); fluorene, benz[a]anthracene and phenanthrene derivatives were identified only in the sample IT02009. Moreover, both samples contained a range of aliphatic hydrocarbons and various aromatic hydrocarbons.



Figure 9. Sacks and barrels jumbled together in the cycle shed. © Greenpeace/Stringer

1.4.6 Sevin structure (Sample IT02001, Figure 6)

This sample contained 0.083 ug/kg of carbaryl and 5 010 000 ug/kg total HCH. 83 organic compounds were isolated and 44 of them (53%) were reliably identified. Organochlorine compounds identified in this sample included chlorinated benzenes (from di- to hexachlorinated), isomers of HCH, hexachloroethane, chloronaphthalene, naphthalenol and its derivatives, PAHs and other aromatic compounds (see Table 3).

1.4.7 The former solar evaporation ponds (Samples IT02029-IT02032, Figure 10)

Between 39 and 84 organic compounds could be isolated from the soil samples from the evaporation ponds (see Table 4). However, only between 20% and 34% of these could be reliably identified, a lower proportion than for the stockpile samples. All contained at least one chlorinated benzene and numerous linear hydrocarbons. Alkyl benzenes, phthalate esters, phenol, 2,4-bis(1,1-dimethylethyl)- and molecular sulphur were also reliably identified in one or more samples. All samples contained 1,4-dichlorobenzene, whereas IT02029, which was the most contaminated of the four, also contained traces of pentachlorobenzene and hexachlorobenzene.

The SEP samples contained chlorinated benzenes and aromatic and aliphatic hydrocarbons. The 1999 Greenpeace survey included two samples from the SEP area (Labunska *et al.* 1999). Both contained traces of 1,4-dichlorobenzene and a small

number of aliphatic compounds. The 2002 data are therefore indicative of more severe contamination than was detected before.

The only data available previous to the closure of the SEPs comes from a single sample collected in 1990, which was found to contain: 87 500 ug/kg of dichlorobenzenes, 9 410 ug/kg of trichlorobenzenes, 59 090 ug/kg of 1-naphthalenol and 9 940 ug/kg of phthalate esters. Oxybis benzene and trimethyl triazintrione were tentatively identified (National Toxics Campaign Fund 1990). This level of contamination has not been detected in the surface soils of the closed SEPs to date, but should further degradation of the extremely poor containment be allowed to occur, there is a very real possibility of far more contaminated materials being unearthed and distributed in the local environment with concomitant risks to the local residents.

The concentrations of metals in the four samples are presented in table 5 and are generally within the range typically found for these metals in uncontaminated soils (Alloway 1990). In addition, the concentrations of each metal do not vary significantly between the four samples.



Figure 10. Children digging soil from the solar evaporation ponds for use as a building material. The shanty settlements, locally known as bustees, can be seen in the background. ©Greenpeace/Yashwant.

The only metal present at concentrations above those typically found in uncontaminated soils was copper. The samples contain copper at concentrations of 40-57 mg/kg, while the average concentration of copper in uncontaminated soils is typically 20-30 mg/kg (Alloway 1990). Variations in concentration can occur locally

and this may be the cause of the slightly elevated copper concentrations in these samples. Consequently it does not appear as though the soil samples from the solar evaporation pond area have been contaminated by metals as a result of the operations of UCIL.

1.5 Discussion

1.5.1 Carbaryl

Carbaryl, perhaps more widely known as sevin, is a broad spectrum insecticide, which was produced at the Union Carbide plant from 1977 until 1984 (NEERI 1990, Chouhan 2000). It belongs to the chemical class of carbamates, which act by disrupting the normal transmission of signals from one nerve cell to another by blocking the action on the enzymes that break down the messenger chemical acetylcholine. It is regarded as non-persistent (Metcalf 1995) and consequently many investigators believe that it would no longer be present at the UCIL site. However, residues were still detectable in eleven of the twelve samples collected from the chemical stockpiles, nearly eighteen years after the abandonment of the manufacturing facility.

Studies on laboratory animals have shown that acute oral, dermal and inhalation exposure of rats and rabbits to carbaryl at doses ranging from 450 to 15 000 mg/kg resulted in transient acetylcholinesterase inhibition in the brain, plasma and erythrocytes ranging from 30% to greater than 65% (Baron 1991). Carbaryl is harmful if swallowed and in contact with skin, harmful to fish and other aquatic life, and also dangerous to bees (CABI 2002). More information on carbaryl is given in Appendix 2.

Carbaryl was detected in all samples with the exception of sample IT02008 from the cycle shed. Other than this, the lowest concentration, 0.013 ug/kg, was found in sample IT02003 from a sack in the first room of BHC store and the highest, at 1.839 ug/kg, was found in sample IT02007 from a sack in the soapstone shed. Levels of carbaryl detected in the sacks from the formulation shed ranged from 0.695 ug/kg in sample IT02011 to 1.122 ug/kg in sample IT02012.

Among samples collected in the BHC store sample IT02005 had the highest concentration of carbaryl at 0.962 ug/kg. A comparatively low level of 0.083 ug/kg of carbaryl was detected in sample IT02001 collected from the residues spilling from the split reaction vessel in the sevin structure. Since carbaryl can be degraded by photooxidation (Howard *et al.* 1991), sevin in the exposed pile of reactants at the sevin structure may have broken down more quickly than at other locations. Furthermore, 1-naphthalenol, also called alpha-naphthol, the main degradation product and metabolite of carbaryl (Metcalf 1995), was also detected in the sample IT02001. However, 1-naphthalenol was also used as a raw material in the carbaryl production, therefore, its presence in sample IT02001 may be as unreacted raw material. If the sevin-producing reaction had not gone to completion at the time processing was abandoned, of course, this would also help to explain the lower carbaryl concentrations in this sample.

1.5.2 Isomers of hexachlorocyclohexane (HCH), chlorinated cyclohexanes and cyclohexenes

Quantitatively, the most significant contaminants in the stockpile samples were isomers of hexachlorocyclohexane (HCH). Today, gamma-HCH is widely sold as the insecticide lindane. It is manufactured by the photochlorination of benzene, which produces impure “technical HCH” from which the gamma isomer can be extracted. Technical HCH has also been employed as an insecticide under the name BHC (benzene hexachloride) (Safe 1993) and though it is banned or severely restricted in many countries, including India (Stringer & Johnston 2001) it is still reported to be on sale in India (Yashwant, pers. comm.).

Historically, India has been one of the largest consumers of technical HCH in both agricultural and public health sectors (Li 1999) and contamination of environmental compartments and human tissues is among the highest levels in the world (Allsopp *et al.* 1995). It is not believed that HCH was manufactured at the UCIL site, being instead purchased by Union Carbide to mix with sevin in pesticide formulations such as sevidol. In the previous Greenpeace study (Labunska *et al.* 1999), isomers of HCH were detected in a ditch running alongside the former UCIL formulation plant and also in the lime covered waste pit. Alpha-, beta- and gamma-HCH were also found in wells, hand-pumps and ponds in and around Bhopal in another study (Dikshith *et al.* 1990b) with alpha-HCH being the most abundant isomer.

Concentrations of alpha-, beta-, gamma- and delta-isomers of hexachlorocyclohexane (HCH) were determined and epsilon HCH was reported as present or absent by the external laboratory conducting the quantitative analyses; see Table 2. Hexachlorocyclohexane isomers, as well as other chlorinated cyclohexane and cyclohexene isomers were detected in the screening analysis (Table 3 and Appendix 3).

Inspection of Table 2 shows that all five isomers under investigation were detected in ten samples of the twelve collected in this study; samples IT02002 (from small shed) and IT02003 (from BHC store) had levels of alpha-, beta-, gamma-, delta-HCH and epsilon-HCH below the analysis detection limit.

HCHs were detected by the GC/MS screening in all samples where their presence was found by the quantitative analyses, ie all samples except IT02002 and IT02003. GC/MS screening is less sensitive than target analysis and consequently epsilon-HCH and, in some cases, one of the other lower concentration isomers could not be detected. However, the screening analysis's strength is its breadth and in four samples it was able to detect the presence of a number of chlorocyclohexanes and chlorocyclohexenes not part of the quantitative analysis suite. These four samples, one (IT02006) from the BHC store and all three (IT020010-12) from the formulation shed, were among those containing the highest total concentrations of HCHs. This is not surprising given that heptachlorocyclohexanes, found in samples IT02010 and IT02012 from the formulation shed, are common contaminants of technical grade HCH and reportedly responsible for the smell of technical HCH (IPCS 1991). Further, pentachlorocyclohexanes, detected in all four of these samples and tetrachlorocyclohexanes (detected in the most HCH-contaminated sample IT02012), are known to result from ultra-violet induced degradation of gamma-HCH (IPCS

1991), although given the general lack of UV-exposure these samples would have experienced, any such degradation would probably have occurred spontaneously. Manufacturing byproduction is another plausible source for these isomers.

Approximate proportions of isomers in technical HCH are: alpha-HCH 60-70%; beta-HCH 7-10%; gamma HCH 14-15%, delta-HCH 7%, epsilon-HCH 1-2% and other components 1% (Safe 1993, IPCS 1991). The ratios of the four quantified isomers in the samples from UCIL are given in Figure 11 below. It shows that the alpha isomer clearly dominates in all samples except one and, as expected, the gamma-isomer is usually the second most abundant. Beta and delta isomers were, in almost all cases, the third and fourth most abundant. Epsilon-HCH was not quantified but traces were detectable, confirming its presence at low concentrations. Given the variability in manufacturing processes such as this, these data are well within the range expected and can be regarded as confirmation of the presence of technical HCH in samples from almost every site sampled. The only sample which deviates significantly from this pattern is IT02005 from the BHC store which is dominated by beta-HCH. Beta-HCH is the most persistent HCH isomer (ATSDR 1997), which might account for its dominance here, but it is perhaps more likely that sample IT02005 simply contains technical HCH of a particularly poor quality.

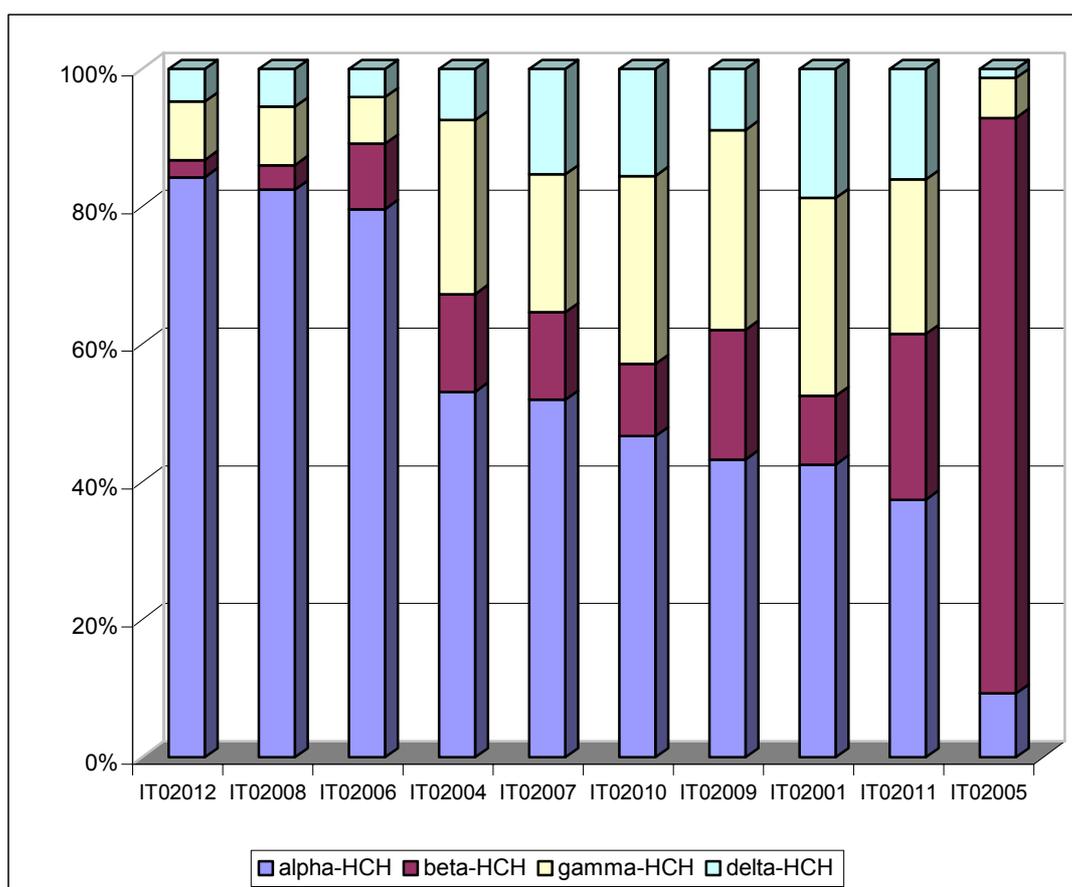


Figure 11. Percentage contribution of each isomer of HCH to the total. Samples are ranked according to percentage of alpha-HCH. No HCHs were detected in samples IT02002 or IT02003.

The summed concentrations of the four quantified isomers are presented in Figure 12, using a logarithmic scale to accommodate the wide range of concentrations in the data set. The concentrations of HCHs in the most heavily contaminated samples, IT02006

from the BHC store and sample IT01012 from the formulation shed were in excess of 10 000 mg/kg or 1%. IT02012, the most heavily contaminated sample actually contains just under 100 000 mg/kg HCH, that is, almost 10% HCH.

The less contaminated samples (IT02007 from the soapstone shed and IT02008 and IT02009 from the cycle shed) contain tens of parts per million, a highly significant level of contamination. Surprisingly high levels of HCHs were found in sample IT02001 collected from the material that had spilled from the sevin reaction vessel. It had not been expected that HCH would be present in this sample, but it was detected by both quantitative and screening analyses, making the chances of analytical error highly unlikely. It is not possible to explain the presence of HCH in this sample, but sacks of hexachlorocyclohexane were observed next to the sevin plant in 1999 by Greenpeace representatives (Labunska *et al.* 1999, Yashwant, pers. comm.) and may have been the source of the contamination. Similarly, HCHs were detectable in sample IT02008, sevin residues from a barrel in the cycle shed, though at one of the lowest concentrations among these stockpile samples. This material was a tarry solid and difficult to sample. The presence of HCHs in sample is thought to be due to contamination from HCH dust on the surface of the residues in the barrel. If this were indeed the case it would represent further proof of the widespread nature of HCH contamination within the UCIL site.

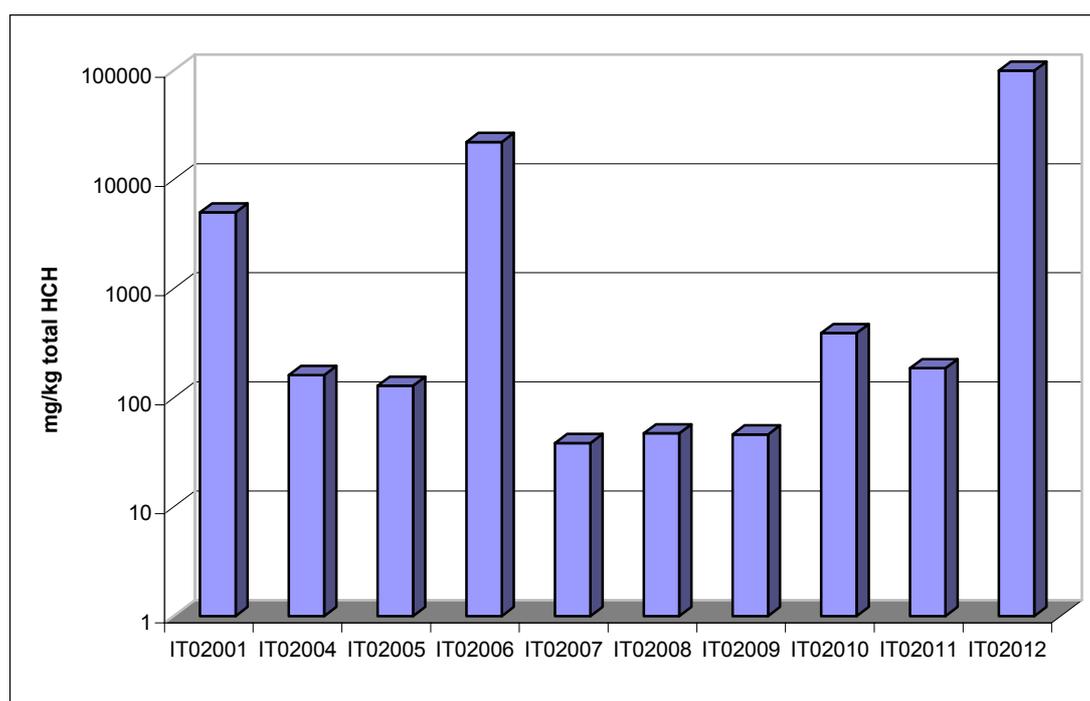


Figure 12. Total concentrations of alpha, beta, gamma and delta HCH isomers in samples. Data are presented in mg/kg (parts per million) dry weight on a logarithmic scale. No HCHs were detected in samples IT02002 or IT02003.

1.5.3 Hexachlorobenzene (HCB) and other chlorinated benzenes

There are twelve possible chlorobenzenes, containing between one and six chlorine atoms. Hexachlorobenzene quantification results are given in Table 2, presence of HCB and other chlorobenzene in samples detected via the screening analysis in Table 3 and Appendix 3.

Because of the extremely high concentration of HCHs present the analytical laboratory undertaking the quantitative analyses were forced to dilute the samples many times before analysis. Consequently, the detection limits for HCB are unusually high and among twelve samples only three had levels of HCB above the analytical detection limit: IT02004 (5 800 ug/kg) and IT02005 (580 ug/kg) from the BHC store; and IT02009 (1 900 ug/kg) from the cycle shed. These values represent high levels of contamination by HCB. Mean concentrations of HCB for uncontaminated soils in Europe were found in range from 0.3 ug/kg in Switzerland to 5.1 ug/kg in a Swedish rural soil (IPCS 1997).

The probable occurrence of hexachlorobenzene in these samples is its formation as an unwanted by-product during the synthesis of the HCHs. It is a well-known fact that HCB is a common component of wastes generated though the manufacture of chlorinated solvents, pesticides and other chlorinated substances (IPCS 1997, Stringer & Johnston 2001). Once introduced into the environment, HCB is strongly absorbed to soil materials and almost no desorption take place (Bahnick & Doucette 1988). HCB is a persistent chemical, although slow photodegradation in air and microbial degradation in soil do occur (IPCS 1997). Therefore, HCB can remain in the environment for many years after its release.

Screening analyses showed a total of between four and ten chlorobenzenes in the ten samples that also contained HCHs. It is known that Union Carbide used dichlorobenzene at Bhopal (Behl *et al.* 1978), and this may have contained higher chlorinated chlorobenzenes as a byproduct of the manufacturing process (Bryant 1993). However, they are also formed during the degradation of HCHs (Johnston 1989) and both pentachlorobenzene and hexachlorobenzene are known to be produced unintentionally in other industrial processes (Stringer & Johnston 2001). Consequently it is likely that at least some of the chlorobenzenes are present, like the chlorinated cyclohexanes and cyclohexenes, as contaminants in technical HCH.

HCB was previously detected by Greenpeace in one sample consisting of soil and lime collected close to the lime covered waste pit located on the UCIL territory. Tri-, tetra- and penta- chlorobenzenes were found at this location and in a ditch near the formulation shed; and dichlorobenzenes were detected at three locations within the factory site and two at the solar evaporation ponds (Labunska *et al.* 1999).

All chlorinated benzenes are toxic and persistent contaminants. More information on this group of chemicals is given in Appendix 2. Internationally, hexachlorobenzene (HCB) is undoubtedly is of the most serious concern because of its persistence, toxicity, bioaccumulation and biomagnification (ATSDR 1997). The UNECE (1998) lists HCB alongside PCDD/Fs and PAHs as being the most important persistent organic pollutants (POPs) emitted from stationary sources and it is one of the twelve persistent organic pollutants regulated by the UNEP Stockholm (POPs) Convention.

1.5.4 Other organochlorines

In addition to the chlorinated cyclohexanes, cyclohexenes and benzenes, a wide range of other organochlorines was also detected. Recognition should be made of the complexity of the solid waste samples collected in this study. The results of the organic screen analysis (see Table 3 and Appendix 3) showed that substantial number

of compounds that were isolated from the samples could not be identified. However, some of the unidentified compounds had mass spectra characteristic of organochlorines. For example, samples IT02005 from the BHC store and IT02011 from the formulation shed contained bis(3,4-dichlorophenyl)methane and other, as yet unidentified, chlorinated homologues or isomers of this compound, as a suite of at least 10 peaks in the region of bis(3,4-dichlorophenyl)methane in the samples' GC/MS traces. Unidentified chlorinated compounds were also present in the sample IT02012, however, the fragmentation pattern of these was different from those in samples IT02005 and IT02011.

Hexachlorobutadiene (detected in three samples) and hexachloroethane (detected in four samples) may be formed as byproducts in a range of industrial processes that involve chlorination (Snedecor 1993, DHHS 2000, ATSDR 1997). Hexachloroethane is also formed during incineration of materials containing chlorinated hydrocarbons. If released to soil, both hexachloroethane and hexachlorobutadiene may persist for many months or even years under aerobic conditions (Howard *et al.* 1991). Persistence is substantially greater under more anaerobic conditions. Both compounds are toxic to humans and may cause damage to animals, birds, fish, and plants (DHHS 2000, ATSDR 1997). Another chlorinated ethane, pentachloroethane, which was detected in one sample (IT02011), is used as an intermediate in some tetrachloroethylene processes. It is a toxic compound and has a strong narcotic effect, even greater than that of chloroform, which was used as a medical anaesthetic for many years. Pentachloroethane is one of the primary metabolites of hexachloroethane in sheep (Snedecor 1993). It is difficult to suggest what the source of this chemical in sample IT02011 could be other than an unintended contaminant.

DDT and its metabolites were detected in two samples: IT02007 from the soapstone shed and IT02010 from the formulation shed. It was found in the soil of the UCIL site during the earlier Greenpeace study (Labunska *et al.* 1999). It was not manufactured by UCIL, but since it has been widely in India for decades, primarily to combat mosquitoes, this may well be the reason for its presence here.

Polychlorinated biphenyls (PCBs), which were detected in four samples, have been used as a heat transfer fluid (Edwards *et al.* 1991, Budavari *et al.* 1989). However, there is no evidence that they were used in this capacity at UCIL; according to the UCIL Operating Manual, instead of PCBs, Dowtherm (a non-chlorinated mixture of diphenyl and diphenyl oxide) was used at the plant as a heat transfer fluid (Behl *et al.* 1978). The PCBs detected in the samples from UCIL were mono and dichlorinated congeners which are neither the most common congeners in technical mixes (de Voogt & Brinkman 1989), nor the most environmentally persistent (see eg Krokos *et al.* 1996, van den Berg 1998, Thomas *et al.* 1999). Conversely, PCBs are known byproducts of several manufacturing and waste disposal processes (Stringer & Johnston 2001) and it is possible that the biphenyls in these samples are byproducts of the manufacturing of the major organochlorine constituents of the samples.

Representatives of the chlorinated naphthalenes (PCNs) were detected in several samples: monochloronaphthalene in samples IT02001 from the sevin structure and IT02008 from the cycle shed, two dichloronaphthalene isomers in sample IT02004 from the BHC store and dichloromethoxynaphthalene in sample IT02007 from the soapstone shed. The presence of PCNs in these samples may be as a result of their

unintentional production in the manufacturing of the BHC. It is known that PCNs may be formed as by-products in the following processes: municipal waste incineration, combustion, chlor-alkali, aluminium smelting, as contaminants of PCBs, "kieselrot" copper slag and magnesium refining (Stringer & Johnston 2001). In the past, chlorinated naphthalenes were produced industrially and had various uses: in the production of gas masks, in the mining industry as water- and fire-resistant insulating materials for detonators, as insulating materials for cables and condensers, as dielectrics in capacitors, in ship-building industry for painting the hulls of the ships and as preservatives for fabrics, wood and paper. The use of chlorinated naphthalenes has now declined substantially because of their toxicity and also due to replacement with other products (e.g. PCBs largely replaced PCNs in capacitors after World War II) (Kimbrough & Grandjean 1989, Hayward 1998, Falandysz 1998). Toxic actions of PCNs are very similar to those of the PCBs, PCDDs and PCDFs. Symptoms include effects on skin, liver, digestive tract and peripheral nervous system.

Chlorinated toluenes were found in one sample (IT02004) collected in the BHC store; three di-chlorinated isomers and four trichlorinated isomers were reliably identified. Chlorinated toluenes, also called chloromethylbenzenes, may be used in the production of fungicides, dyes and pharmaceuticals, preservatives and peroxides and as an intermediate in herbicide manufacture (Stringer & Johnston 2001). It is presumed that these were present as contaminants of the hexachlorocyclohexanes.

1,2,4-trichloro-5-[(4-chlorophenyl)thio]benzene, also called Tetrasul, was detected in single sample (IT02005) collected from BHC store. This compound used as an acaricide for control of spider mites in fruit cultivation and horticulture. Tetrasul has low toxicity to man and fish though it is moderately toxic to bees (RSC 1986). The reason for its presence here is not known.

1.5.5 PAHs

A wide range of PAHs were reliably identified in the samples of chemical stockpiles, mainly dominated by naphthalene and/or substituted naphthalenes, which were detected in eleven out of twelve samples (only sample IT02002 contained no PAHs). Naphthalene is used in production of sevin and also in moth repellents and toilet deodorant blocks, for making dyes, resins and leather-tanning agents (ATSDR 1997).

1-Naphthalenol, also known as alpha-naphthol, is both a raw material in the production of sevin and its most persistent breakdown product. 1-Naphthalenol and related compounds were detected in the samples IT02001 (sevin structure), IT02004 (BHC store), IT02007 (soapstone shed), IT02009 (cycle shed) and IT02011 (formulation shed). 1-Naphthalenol was previously detected in soil and water samples from Bhopal in another study (Dikshith *et al.* 1990a). 1-Naphthalenol has been found to cause severe alterations in lysosomal system structure of the common periwinkle *Littoria littorea*, even in extremely short periods of time (Cajaraville *et al.* 1989a & b, 1990). More information on this class of compounds is to be found in Appendix 2.

The simplest alkyl derivatives of naphthalene, 1-methylnaphthalene and 2-methylnaphthalene are used to make other chemicals such as dyes, resins, and, for 2-methylnaphthalene, vitamin K. Along with naphthalene, they are present in

cigarette smoke, wood smoke, tar and asphalt, and at some hazardous waste sites (ATSDR 1997). Naphthalene and its methyl derivatives are a part of the water-soluble fraction of various crude oils and are probably responsible for much of their toxicity (Falk-Petersen *et al.* 1982).

Alkyl-naphthalenes are ubiquitous micropollutants in drinking water. 2-Methylnaphthalene is of relatively low toxicity, though at high doses it is selectively toxic to the Clara cells of the lungs (Fawell & Hunt 1988). Exposure to a large amount of naphthalene may damage or destroy human red blood cells. People, particularly children, have developed this problem after eating naphthalene-containing mothballs or deodorant blocks. Anaemia has also occurred in infants wearing diapers that had been stored in mothballs (ATSDR 1997). Mono- and dimethylated derivatives of naphthalene are toxic to aquatic organisms with their toxic effects dependent on specific ring position rather than on the number of the methyl groups alone. 1,3-dimethylnaphthalene was found to be the most toxic and 1,8-dimethylnaphthalene the least toxic to newly fertilised sea urchin and cod eggs (Sæthre *et al.* 1984).

Benz[a]anthracene was detected in one sample (IT02009). This compound is listed among fifteen PAHs that are reasonably anticipated to be human carcinogens based on sufficient evidence of carcinogenicity in experimental animals (DHHS 2000). Fluorene and its derivatives were detected in five samples: IT02001, IT02004, IT02005, IT02009 and IT02011. Fluorene is a constituent of coal tar. There is no known commercial production or use of this compound. It can be detected in raw waters and in drinking water samples, though at low ng/l levels. It was also found in food and cigarette smoke (Fawell & Hunt 1988). There is very little information on the toxicity of fluorene.

Phenanthrene and its derivatives were detected in three samples: IT02004, IT02009, and IT02011. Phenanthrene is also a constituent of coal tar and can be isolated from several types of crude petroleum. Very little toxicological information is available on phenanthrene, though it is mutagenic in bacterial systems under specialised conditions. Also, phenanthrene is known to be a human skin photosensitiser and mild allergen (Fawell & Hunt 1988).

1.5.6 Other aromatic hydrocarbons

1,1'-Biphenyl, also called diphenyl, was detected in four samples (see Table 3). This chemical has been used as a heat transfer fluid, a fungistat for oranges (applied to inside of shipping container or wrappers) and in organic synthesis (Edwards *et al.* 1991, Budavari *et al.* 1989). According to the UCIL Operating Manual, Dowtherm (a mixture of diphenyl and diphenyl oxide) was used at the plant as a heat transfer fluid in the phosgene and monomethylamine pre-heaters and was also used in the reactivation heater (Behl *et al.* 1978). Overexposure to 1,1'-biphenyl may cause irritation of throat and eyes, headache, nausea, fatigue and numb limbs and also liver damage (Budavari *et al.* 1989).

Various alkyl-substituted benzenes were detected in six samples (see Table 3). These compounds can be found in petroleum (Overton *et al.* 1994) and some of them are produced industrially and used as solvents in large quantities, including

methylbenzene (toluene), dimethylbenzenes (xylenes), trimethylbenzene (mesitylene) and ethylbenzene (Hume & Ho 1994). Most toxicity data is available for these most common compounds, which are nervous system depressants, also irritating the eyes and causing developmental toxicity (Hume & Ho 1994, Ritchie *et al.* 2001), but no specific data were available for the compounds which were found in the samples from the stockpiles, though they are anticipated to exhibit lower toxicity.

Diethylhexyl phthalate (DEHP) was detected in two samples, IT02004 from the BHC store and IT02031 from the solar evaporation pond area. Di-n-butyl phthalate (DnBP or DBP) and diisobutyl phthalate (DiBP) were detected in sample IT02029 (also from the evaporation pond area). These chemicals are well known plasticisers and 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 (Jobling *et al.* 1995). In the past DEHP and DBP were the phthalates produced in the greatest quantities (Menzert & Nelson 1986). DEHP and DnBP 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 be affected by DnBP (Chan & Meek 1994, ATSDR 1997) and DEHP (ATSDR 1997). Because of their recognised toxicity and widespread distribution, 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).

1.5.7 Aliphatic hydrocarbons

Aliphatic hydrocarbons are components of mineral oils. In addition to fuel and lubricant applications, the lighter components may be used as solvents and the heavier ones as waxes. They are widespread environmental contaminants. The longer chain compounds most commonly found here generally exhibit low toxicity and are used as solvents, degreasing agents, dry-cleaning fluids and lubricants though they may irritate the skin and can promote skin cancers in mice (Fawell & Hunt 1988). See Appendix 2 for more details on this class of compounds.

1.6 Conclusions

The current survey represents the most comprehensive and detailed description available on the chemical stockpiles at the UCIL facility. The combination of quantitative and qualitative analyses allows a broad understanding of the contents of the individual stockpiles. Organic compounds detected in the solid wastes left unattended and insecure on the territory of the former UCIL plant are variously toxic, persistent and/or bioaccumulative. Confirmation of contamination outside the factory walls is moreover provided by the four samples from the SEP area.

In terms of immediate threat to human health the carbaryl and BHC must be regarded as of the greatest concern. These were found at almost every site sampled. The presence of sevin, widely regarded as insufficiently persistent to remain so many years after the abandonment of the plant, is notable. Whilst its biodegradability does

mean that there is limited risk of dispersal to the wider environment, the fact that concentrations are low does not necessarily preclude the presence of more heavily contaminated materials and there remains the risk of exposure to any person or persons who may come into contact with the stockpiled wastes. The toxic action of carbaryl results from its inhibition of an enzyme critical to regulation of the passage of signals between nerve cells. Large doses can be fatal to humans unless an antidote is administered.

The hazard posed by the carbaryl is exacerbated by its combination with HCH isomers which were found in concentrations ranging from part per million to percent levels. These isomers have differing modes of toxicity. Gamma-HCH (lindane) is the member of the group for which toxicological actions are best understood. Human deaths have only rarely been recorded subsequent to lindane exposure but are not unknown. Its toxic actions result from nervous system stimulation (IPCS 1991, Smith 1991). However, alpha-HCH, which predominates in almost all samples, is a nervous system depressant, as are the beta- and delta isomers (Willett *et al.* 1998, Smith 1991). The combined effects of these and the other contaminants is consequently extremely difficult to predict.

In addition to the immediate threat to health, HCHs, once absorbed in the body, can be retained for years and have the potential to cause long-term health effects. HCHs are also reasonably anticipated to be human carcinogens by the US Department of Health and Human Services (DHHS 2000); the International Agency for Research on Cancer regards them as possible human carcinogens (Group 2B).

HCH isomers are persistent not only in the body but in environmental systems as well. The contamination of the soil around the UCIL site will therefore be expected to represent a long-term issue that could be significantly exacerbated by the continued spread of materials from the stockpiles given the parlous state of their containment. Furthermore, under Indian climatic conditions they can evaporate quite quickly (Samuel *et al.* 1988) and these volatilised residues may be transported to distant areas and contribute to global atmospheric contamination. This dispersal mechanism has over recent decades caused widespread contamination of food products and most human exposure can take place through consumption of contaminated food products or through transfer from mother to child transplacentally or via breastfeeding (Willett *et al.* 1998). Many of the other contaminants, notably the other organochlorines, are anticipated to behave in a similar fashion.

In the context of the UCIL site, routes of population exposure to these chemicals include inhalation of or dermal contact with contaminated dusts on the site or blown on the wind and consumption of dairy products from cattle grazing in and around the site, in addition to the more conventional routes. The easy access to the site and sheds and buildings within it also raises the possibility of material being removed, distributed and accidentally misused. Children playing in the site may also come into direct contact with any of the unsecured material described in this report.

Exposure of the local population to the contaminants buried in the former evaporation ponds must also be considered. The plastic liner has been breached in at least three locations and the samples collected as part of this survey show traces of chlorobenzenes in the soil at this location. Local residents are known to take soil

from here to use in the construction of the floors of the porches outside their houses and may therefore be exposed to contaminants either dermally or through inhalation of dust. Although the concentrations are not believed to be very high, insofar as this can be determined from the non-quantitative screening analysis employed, the presence of far higher concentrations of di- and trichlorobenzenes was established in 1990 (National Toxics Campaign Fund 1990) and further breaching of the already damaged containment liner is likely to increase the levels of exposure.

In 1999, the extent and severity of the contamination well water near the former plant was documented. Chlorinated methanes, ethanes and benzenes were found in concentrations in excess of WHO drinking water guidelines at most of the sites sampled. For example, the worst well, situated between the northern wall of the plant and the evaporation ponds contained carbon tetrachloride 1 700 times the World Health Organisation (WHO) guidelines (Labunska *et al.* 1999). Since then, clean drinking water has been provided to these populations. However, well water is still used for washing and bathing and inhalation and dermal exposure to waterborne organochlorines can equal or exceed the intake from ingestion (McKone 1987, Wallace 1997, Moody & Chu 1995). Some risk to the inhabitants of the bustees (shanty settlements) is therefore to be expected and will probably not be eliminated until full cleanup of the groundwater resources is completed.

In 1989, Union Carbide paid US\$ 470 million in compensation for gas-related injuries and deaths (Chouhan *et al.* 1994) though according to non-governmental organisations involved in the court cases, many claims remain unsettled and the individual sums received are extremely small; on average US\$400 for injury and a maximum of \$1250 for death of a family member. Legal proceedings currently underway in the US and Indian courts relate to the criminal liability of Union Carbide and nine executives in place at the time of the disaster. Moreover, the issue of ongoing toxic exposure from contamination of soil and water around the factory site has been raised as separate grounds for damages and environmental cleanup in the US case.

This report, in combination with previous works (eg Labunska *et al.* 1999, National Toxics Campaign Fund 1990), provide unequivocal evidence of a continuing risk to the local population and the environment, with the potential for these to increase, rather than decrease, over time, as degradation of the various structures in and around the plant and the continuing action of physicochemical dispersion processes lead to the further dispersion of the contaminant and stockpile inventory. Greenpeace has recently published guidelines on the standards that will be required in the cleanup of the site, the nearby solar evaporation ponds and the groundwater resources (Stringer & Johnston 2002). Our current findings underscore the urgency of action to carry out this cleanup.

1.7 References

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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 an oven overnight at 105°C and rinsed three times with low haloform pentane.

In preparation for analysis of extractable organic compounds, approximately 30 g (wet weight) of the sample 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. 15 ml of pentane was added, followed by 5 ml of acetone. All samples were then sonicated for two hours.

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
Benzene, hexachloro-	284, 286, 282, 249
Atrazine	200, 215, 202, 217
alpha-HCH	181, 183, 219, 217
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 A1. List of compounds in the Standard I used for SIM analysis

Compound	Ions to monitor
Phenol	94, 66, 65, 95
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-nitro-	139, 65, 81, 109
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
Phenol, 4-chloro-3-methyl-	107, 142, 77, 144
Phenol, 2,3,5-trichloro-	196, 198, 160, 97
Phenol, 2,4,6-trichloro-	196, 198, 97, 132
Phenol, 2,4,5-trichloro-	196, 198, 97, 132
Phenol, 2,3,4-trichloro-	196, 198, 97, 160
Phenol, 2,3,6-trichloro-	196, 198, 97, 132
Phenol, 3,5-dichloro-	162, 164, 99, 63
Phenol, 3,4-dichloro-	162, 164, 99, 63
Phenol, 2,3,5,6-tetrachloro-	232, 234, 230, 131
Phenol, 2,3,4,6-tetrachloro-	232, 234, 230, 131
Phenol, pentachloro-	266, 268, 264, 165
Butadiene, hexachloro-	225, 190, 260, 118
Dinoseb	211, 163, 147, 117
Heptachlor	100, 272, 274, 137
Octachlorostyrene	308, 310, 380, 378
Aldrin	66, 263, 265, 261
Dieldrin	79, 81, 263, 265
Endrin	67, 317, 319, 345
Chlordane I	373, 375, 272, 237
Chlordane II	373, 375, 272, 237
PCB-28	256, 258, 186, 150
PCB-52	292, 220, 290, 222
PCB-77	292, 290, 294, 220
PCB-81	292, 290, 294, 220
PCB-101	326, 324, 254, 328
PCB-105	326, 324, 254, 328
PCB-114	326, 324, 256, 328
PCB-118	326, 324, 256, 328
PCB-123	326, 324, 254, 328
PCB-126	326, 324, 254, 328
PCB-138	360, 362, 290, 358
PCB-153	360, 362, 290, 358
PCB-156	360, 362, 290, 358
PCB-157	360, 362, 290, 358
PCB-167	360, 362, 290, 358
PCB-169	360, 362, 358, 145
PCB-170	396, 394, 324, 326
PCB-180	396, 394, 324, 162
PCB-189	396, 394, 398, 324

Table A2. List of compounds in the Standard II used for SIM analysis.

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 15 ml of pentane was added, followed by 5 ml of acetone 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 a Florisil column, eluted with a 95:5 mixture of pentane: toluene and evaporated down to a volume of 2 ml under a stream of analytical grade nitrogen. 1-Bromonaphthalene was then added at a concentration of 10 mg/l to provide an indication of GC/MS performance.

A1.1.2 Organic Screen Chromatographic Analysis

Organic compounds were identified qualitatively using Gas Chromatography Mass Spectrometry (GC-MS). Instrumentation was an Agilent 6890 Series gas chromatograph, interfaced with an Agilent Enhanced Chem-Station data system and linked to an Agilent 5973 Mass Selective Detector operated in SCAN mode. The identification of compounds was carried out by computer matching against Agilent Wiley7N and Pesticides Libraries of over 390 000 mass spectra combined with expert interpretation. Moreover all extracts were analysed using selective ion monitoring (SIM) method against two standard solutions. The lists of compounds in Standard I and Standard II are presented in Tables A1 & A2. 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 Agilent Wiley7N and Pesticides Libraries 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 match qualities between 51% and 90% against Agilent Wiley7N and Pesticides Libraries only. Analytes yielding match qualities of 50% or less are assumed to be unidentified.

A1.1.2 Quantitative analysis for carbaryl, hexachlorobenzene and isomers of hexachlorocyclohexane.

The sediment samples are registered at sample reception and stored in a refrigerator until ready for extraction and analysis. The sample is mixed thoroughly to obtain the best homogenous mix possible. All stones and rocks are removed.

One gram is weighed and then dried using an aliquot of sodium sulphate. This mix is then extracted using dichloromethane on a Dionex Accelerated Solvent Extractor (ASE). The extract is then concentrated and put through a clean up column. The column is made up of some silver nitrate/alumina mix and 5% activated alumina. The extract is eluted using iso-hexane and then further concentrated.

The final extract is run on a GC/MS system (HP 5973) in single ion monitoring mode. The instrument is set to run in pulsed splitless mode, constant flow. The chromatography column is a 30 m HT-8 column. All calibrations and quality control checks are extracted sediment matrices and run with every batch of samples. A blank sediment matrix is also run with every batch. The range of the calibration extends

from the minimum reporting limit to a value of 250 ug/kg. Any values exceeding this range are analysed by diluting the final extract.

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.

Samples were homogenized and split into two fractions. One fraction was dried in an oven at 60°C until weighing readings became constant. The second fraction was dried at room temperature until weighing readings became constant and used for mercury content analysis. All dried samples were then crushed using a pestle and mortar until homogenous and sieved through a 2-mm mesh.

0.5 g of oven dried 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 prior to analysis for all metals other than mercury. 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.

This procedure was repeated using the fraction dried at room temperature, using an identical method other than a digestion reflux temperature of 80°C. Solutions from this digest method were used for mercury content analysis.

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 Certified Reference Material, No. 7004 (Loam with elevated analyte levels, certified by the Czech Metrological Institute) 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.

A1.2.2 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.

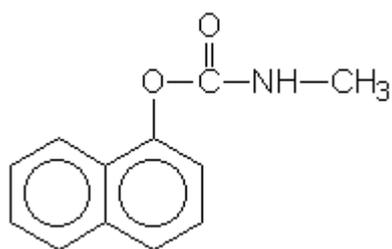
Mercury (Hg) was determined using Cold Vapour Generation ICP-AES. Hg (II) was reduced to Hg (0) vapour, following reduction of the samples with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The vapour was carried in a stream of argon into the spectrometer. 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 ORGANIC COMPOUNDS

A2.1 Carbaryl (sevin)

Carbaryl, also known as sevin or 1-naphthyl N-methylcarbamate, is a wide-spectrum insecticide from the carbamate family. Carbamate insecticides are structurally optimised derivatives of the unique plant alkaloid physostigmine, a cholinergic drug isolated from *Physostigma venenosum* (Metcalf 1995). The carbamates may be considered synthetic derivatives of the synaptic neurotransmitter acetylcholine. The carbamate insecticides represent the third principal group of synthetic organic insecticides developed after World War II. They are highly biodegradable and their toxic action as inhibitors of acetylcholinesterase is rapidly reversible. The chemical structure of carbaryl is presented below.



Carbaryl was used extensively as a replacement for DDT and other products that became environmentally unacceptable (Mason 1995). It is utilised in the control of *Lepidoptera*, *Coleoptera* and other chewing and sucking insects on more than 120 different crops, including vegetables, citrus, fruit, cotton, forests and nuts as well as lawns, ornamentals and shade trees. It was found that pre-treatment with other insecticides, such as pentachlorophenol, could affect the toxicity of carbaryl to the mosquito *Aedes albopictus* (Suwanchaichinda & Brattsten 2001). Other applications include uses as an animal ectoparasiticide, as a growth regulator for fruit thinning of apples and to control earthworms in turf (Royal Society of Chemistry 1987, Cutler 1993). Carbaryl works whether it is ingested into the stomach of the pest or absorbed through direct contact. It has low soil persistence with a half-life of 1-2 weeks (Metcalf 1995).

The main manufacturers of the carbaryl insecticide are Union Carbide, BASF, Makhteshim-Agan, Cequisa and Drexel (Royal Society of Chemistry 1987).

Carbaryl can be produced by more than one method. One is via reaction of 1-naphthol with methyl isocyanate. Methyl isocyanate, in turn, is usually prepared by treating of methylamine with phosgene (Talukder & Kates 1995). Methyl isocyanate is a very toxic compound, boiling at 38°C, and should not be stored for long period of time because of high risk of accident. India has developed a process for the preparation of aryl esters of N-alkyl carbamic acids. Thus, carbaryl is prepared by refluxing of 1-naphthol with ethyl methylcarbamate and phosphoryl oxychloride in toluene (Talukder & Kates 1995).

In the Bhopal accident in 1984 nearly 40 metric tons of methyl isocyanate and reaction products was released from Union Carbide pesticide plant. As a result, thousands of people died of pulmonary oedema and follow-up studies revealed pulmonary, ophthalmic, reproductive, immunological, neurological and hematologic toxicity among survivors (Varma & Guest 1993).

1-Naphthol is usually obtained from coal tar (Talukder & Kates 1995). This compound is also the main degradation product and metabolite of carbaryl (Dikshith *et al.* 1990), which was identified in the soil, surface and ground water in and around Bhopal, India, where carbaryl was produced on a large scale.

Other raw materials that can be used in the production of carbaryl, depending on the method employed are alkylamines and naphthalene. Alkylamines are generally toxic compounds. Both liquids and vapours can cause severe irritation of mucous membranes, eyes and skin (Layer 1993). Naphthalene, a representative of the polycyclic aromatic hydrocarbons (PAHs), can be obtained from crude or semi-refined coal-tar or from petroleum (Mason 1995).

Carbaryl is a toxic compound that can cause toxicity if breathed in, by oral intake and by passing through skin. Exposure to carbaryl can cause nausea, vomiting, diarrhoea, bronchoconstriction, blurred vision, excessive salivation, muscle twitching, cyanosis, convulsions, coma and respiratory failure (Budavari *et al.* 2000). Acute intoxication of experimental animals by carbaryl resulted in acetylcholinesterase inhibition in brain, plasma and erythrocytes. Repeated exposures may affect the liver, kidney and nervous system (Baron 1991). Carbaryl has a rat oral LD₅₀ of 233-850 mg/kg, dermal of 2 000-5 000 mg/kg and inhalation of 0.005-0.023 mg/kg (Metcalf 1995, Budavari *et al.* 2000, Baron 1991).

Toxic effects of carbaryl are increased if administered after malathion. Pretreatment of hybrid red-legged partridges with a single oral dose of 167 mg/kg malathion resulted in a marked potentiation of the toxicity of the carbaryl, given 1 hour after malathion. Oral administration of 200 mg/kg of carbaryl was lethal to 33% of malathion pretreated birds, and further 67% showed symptoms of cholinesterase poisoning (Johnston *et al.* 1994).

Carbaryl was also found to be toxic to juveniles of *Macrobrachium malcolmsonii*, an economically important prawn. Laboratory investigations suggested that carbaryl caused an alteration in basic biochemical metabolism, ultimately posing a detrimental effect on survival, growth and maturation of exposed prawns. Severe energy crisis in test prawns occurred as a consequence of the detoxification processes. Alterations recorded in various biochemical constituents in test prawns can be taken as an indicator for monitoring water pollution in the natural environment (Bhavan & Geraldine 2002).

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A2.3 Hexachlorocyclohexane (HCH)

Technical grade HCH comprises of a mixture of different isomeric forms of HCH. The approximate isomer content is alpha-HCH (65-70%), beta-HCH (7-10%), gamma-HCH (14-15%), delta-HCH (approximately 7%), epsilon-HCH (1-2%) and other components (1-2%) (IPCS 1991). One of the other components present in technical grade HCH is heptachlorocyclohexane, to which the smell of this mixture is attributed (IPCS 1991).

Lindane, the gamma isomer of HCH, is commercially produced by purification of the technical HCH mixture (Thomas & Colborn 1992, Safe 1993). This insecticide is used for the control of grasshoppers, cotton insects, rice insects, wireworms and other soil pests. Lindane has been used for protection of seeds, for treatment of poultry and livestock and for control of household insects. It is still used as a scabicide and pediculocide, usually as lotions, creams, and shampoos.

Quantitatively, the most important isomers are alpha-, beta-, gamma- and delta-HCH. Bioaccumulation of alpha, beta and gamma isomers in tissues of some animals has been recorded, although the alpha- and gamma-isomers do not concentrate highly through the food chain. The beta-isomer, however, is more persistent (Johnston, 1989). Human intake of HCH compounds is largely through food consumption (Toppari *et al.* 1995). Alpha-, beta- and gamma-HCH have been recorded in human breast-milk with the beta-isomer being the most ubiquitous. The generally less

widespread nature of the alpha- and gamma-isomers in comparison to beta-HCH is due to the more rapid clearance of these isomers from the body (National Research Council 1993). However, alpha-HCH has been found to concentrate mainly in the white matter of the brain after intraperitoneal injection to experimental animals and stayed in the brain for more than 24 hours (Smith 1991). Like many persistent organochlorines, HCH levels in the body have been found to increase with age (ATSDR 1997). Lindane has been detected in air and water (Bidelman *et al.* 1995), plants (Strachan *et al.* 1994), birds and mammals (Smith 1991, Junqueira *et al.* 1994) and humans (Pesendorfer *et al.* 1973, Acker 1974, Inoue *et al.* 1974, Pramanik & Hansen 1979). In humans lindane mostly concentrates in adipose tissue. Women chronically exposed to lindane or living in areas of intense usage have been found to contain residues of different chloroorganic compounds, including lindane, in breast milk (Larsen *et al.* 1994, Schlaud *et al.* 1995, Schoula *et al.* 1996). It was found that lindane and other organochlorine compounds can be transferred through the pathway soil-earthworm-bird/mammal (Romijn *et al.* 1994) causing secondary poisoning.

All isomers of HCH are toxic compounds. The alpha, beta- and delta-HCH mainly act as depressants of the nervous system (Smith 1991, Nagata *et al.* 1996). Poisoning by alpha-HCH is characterised by tremors of the extremities and inability of the animals to make coordinated movements. The beta-isomer produces lameness and a peculiar flaccidity in the entire musculature. Poisoning by the delta-isomer is characterised by prostration, the animals remaining motionless for days. All of the isomers of HCH induce liver microsomal enzymes.

Lindane and other HCH isomers are reasonably anticipated to be human carcinogens (DHHS 2000). It was found that alpha-HCH is more tumorigenic in mice and rats than beta-, gamma- and delta-isomers; it was suggested that the alpha-isomer is probably responsible for the tumorigenic action of technical grade hexachlorocyclohexane. Beta-HCH was found to be carcinogenic only when administered together with a polychlorinated biphenyl (Smith 1991). Beta-hexachlorocyclohexane was reported as a possible representative of a new class of xenobiotics that produces oestrogen-like effects through nonclassic mechanisms and, therefore, may be of concern with regard to breast and uterine cancer risk (Steinmentz *et al.* 1996).

Such substances may also have the potential for causing reproductive damage in humans. Several authors reported that the genotoxicity of lindane and other isomers of hexachlorocyclohexane is clearly established (Mattioli *et al.* 1996, Dubois *et al.* 1997).

Lindane is toxic to animals, humans, and aquatic species. Acute animal poisoning by lindane causes an increased respiratory rate, restlessness accompanied by increased frequency of micturition, intermittent muscular spasms of the whole body, salivation, grinding of teeth and consequent bleeding from the mouth, backward movement with loss of balance and somersaulting, retraction of the head, convulsions, gasping and biting and collapse and death usually within a day (Smith 1991). The chronic (long-term) health effects can occur at some time after exposure to lindane and can last for months or years. Lindane has been shown to cause liver, lung, endocrine gland and other types of cancer in animals (Bunton 1996, Smith 1991). It is expected that humans chronically exposed to gamma-HCH or similar insecticides and pesticides are

much more susceptible to liver damage when using paracetamol as a pain reliever. Exposure may also cause a serious drop in the blood cell count (aplastic anaemia) or in the white blood cell count (agranulocytopenia) (Itinose *et al.* 1995).

Hexachlorocyclohexane introduced to the environment from industrial discharges, insecticide applications, or spills, can cause significant damage. Acute toxic effects may include the death of animals, birds, or fish, and death or low growth rate in plants (Bunton 1996, Smith 1991). Acute effects are seen two to four days after animals or plants come in contact with a toxic chemical substance. Chronic toxic effects may include shortened lifespan, reproductive problems, lower fertility and changes in appearance or behaviour. Chronic effects can be seen long after the first exposure(s) to a toxic chemical. Lindane has high chronic toxicity to aquatic life. The insecticide load in surface waters does not ordinarily reach concentrations acutely toxic to aquatic fauna. The effects of the low insecticide concentrations often appear only after relatively long exposure times. Chronic exposure to insecticides, such as lindane, (Schulz *et al.* 1995) can be hazardous to freshwater macroinvertebrates even at unexpectedly low concentrations. The low-concentration effects may depend on both species and substance and therefore cannot be predicted from toxicity data at higher concentrations.

Hexachlorocyclohexane is a subject to European Community legislation as a toxic, persistent and bioaccumulative chemical. Stringer & Johnston (2001) present a comprehensive overview of hexachlorocyclohexane legislation including materials of EU Council Directives, OSPAR, LRTAP and PIC Conventions. The limit values and quality objectives for discharges of hexachlorocyclohexane in the European Union are set by Council Directive 84/491/EEC (EEC 1984) as amended. The uses of hexachlorocyclohexane (including lindane) were severely restricted under the LRTAP Persistent Organic Pollutants (POPs) Protocol, which was adopted in 1998 and has 36 contracting parties encompassing not only Europe but also Canada and the United States of America (UNECE 1998). The LRTAP POPs Protocol is part of the 1979 Convention on Long-Range Transboundary Air Pollution (LRTAP), which is under the auspices of the United Nations Economic Council for Europe. Lindane is also included in Annex III of the 1998 Rotterdam Convention on the Prior Informed Consent procedure (PIC procedure) among 27 other chemicals (FAO/UNEP 1998). Under the PIC procedure countries should not export any chemical to any other country without first receiving explicit permission. In order to avoid unfair trade barriers arising through the implementation of the Convention, any country that has denied import of any chemical must also stop producing it domestically and may not import it from any country that is not a Party to the convention.

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A2.2 Chlorinated benzenes

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

- | | |
|-------------|---|
| 1 chlorine | monochlorobenzene |
| 2 chlorines | 1,2-, 1,3- and 1,4-dichlorobenzenes |
| 3 chlorines | 1,2,3-, 1,2,4- and 1,3,5-trichlorobenzenes |
| 4 chlorines | 1,2,3,4-, 1,2,3,5,- and 1,2,4,5-tetrachlorobenzenes |
| 5 chlorines | pentachlorobenzene |
| 6 chlorines | hexachlorobenzene |

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.

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 1,4-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).

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

Ware (1988b) reports human symptoms after exposure to dichlorobenzenes, 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 (ortho- or o-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 diisocyanates, 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 that were overtly toxic to the mother. Human toxicity data are sparse, but chromosomal aberrations, anaemia and leukaemia have been reported (Meek *et al.* 1994b). Mammals metabolise 1,2-dichlorobenzene to phenols and catechols, most of which are excreted after conjugation with glucuronic 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 (meta- or m-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-dichlorobenzene above, but generally little is known about 1,3-dichlorobenzene in comparison to the more commercially important dichlorobenzenes.

1,4-Dichlorobenzene (para- or 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 through consumption of contaminated food. Human symptoms include damage to the liver, kidneys and lungs. Accidental poisoning of children, presumed to 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 adipose tissue and blood (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.

Trichlorobenzenes

1,2,3- and 1,2,4-trichlorobenzene have been produced from the dehydrohalogenation of the unwanted isomers of the production of the pesticide 1,2,3,4,5,6-hexachlorocyclohexane (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 gland. 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 human 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 are 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 in air, drinking water, food and 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 the PVC industry (Johnston *et al.* 1993).

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 in behaviour between 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-tetrachlorobenzene 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).

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. Pentachlorobenzene 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.

Hexachlorobenzene

Hexachlorobenzene (HCB), as an intentionally manufactured compound, has been 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 and from high-temperature sources (Newhook & Meek 1994, Sala *et al.* 1999). The UNECE (1998) lists HCB alongside PCDD/Fs and PAHs as being the most important persistent organic pollutants (POPs) emitted from stationary sources. HCB emissions from waste incineration, metallurgical industries and burning of chlorinated fuels are highlighted (UNECE 1998)(Annex V).

HCB is toxic to aquatic life, land plants, land animals and humans. It is listed by the International Agency for Research on Cancer (IARC) as a Group 2B carcinogen, i.e. a possible carcinogen to humans and also appears to be a tumour promoter. Hexachlorobenzene may damage the developing foetus, liver, immune system, thyroid and kidneys and central nervous system. The liver and nervous system are the most sensitive to its effects. Porphyria is a common symptom of HCB toxicity. High or repeated exposure may damage the nervous system and can cause irritability, difficulty with walking and co-ordination, muscle weakness, tremor and/or a feeling of pins and needles on the skin. Repeated exposure can lead to permanent skin changes, such as changes in pigmentation, tight, thickened skin, easy wrinkling, skin scarring, fragile skin and increased hair growth, especially on the face and forearms (ATSDR 1997, Newhook & Meek 1994, van Birgelen 1998). Recent research (van Birgelen 1988) suggests that HCB has dioxin-like toxicity and that, based on a preliminary toxic equivalence factor (TEF) of 0.0001, HCB could contribute significantly to the dioxin-type toxicity of human milk based on PCB/PCDD/PCDF toxicity equivalents. In many countries, this could mean an increase of 10%-60%, but in countries with high HCB exposure levels, the effects could be even greater. In

Spain and the Czech Republic, inclusion of HCB in total breastmilk TEQ estimates could lead to totals 6 times higher than those based only on PCBs and PCDFs. Slovakia and India also have very high HCB levels; other countries (eg Austria) had high levels in previous decades. It has been suggested that more epidemiological studies should be undertaken, especially in the most highly contaminated countries.

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

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

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

HCB is further included in the list of priority hazardous substances agreed by the Third and Fourth North Sea Conferences (MINDEC 1990, 1995), where continuous reduction of all hazardous substances was agreed with the ultimate aim of reducing environmental concentrations of hazardous substances to near background levels (synthetic substances to zero) within the next 25 years. The 1998 Ministerial Meeting of the OSPAR Commission (OSPAR 1998a) further reinforced these objectives. HCB is included on the OSPAR 1998 List of Candidate Substances, Annex 3 of the OSPAR Strategy with regard to Hazardous Substances (OSPAR 1998b). In addition, HCB is regulated under the 1995 Barcelona Convention, the Rotterdam (PIC) Convention and the International Joint Commission on the Great Lakes of Canada and the USA has called for all uses to be eliminated.

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A2.4 Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons occur in a variety of materials such as soot, coal, tar, tobacco smoke, petroleum and cutting oil. They are commonly found as products of incomplete combustion (DHHS 2000). It was shown that variety of PAHs (chrysene, benz[a]anthracene, benzo[c]phenanthrene, benzo[a]fluorene, benzo[b]fluorene, naphthalene and benzofulvene) could be formed from indene in a flow reactor over a temperature range of 650-850°C (Mingming & Mulholland 2001). It was also found that PCDD/Fs, PCBs and PCNs could be formed in de novo synthesis from PAHs in fluidised bed incinerators (Weber *et al.* 2001).

PAHs are prevalent pollutants in both terrestrial and aquatic environment and can cause a wide range of toxic effects. The anthropogenic contribution usually outweighs the inputs from other sources. PAHs together with alkylbenzenes are considered to be the most toxic and prevalent compounds in the initial phase of a crude oil spill (Overton, 1994). PAHs are toxic to soil organisms. It was shown that eight PAHs (naphthalene, acenaphthene, fluorene, acenaphthylene, anthracene, phenanthrene, pyrene, and fluoranthene), which have moderate lipophilicity ($\log K_{ow} = 3.3-5.2$), are toxic to soil-dwelling springtail *Folsomia fimetaria* with a narcotic mode of toxic action (Sverdrup *et al.* 2002).

The toxicity of certain PAHs to aquatic organisms can be greatly increased upon exposure of the organisms to ultraviolet (UV) radiation present in sunlight (Monson *et al.* 1995, Ankley *et al.* 1995, Arfsten *et al.* 1996, McConkey *et al.* 1997). It was

found that phototoxicity clearly was a function both of PAH dose and light intensity (Ankley *et al.* 1995, Huang *et al.* 1997). More recent investigations have shown that sunlight increases toxicity of both individual PAHs and PAH mixtures to marine organisms by a factor of 1 000. This finding may explain widespread deformities seen in fish larvae in coastal waters and lead to greater pressure for reductions in emissions. Unlike chlorinated organic contaminants such as dioxins and polychlorinated biphenyls, environmental levels of PAHs have shown little decline in recent years. Current PAH levels in air are estimated to be up to 20 times pre-industrial levels (ENDS 2000).

PAHs are harmful to human health. Individuals exposed by breathing or skin contact for long periods of time to mixtures of PAHs and other compounds can develop cancer (ATSDR 1997). Many of the carcinogenic polycyclic aromatic hydrocarbons are derived from a benz[a]anthracene skeleton. Anthracene itself is not carcinogenic, but benz[a]anthracene appears to have weak carcinogenicity. Addition of another benzene ring in select positions result in agents with powerful carcinogenicity such as dibenz[a,h]anthracene or benzo[a]pyrene. Moreover, substitution of methyl groups on specific carbons of the ring also enhances carcinogenicity. Thus, 7,12-dimethylbenz[a]anthracene (DMBA) is one of the most powerful synthetic, polycyclic aromatic hydrocarbon carcinogens known (Williams 1986).

Fifteen PAHs are reasonably anticipated to be human carcinogens based on sufficient evidence of carcinogenicity in experimental animals (DHHS 2000), they are:

Benz[a]anthracene	Benzo[b]fluoranthene
Benzo[j]fluoranthene	Benzo[k]fluoranthene
Benzo[a]pyrene	Dibenz[a,h]acridine
Dibenz[a,j]acridine	Dibenz[a,h]anthracene
Dibenzo[c,gh]carbazole	Dibenzo[a,e]pyrene
Dibenzo[a,h]pyrene	Dibenzo[a,i]pyrene
Dibenzo[a,l]pyrene	Indeno[1,2,3-cd]pyrene
5-Methylchrysene	

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

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

Laboratory rabbits, guinea pigs, mice and rats sometimes develop cataracts (cloudiness) in their eyes after swallowing naphthalene. It is not clear if cataracts also

develop in humans exposed to naphthalene, but the possibility exists. The carcinogenicity of naphthalene has not been determined. The US Department of Health and Human Services (DHHS) has determined that naphthalene may cause cancer in female mice but not in male mice or rats of either sex. The International Agency for Research on Cancer (IARC) has determined that naphthalene is not classifiable as to its carcinogenicity to humans. The USEPA has determined that naphthalene is not classifiable as to its carcinogenicity to humans (ATSDR 1997).

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A2.5 Aliphatic hydrocarbons

Aliphatic hydrocarbons, also called alkanes or paraffins, are one of the components of petroleum, a complex mixture of hydrocarbons that is formed from the partial decomposition of biological material, over geological time-scales. They could be arranged as either straight-chained, branched or cyclic hydrocarbon structures. Refined petroleum products principally contain the alkanes. In crude oil alkanes are present together with monocyclic aromatic hydrocarbons (alkyl benzenes), polycyclic aromatic hydrocarbons (naphthalene and others) and different nonhydrocarbons (compounds made up of carbon, hydrogen and other elements such as sulphur, nitrogen and oxygen). The most abundant element in crude oil by weight is carbon,

followed by hydrogen and then sulphur. Most oils contain a low percentage of sulphur and are called "sweet crudes". Sulphur compounds in crude oils are present as cyclic sulphides and thiophenes (Overton 1994).

Alkanes are the major components of petroleum commonly found in contaminated environments. Petroleum hydrocarbons are released into the environment through natural seeps, non-point source urban runoffs and by large quantities of accidentally released oil. Long-chain petroleum hydrocarbons (with more than nine carbons) are predominant components of weathered hydrocarbon fuel spills (Ritchie *et al.* 2001, So & Young 2001).

Aliphatic hydrocarbons exhibit only slight acute toxicity by all routes of exposure. The liquid may cause irritation upon contact with skin or eyes. Ingestion of aliphatic hydrocarbons may lead to aspiration of the substance into the lungs, causing pneumonia. Prolonged skin exposure may cause irritation due to the ability of these solvents to remove fats from the skin (Ritchie *et al.* 2001).

n-Hexane, a linear aliphatic hydrocarbon with six carbons (C_6H_{14}), can be found in many hydrocarbon fuels. As an individual compound, it is largely used as a solvent for adhesives, dry cleaning and vegetable oil extraction. Repeated exposure to n-hexane has been shown to induce neuropathology in humans, animals and tissue cultures. Neurotoxicity in humans is related to the parent compound and to its main metabolite, 2,5-hexanedione. n-Hexane vapour (and the vapour of other volatile hydrocarbons) at high concentrations (>1000 ppm) is a narcotic and inhalation may result in light-headedness, giddiness, nausea and headache (Ritchie *et al.* 2001, Fawell & Hunt 1988).

n-Heptane, a linear aliphatic hydrocarbon with seven carbons (C_7H_{16}), is used as a standard in testing "knocking" of gasoline engines. As a component of a mixture of hydrocarbons, it is also used as a fuel, solvent, thinner, degreasant, dry-cleaning agent and lubricant. There is relatively little toxicological information available on heptane and none at all by the oral route. However, heptane does not appear to possess the neurotoxic properties of hexane (Fawell & Hunt 1988).

n-Octane (C_8H_{18}) is widely used in organic synthesis, in the rubber industry, the paper processing industry and as a solvent. Laboratory studies on experimental animals have shown that octane is capable of lowering hepatic mixed function oxidase activity in rats after intraperitoneal injection of 1.0 ml/kg/day (700 mg/kg) for 2 or 7 days. Depression of body weight and an increase in relative liver weight were reported after treatment for 7 days. Additionally, application of octane solution in cyclohexane (75% v/v) to the initiated skin of male C3H mice for up to 50 weeks was found to produce an increase in the number of skin tumours compared to a solvent control group (Fawell & Hunt 1988).

n-Nonane (C_9H_{20}) is used in the manufacture of paraffin products and in the rubber and paper processing industries. In experimental studies on animals exposed to higher linear aliphatic hydrocarbons (n-nonane, n-decane, n-undecane, n-dodecane, or n-tridecane) in air, it was shown that only n-nonane exhibited high toxic effects on male adult rats. At 5 280 ppm, 90% of rats exposed to n-nonane died, while among rats exposed to 4 438 ppm, 40% died and at 2 414 ppm all animals survived.

Lethality induced by n-nonane exposure typically followed tremor, ataxia, spasms, and limb paralysis and was hypothesized to result from cardiopulmonary stress and/or direct neurotoxicity. Exposures to n-undecane, n-dodecane, or n-tridecane (41-1 369 ppm) were without obvious behavioural consequences and induced no detectable neurotoxicity (Ritchie *et al.* 2001, Fawell & Hunt 1988).

The higher alkanes (C₁₀ to C₂₀), as a complex mixture, are used as fuels, solvents, thinners, degreasants, dry-cleaning agents and lubricants. Toxicological data on these compounds are very sparse. The information available suggests that they are of low toxicity and do not appear to have genotoxic potential. However, these compounds are irritants to the skin at high dose levels and have been shown to have tumour-promoting activity in the mouse skin system (Fawell & Hunt 1988).

1-Alkenes are aliphatic hydrocarbons with one unsaturated bond and they also called olefins. They do not occur frequently in crude oil but are a feature of refined petroleum products, being produced either by petroleum cracking or pyrolysis of paraffins. They are used as raw materials for polymers, petrochemicals and detergents (Fawell & Hunt 1988). It was found that 1-alkenes, containing eight to ten carbons, exhibited increasingly efficient absorption in the blood and higher concentrations in brain, liver and fats as a function of greater number of carbons (Ritchie *et al.* 2001). In general, the alkenes are of low acute toxicity in experimental animals. Within the group, chain branching and di-unsaturation tend to increase their toxicity (Fawell & Hunt 1988). Three out of ten alkenes were shown to inhibit hepatic cytochrome P-450 activity in the rat. The three active compounds, 4-ethyl-1-hexene, 1-heptene and 3-methyl-1-octene, also led to the formation of identical abnormal hepatic pigments. It was further found that male rats exposed by inhalation to 215-2 049 ppm of polymerisation naphtha (alkenes comprise about 92% of the mixture) had evidence of kidney damage (Fawell & Hunt 1988).

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APPENDIX 3

**Results of organic compounds qualitative GC/MS analysis for individual samples
IT02001-IT02012 and IT02029-IT02032**

ANALYTICAL RESULTS

Sample Number: **IT02001**
Sample Type: **Solid waste**
Location: **Union Carbide plant, Bhopal, India**
Sampling Date: **29.03.02**
Sample Information: **From reaction vessel, sevin structure**

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen
Prepared by Iryna Labunska

Number of compounds isolated: 83

Compounds identified to better than 90%:

1,1'-Biphenyl
1-Naphthalenol
2-Naphthalenol, 5,6,7,8-tetrahydro-
9H-Fluorene
Benzene, 1,1'-(1,4-butanediyl)bis-
Benzene, 1,1'-cyclopropylidenebis-
Benzene, 1,1'-oxybis-
Benzene, 1,2,3,4-tetrachloro- (SIM)
Benzene, 1,2,3,5-tetrachloro- (SIM)
Benzene, 1,2,3-trichloro- (SIM)
Benzene, 1,2,4,5-tetrachloro- (SIM)
Benzene, 1,2,4-trichloro- (SIM)
Benzene, 1,2-dichloro- (SIM)
Benzene, 1,3-diethyl-
Benzene, 1,3-diethyl-5-methyl-
Benzene, 1,4-dichloro- (SIM)
Benzene, 1-ethyl-3,5-dimethyl-
Benzene, 1-methyl-2-propyl-
Benzene, hexachloro- (SIM)
Benzene, pentachloro- (SIM)
Cyclohexane, .alpha.-hexachloro- (SIM)
Cyclohexane, .beta.-hexachloro- (SIM)

Cyclohexane, .gamma.-hexachloro- (SIM)
Cycloprop[a]indene, 1,1a,6,6a-tetrahydro-
Decane, 3,6-dimethyl-
Docosane
Eicosane
Ethane, hexachloro-
Hexacosane
Hexadecane, 2-methyl-
Indane
Naphthalene
Naphthalene, 1,1'-oxybis-
Naphthalene, 1,2,3,4-tetrahydro-
Naphthalene, 1-chloro-
Naphthalene, 1-ethyl-
Naphthalene, 1-hexyl-
Naphthalene, 1-methoxy-
Naphthalene, 1-methyl-
Naphthalene, 2-ethyl-
Naphthalene, 2-methyl-
Naphtho[1,2-c]furan
Octadecane
Tetracosane

Compounds tentatively identified:

2,3-Dihydro-1H-phenalene
2-Methyl-1,1-diphenyl-1-propene
2-Naphthalenol
5H-Dibenzo(a,d)cyclohepten-5-ol
Benzene, (nitromethyl)-
Benzene, 1,1'-(1-butenylidene)bis-
Benzene, 1-methyl-4-(1-methylethyl)-
Decane
Decane, 2-methyl-
Decane, 3,8-dimethyl-
Docosane, 11-decyl-
Heptadecane, 2-methyl-
Tridecane, 6-propyl-
Tridecanol, 2-ethyl-2-methyl-
Undecane, 2,3-dimethyl-
Undecane, 2,9-dimethyl-
Undecane, 4-ethyl-

ANALYTICAL RESULTS

Sample Number: **IT02002**
Sample Type: **Solid waste**
Location: **Union Carbide plant, Bhopal, India**
Sampling Date: **30.03.02**
Sample Information: **From sacks in small shed**

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen
Prepared by Iryna Labunska

Number of compounds isolated: 26

Compounds identified to better than 90%:

Benzene, (1-butylnonyl)-
Benzene, (1-ethyldecyl)-
Benzene, (1-ethylnonyl)-
Benzene, (1-hexylheptyl)-
Benzene, (1-pentylheptyl)-
Benzene, (1-propyldecyl)-
Benzene, (1-propylnonyl)-
Docosane
Heneicosane
Tetracosane

Compounds tentatively identified:

Benzene, (1-butyloctyl)-
Benzene, (1-methyldodecyl)-
Benzene, (1-methylundecyl)-
Dodecane
Heptadecane, 2-methyl-
Nonane, 5-methyl-5-propyl-
Undecane, 5,7-dimethyl-

ANALYTICAL RESULTS

Sample Number: **IT02003**
Sample Type: **Solid waste**
Location: **Union Carbide plant, Bhopal, India**
Sampling Date: **30.03.02**
Sample Information: **From sacks in BHC store; pile on right hand side of first room**

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen

Prepared by Iryna Labunska

Number of compounds isolated: 19

Compounds identified to better than 90%:

Eicosane
Heptadecane
Hexadecane
Naphthalene
Nonadecane
Octadecane
Pentadecane
Tetradecane
Tridecane

Compounds tentatively identified:

Docosane

ANALYTICAL RESULTS

Sample Number: **IT02004**
Sample Type: **Solid waste**
Location: **Union Carbide plant, Bhopal, India**
Sampling Date: **30.03.02**
Sample Information: **From sacks in BHC store; third pile on left hand side of first room**

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen

Prepared by Iryna Labunska

Number of compounds isolated: 168

Compounds identified to better than 90%:

1(2H)-Naphthalenone, 3,4-dihydro-
1,1'-Binaphthalene
1,1'-Biphenyl
1,1'-Biphenyl, 2,2'-dichloro-
1,1'-Biphenyl, 2-chloro-
1,1'-Biphenyl, 2-ethyl-
1,1'-Biphenyl, 2-methyl-
1,1'-Biphenyl, 4-chloro-
1,2'-Binaphthalene
1,2-Benzenecarboxylic acid, bis(2-ethylhexyl) ester
1,3-Butadiene, 1,1,2,3,4,4-hexachloro-
1-Hexacosene
1-Naphthalenol
2-Naphthalenol
1H-Indane, 2-ethyl-2,3-dihydro-
1H-Indene, 2,3-dihydro-4,7-dimethyl-
1H-Indene, 2,3-dihydro-5-methyl-
1H-Indene, 3-(2-methyl-propenyl)-
9H-Fluoren-9-ol
9H-Fluorene
Benz[e]acephenanthrylen-9-ol

Benzene, (1-methyl-1-propenyl)-
 Benzene, 1,1'-(1,4-butanediyl)bis-
 Benzene, 1,1',1''-methylidynetris-
 Benzene, 1,1'-(1-propylidene)bis-
 Benzene, 1,1'-methylenebis-
 Benzene, 1,1'-methylenebis-
 Benzene, 1,1'-oxybis-
 Benzene, 1,2,3-trichloro-
 Benzene, 1,2,3-trichloro-4-methyl-
 Benzene, 1,2,4,5-tetrachloro-
 Benzene, 1,2,4-trichloro-
 Benzene, 1,2,4-trichloro-3-methyl-
 Benzene, 1,2,4-trichloro-5-(chloromethyl)-
 Benzene, 1,2-dichloro-
 Benzene, 1,2-dichloro-3-methyl-
 Benzene, 1,2-diethyl-
 Benzene, 1,3,5-trichloro-
 Benzene, 1,3,5-triethyl-
 Benzene, 1,3-dichloro-
 Benzene, 1,3-dichloro-2-methyl-
 Benzene, 1,3-diethyl-5-methyl-
 Benzene, 1,4-dichloro-
 Benzene, 1-chloro-4-phenoxy-
 Benzene, 1-ethyl-2,4,5-trimethyl-
 Benzene, 1-ethyl-2-methyl-
 Benzene, 1-methyl-2-(2-propenyl)-
 Benzene, 1-methyl-2-propyl-
 Benzene, 1-methyl-4-(1-methylethyl)-
 Benzene, 1-methyl-4-(2-propyl)-
 Benzene, 2,4-dichloro-1-methyl-
 Benzene, 4-ethyl-1,2-dimethyl-
 Benzene, 4-ethyl-1,2-dimethyl-
 Benzene, diethylmethyl-
 Benzene, ethyl-1,2,4-trimethyl-
 Benzene, hexachloro- (SIM)
 Benzene, pentachloro-
 Benzene, trichloro(chloromethyl)-
 Benzeneacetaldehyde, .alpha.,2,5-trimethyl-
 Cyclohexane, .alpha.-hexachloro-
 Cyclohexane, .beta.-hexachloro-
 Cyclohexane, .gamma.-hexachloro-
 Cyclohexene, .delta.-pentachloro-
 Cycloprop[a]indene, 1,1a,6,6a-tetrahydro-
 Cyclotetradecane, 1,7,11-trimethyl-
 Decane, 3,6-dimethyl-
 Dibenzofuran
 Dibenzothiophene, 4-methyl-
 Dinaphtho[1,2-b:1',2'-d]furan
 Docosane
 Eicosane

Ethane, hexachloro-
Heneicosane
Heptadecane
Hexadecane
Indeno[2,1-a]indene, 4b,5,9b,10-tetrahydro-
Naphthalene
Naphthalene, 1-(phenylmethyl)-
Naphthalene, 1,1'-oxybis-
Naphthalene, 1,2,3,4-tetrahydro-
Naphthalene, 1,4-dichloro-
Naphthalene, 1,6-dimethyl-
Naphthalene, 1-ethoxy-
Naphthalene, 1-methoxy-
Naphthalene, 1-methyl-
Naphthalene, 1-phenyl-
Naphthalene, 2-(phenylmethyl)-
Naphthalene, 2,3-dichloro-
Naphthalene, 2,6-dimethyl-
Naphthalene, 2,7-dimethyl-
Naphthalene, 2-ethyl-
Naphthalene, 2-hexyl-
Naphthalene, 2-methyl-
Naphthalene, 6-ethyl-1,2,3,4-tetrahydro-
Nonadecane
Octacosane
Octadecane
o-Terphenyl
Phenanthrene, 9-allyl-10-methyl-
Tetracosane
Tricosane
Tridecane

Compounds tentatively identified:

2,3-Dihydro-1h-phenalene
2-Naphthalenemethanol
5-Ethylindan
6-Fluorobicyclo[3.3.0]octan-3-ol
7H-Cyclohepta[b]naphthalen-7-one
Acenaphthene
Benzene, (2-chloro-2-butenyl)-
Benzene, 1,2-dichloro-4-[(3,4-dichlorophenyl)sulphonyl]-
Benzene, 1,4-diethyl-
Cyclohexene, .gamma.-2,3,4,5,6-pentachloro-
Docosane, 2,21-dimethyl-
Heptadecane, 3-methyl-
Hexadecane, 2,6,10,14-tetramethyl-
Naphthalene, 2-butyl-
Naphthalene, 2-chloro-3-(chloromethyl)-

ANALYTICAL RESULTS

Sample Number: **IT02005**
Sample Type: **Solid waste**
Location: **Union Carbide plant, Bhopal, India**
Sampling Date: **30.03.02**
Sample Information: **From sacks in BHC store; pile D/A 10 in second room**

ORGANIC ANALYTICAL RESULTS

Analysis method: **GC/MS screen**
Prepared by **Iryna Labunska**

Number of compounds isolated: 60

Compounds identified to better than 90%:

9H-Fluorene, 4a,9a-methano-
Anthracene, 1,2-dihydro-
Benzene, 1,1'-oxybis-
Benzene, 1,2,3,4-tetrachloro-
Benzene, 1,2,3,4-tetrachloro- (SIM)
Benzene, 1,2,3,5-tetrachloro- (SIM)
Benzene, 1,2,3-trichloro- (SIM)
Benzene, 1,2,4-trichloro-5-[(4-chlorophenyl)thio]- (Tetrasul)
Benzene, 1,2-dichloro- (SIM)
Benzene, 1,3,4-trichloro-
Benzene, 1,4-dichloro- (SIM)
Benzene, hexachloro- (SIM)
Benzene, pentachloro- (SIM)
Bis-(3,4-dichlorophenyl)methane
Cyclohexane, .alpha.-hexachloro-
Cyclohexane, .beta.-hexachloro-
Cyclohexane, .gamma.-hexachloro-
Decane, 3,6-dimethyl-
Eicosane
Heneicosane
Heptadecane
Hexadecane

Naphthalene
Nonadecane
Octacosane
Octadecane
Pentadecane
Tetracosane
Tetradecane
Tridecane

Compounds tentatively identified:

Benzene, 1,1'-(1,2-ethenediyl)bis-
Decane, 3,8-dimethyl-
Eicosane, 10-methyl-
Heptadecane, 2-methyl-
Heptadecane, 8-methyl-
Isocopalane
Methylnaphthalene
Nonacosane
Undecane, 4,7-dimethyl-

NOTE: There are 4 groups of unidentified compounds in this sample and each group has very similar fragmentation pattern typical for chlorine containing isomers (the same main fragments but at different abundance). Only one compound from one group was reliably identified as bis-(3,4-dichlorophenyl)methane; all the rest have no match with the library spectra.

ANALYTICAL RESULTS

Sample Number: **IT02006**
Sample Type: **Solid waste**
Location: **Union Carbide plant, Bhopal, India**
Sampling Date: **30.03.02**
Sample Information: **From sacks in BHC store; pile D/A 4 in second room**

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen
Prepared by Iryna Labunska

Number of compounds isolated: 25

Compounds identified to better than 90%:

Benzene, 1,2,3,4-tetrachloro-
Benzene, 1,2,4-trichloro-
Benzene, 1,2-dichloro-
Benzene, 1,3-dichloro- (SIM)
Benzene, 1,4-dichloro-
Cyclohex-1-ene, pentachloro- (2 isomers)
Cyclohexane, .alpha.-hexachloro-
Cyclohexane, .beta.-hexachloro-
Cyclohexane, .gamma.-hexachloro-
Cyclohexane, .delta.-hexachloro-
Naphthalene, 1,2,3,4-tetrahydro-

Compounds tentatively identified:

Cyclohex-1-ene, pentachloro- (3 isomers)
Cyclohexane, heptachloro- (2 isomers)
Cyclohexene, .gamma.-tetrachloro-

ANALYTICAL RESULTS

Sample Number: **IT02007**
Sample Type: **Solid waste**
Location: **Union Carbide plant, Bhopal, India**
Sampling Date: **30.03.02**
Sample Information: **From sacks in soapstone shed**

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen
Prepared by Iryna Labunska

Number of compounds isolated: 53

Compounds identified to better than 90%:

Benzene, 1,2,3,4-tetrachloro- (SIM)
Benzene, 1,2,3,5-tetrachloro- (SIM)
Benzene, 1,2,3-trichloro- (SIM)
Benzene, 1,2,4,5-tetrachloro- (SIM)
Benzene, 1,2,4-trichloro- (SIM)
Benzene, 1,2-dichloro- (SIM)
Benzene, 1,4-dichloro- (SIM)
Benzene, hexachloro- (SIM)
Benzene, pentachloro- (SIM)
Cyclohexane, .alpha.-hexachloro-
Cyclohexane, .beta.-hexachloro-
Cyclohexane, .gamma.-hexachloro-
Cyclohexane, .delta.-hexachloro-
Docosane, 11-decyl-
Heneicosane
Heptadecane
Hexadecane
Hexadecane, 2-methyl-
Naphthalene
Naphthalene, 1,2,3,4-tetrahydro-
Naphthalene, 1-methoxy-
Naphthalene, 2,4-dichloro-1-methoxy-

p,p'-DDE	(SIM)
o,p'-DDD	(SIM)
p,p'-DDD	(SIM)
o,p'-DDT	(SIM)
p,p'-DDT	
Pentadecane	
Pentadecane, 2,6,10,14-tetramethyl-	
Tridecane	

Compounds tentatively identified:

1-Isopropenyl naphthalene
2,3,5-Trichloropyridine
Cyclohexene, .delta.-pentachloro-
Cyclohexene, .gamma.-pentachloro-
Decane, 2-methyl-
Docosane
Octadecane
Octane, 2-methyl-
Pentadecane, 2-methyl-
Undecane, 5,7-dimethyl-
Undecane, 5-methyl-

ANALYTICAL RESULTS

Sample Number: **IT02008**
Sample Type: **Solid waste**
Location: **Union Carbide plant, Bhopal, India**
Sampling Date: **30.03.02**
Sample Information: **From barrels in cycle shed**

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen
Prepared by Iryna Labunska

Number of compounds isolated: 66

Compounds identified to better than 90%:

Benz[e]acephenanthrylen-8-ol
Benzene, 1-(1,1-dimethylethyl)-
Benzene, 1,1'-cyclopropylidenebis-
Benzene, 1,1'-oxybis-
Benzene, 1,2,3,4-tetrachloro- (SIM)
Benzene, 1,2,4-trichloro- (SIM)
Benzene, 1,2-dichloro- (SIM)
Benzene, 1,4-dichloro- (SIM)
Benzene, 1-methyl-2-(1-methylethyl)-
Benzene, 1-methyl-3,5-bis(1-methylethyl)-
Benzene, 1-methyl-3,5-bis(1-methylethyl)-
Benzene, 1-methyl-4-(1-methylethyl)-
Benzene, 2-methyl-1,4-bis(1-methylethyl)-
Cyclohexane, .alpha.-hexachloro-
Cyclohexane, .beta.-hexachloro- (SIM)
Cyclohexane, .delta.-hexachloro- (SIM)
Decane, 3,6-dimethyl-
Dinaphtho[1,2-b:1',2'-d]furan
Docosane
Docosane, 11-decyl-
Eicosane
Heneicosane

Heneicosane, 3-methyl-
Heptacosane
Heptadecane
Heptadecane, 2-methyl-
Heptadecane, 3-methyl-
Hexadecane
Hexadecane, 2-methyl-
Naphthalene
Naphthalene, 1,1'-oxybis-
Naphthalene, 1,2,3,4-tetrahydro-
Naphthalene, 1-chloro-
Naphthalene, 1-isopropenyl-
Naphthalene, 2,2'-oxybis-
Nonacosane
Octacosane
Octadecane
Pentacosane
Pentadecane
Tricosane

Compounds tentatively identified:

9-Anthracenemethanol
Benzene, 1-ethyl-2,3-dimethyl-
Decane, 2,3,6-trimethyl-
Decane, 2-methyl-
Nonadecane
Octadecane, 2-methyl-
Pentadecane, 2-methyl-
Undecane, 2,8-dimethyl-
Undecane, 4-ethyl-
Undecane, 4-methyl-

ANALYTICAL RESULTS

Sample Number: **IT02009**
Sample Type: **Solid waste**
Location: **Union Carbide plant, Bhopal, India**
Sampling Date: **30.03.02**
Sample Information: **From sacks in cycle shed**

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen
Prepared by Iryna Labunska

Number of compounds isolated: 101

Compounds identified to better than 90%:

1,1'-Biphenyl
1,2'-Binaphthalene
1,3-Butadiene, 1,1,2,3,4,4-hexachloro-
1H-Indene
1H-Indene, 2,3-dihydro-4,7-dimethyl-
1-Naphthalenol
2,2'-Binaphthalene
2,3-Dihydro-1H-phenalene
9H-Fluoren-9-ol
9H-Fluorene, 9-(phenylmethylene)-
Benz[a]anthracene
Benz[e]acephenanthrylen-1-ol
Benz[e]acephenanthrylen-8-ol
Benzene, 1,1'-oxybis-
Benzene, 1,2,3,4-tetrachloro- (SIM)
Benzene, 1,2,3-trichloro-
Benzene, 1,2,4,5-tetrachloro- (SIM)
Benzene, 1,2-dichloro-
Benzene, 1,3-dichloro- (SIM)
Benzene, 1,4-dichloro-
Benzene, ethyl-1,2,4-trimethyl-
Benzo[b]naphtho[2,3-d]furan

Benzo[c]phenanthrene 5,6-oxide
Cyclohexane, .alpha.-hexachloro-
Cyclohexane, .beta.-hexachloro-
Cyclohexane, .gamma.-hexachloro- (SIM)
Dibenzofuran
Dinaphtho[1,2-b:1',2'-d]furan
Docosane
Eicosane
Ethane, hexachloro-
Heneicosane
Heptadecane
Hexadecane
Naphthalene
Naphthalene, 1-(2-naphthalenylmethyl)-
Naphthalene, 1-(phenylmethyl)-
Naphthalene, 1,1'-methylenebis-
Naphthalene, 1,1'-oxybis-
Naphthalene, 1,2,3,4-tetrahydro-
Naphthalene, 1,2-dihydro-
Naphthalene, 1-ethyl-
Naphthalene, 1-methoxy-
Naphthalene, 1-methyl-
Naphthalene, 1-phenyl-
Naphthalene, 2-(phenylmethyl)-
Naphthalene, 2-ethyl-
Naphthalene, 2-methyl-
Nonadecane
Octadecane
Pentadecane
Pentadecane, 2,6,10,14-tetramethyl-
Tetracosane
Tetradecane
Tricosane
Tridecane
Undecane

Compounds tentatively identified:

1-Ethyl-1,2,3,4-tetrahydronaphthalene
2,2'-Dinaphthyl ether
2-Methylindene
2-Naphthalenol
2-Phenylnaphthalene
4-Benzylbiphenyl
5-Ethylindan
9H-pyrido[3,4-b]indole
Dibenz[a,j]anthracene, 5,6,8,9-tetrahydro-
Docosane, 11-decyl-
Dodecane

Dodecane, 2,5-dimethyl-
Naphthalene, 1,2,3,4-tetrahydro-
Pentadecane, 2-methyl-
Tetratriacontane

ANALYTICAL RESULTS

Sample Number: **IT02010**
Sample Type: **Solid waste**
Location: **Union Carbide plant, Bhopal, India**
Sampling Date: **30.03.02**
Sample Information: **From sacks in formulation shed**

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen
Prepared by Iryna Labunska

Number of compounds isolated: 66

Compounds identified to better than 90%:

Benzene, 1,2,3,4-tetrachloro-
Benzene, 1,2,3,5-tetrachloro- (SIM)
Benzene, 1,2,3-trichloro- (SIM)
Benzene, 1,2,4,5-tetrachloro- (SIM)
Benzene, 1,2,4-trichloro-
Benzene, 1,2-dichloro-
Benzene, 1,3,5-trichloro- (SIM)
Benzene, 1,3-dichloro- (SIM)
Benzene, 1,4-dichloro-
Benzene, pentachloro- (SIM)
Cyclohexane, .alpha.-heptachloro-
Cyclohexane, .beta.-heptachloro-
Cyclohexane,.alpha.-hexachloro-
Cyclohexane,.beta.-hexachloro-
Cyclohexane,.gamma.-hexachloro-
Cyclohexane,.delta.-hexachloro-
Cyclohexene, 1,2,3,4,5-pentachloro-
Cyclohexene, 1,3,4,5,6-pentachloro-
Cyclohexene, 2,3,4,5,6-pentachloro-
Docosane
Eicosane
Heneicosane

Hexacosane
Hexadecane
Naphthalene, 1,4-dihydro-
Naphthalene, 1-methoxy-
Nonadecane
Octacosane
Octadecane
p,p'-DDE (SIM)
o,p'-DDD (SIM)
o,p'-DDT (SIM)
p,p'-DDT (SIM)
Pentacosane
Pentadecane, 2,6,10,14-tetramethyl-
Tetracosane

Compounds tentatively identified:

Benz[e]acephenanthrylen-1-ol
Benzene, 1,1'-(1,2-ethanediyl)bis-
Hexadecane, 2-methyl-
Hexadecane, 7,9-dimethyl-
Octadecane, 3-methyl-
Undecane, 4,7-dimethyl-

ANALYTICAL RESULTS

Sample Number: **IT02011**
Sample Type: **Solid waste**
Location: **Union Carbide plant, Bhopal, India**
Sampling Date: **30.03.02**
Sample Information: **From sacks in formulation shed**

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen
Prepared by Iryna Labunska

Number of compounds isolated: 214

Compounds identified to better than 90%:

1,1'-Biphenyl, 2',3,4-trichloro-
1,1'-Biphenyl, 2-ethyl-
1,1'-Biphenyl, 2-methyl-
1,2'-Binaphthalene
1,3-Butadiene, 1,1,2,3,4,4-hexachloro-
1,3-Butadiene, 1,4-diphenyl-
1H-indene, 2,3-dihydro-
1H-indene, 2,3-dihydro-1,1,5-trimethyl-
1H-indene, 2,3-dihydro-2-methyl-
1H-indene, 2,3-dihydro-4,7-dimethyl-
1H-indene, 2,3-dihydro-5-methyl-
1-Naphthalenol
1-Naphthalenol, 2,4-dichloro-
2,2-Dimethylindene, 2,3-dihydro-
6,8-Dimethylbenzocyclooctene
9H-Fluoren-2-ol
9H-Fluorene
9H-Fluorene, 9-(phenylmethylene)-
Benz[e]acephenanthrylen-1-ol
Benz[e]acephenanthrylen-2-ol
Benzene, (2-methyl-1-propenyl)-
Benzene, 1,1'-(1,4-butanediyl)bis-

Benzene, 1,1'-(1-butenylidene)bis-
 Benzene, 1,1'-(1-propylidene)bis-
 Benzene, 1,1'-methylenebis-
 Benzene, 1,1'-oxybis-
 Benzene, 1,2,3,4-tetrachloro- (SIM)
 Benzene, 1,2,3,5-tetrachloro- (SIM)
 Benzene, 1,2,3-trichloro- (SIM)
 Benzene, 1,2,3-trimethyl-
 Benzene, 1,2,4,5-tetrachloro- (SIM)
 Benzene, 1,2,4-trichloro-
 Benzene, 1,2,4-triethyl-
 Benzene, 1,2-dichloro-
 Benzene, 1,3,5-triethyl-
 Benzene, 1,3-dichloro-
 Benzene, 1,3-diethyl-
 Benzene, 1,3-diethyl-5-methyl-
 Benzene, 1,4-dichloro-
 Benzene, 1,4-diethyl-
 Benzene, 1-ethyl-2-methyl-
 Benzene, 1-methyl-2-propyl-
 Benzene, 1-methyl-3-(1-methylethyl)-
 Benzene, 1-methyl-4-(1-methylethyl)-
 Benzene, 1-propynyl-
 Benzene, 4-ethyl-1,2-dimethyl-
 Benzene, ethyl-1,2,4-trimethyl- (SIM)
 Benzene, pentachloro- (SIM)
 Bis-(3,4-dichlorophenyl)methane
 Cyclohex-1-ene, 1,2,3,4,5-pentachloro-
 Cyclohexane, .alpha.-hexachloro-
 Cyclohexane, .beta.-hexachloro-
 Cyclohexane, .delta.-hexachloro-
 Cyclohexane, .gamma.-hexachloro-
 Dinaphtho[1,2-b:1',2'-d]furan
 Docosane
 Docosane, 11-decyl-
 Eicosane
 Ethane, hexachloro-
 Ethane, pentachloro-
 Heneicosane
 Heptadecane, 2-methyl-
 Hexadecane
 Naphth[2,3-a]azulen-5(12h)-one
 Naphthalene
 Naphthalene, 1-(phenylmethyl)-
 Naphthalene, 1,1'-methylenebis-
 Naphthalene, 1,1'-oxybis-
 Naphthalene, 1,2,3,4-tetrahydro-
 Naphthalene, 1-ethoxy-
 Naphthalene, 1-ethyl-1,2,3,4-tetrahydro-
 Naphthalene, 1-hexyl-

Naphthalene, 2-(phenylmethyl)-
Naphthalene, 2-butyl-
Naphthalene, 2-ethyl-
Naphthalene, 2-ethyl-1,2,3,4-tetrahydro-
Naphthalene, 2-hexyl-
Naphthalene, 2-methoxy-
Naphthalene, 2-methyl-
Naphthalene, 5-ethyl-1,2,3,4-tetrahydro-
Naphthalene, 6-butyl-1,2,3,4-tetrahydro-
Nonadecane
Pentacosane
Tetracosane
Tetradecane

Compounds tentatively identified:

(1,4-Dimethylpent-2-enyl)benzene
1,1'-Biphenyl, 4-pentyl-
1-Chloro-2-naphthol
1H-indene, 1,3-dimethyl-
1H-indene, 1-ethenyl-2,3-dihydro-
1H-indene, 2,3-dihydro-1,1,3-trimethyl-
1H-indene, 5-hexyl-2,3-dihydro-
2,3-Dihydro-1h-phenalene
2-(.Betya.-naphthyl)benzo[b]furan
2-Cyclohexen-1-one, 3-phenyl-
5,10,12-Trimethyl-10,11-dihydro-
6,7-Didehydro-4-t-butyl dimethyl-
Benzene, (methylenecyclopropyl)-
Benzene, 1,1'-(2-methyl-1-propenyl)-
Benzene, 1,2-diethyl-
Benzene, 1,2-diethyl-4,5-dimethyl-
Benzene, 1,3,5-trimethyl-2-propyl-
Benzene, 1,4-diethyl-2-methyl-
Benzene, 1-hexynyl-
Benzene, 1-methyl-2-(1-methylethyl)-
Benzene, 2,4-dimethyl-1-(1-methyl)-
Benzene, diethenyl-
Bibenzyl
Decane, 2-methyl-
Decane, 3,8-dimethyl-
Decane, 3-methyl-
Dodecane, 2,6,10-trimethyl-
Ethyl naphthalene
Heptacosane
Heptadecane, 3-methyl-
Hexadecane, 2,6,10,14-tetramethyl-
Hexadecane, 2-methyl-
Hexadecane, 7,9-dimethyl-

Naphthalene, 1,2(or 2,3)-diethyl-
Naphthalene, 1,4-dimethyl-
Naphthalene, 1-propyl-
Naphthalene, 2-chloro-3-(chloromethyl)-
Naphthalene, 2-methyl-1-propyl-
Naphthalene, 6-ethyl-1,2,3,4-tetramethyl-
Naphtho[1,2-c]furan
Octadecane
Triacontane
Tricosane, 2-methyl-

NOTE: There are five more compounds with the fragmentation pattern very similar to bis-(3,4-dichlorophenyl)methane. These might be an isomeric mixture.

ANALYTICAL RESULTS

Sample Number: **IT02012**
Sample Type: **Solid waste**
Location: **Union Carbide plant, Bhopal, India**
Sampling Date: **30.03.02**
Sample Information: **From sacks in formulation shed**

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen
Prepared by Iryna Labunska

Number of compounds isolated: 57

Compounds identified to better than 90%:

Benzene, 1,2,3,5-tetrachloro-
Benzene, 1,2,3-trichloro-
Benzene, 1,2,4,5-tetrachloro-
Benzene, 1,2,4-trichloro-
Benzene, 1,2-dichloro-
Benzene, 1,3-dichloro-
Benzene, 1,4-dichloro-
Benzene, 1-methyl-2-nitro-
Benzene, pentachloro-
Cyclohexane, .alpha.-hexachloro-
Cyclohexane, .beta.-hexachloro-
Cyclohexane, .gamma.-hexachloro-
Cyclohexane, .delta.-hexachloro-
Cyclohexane, heptachloro- (4 isomers)
Cyclohexene, pentachloro- (6 isomers)
Cyclohexene, tetrachloro- (2 isomers)
Eicosane
Heneicosane
Naphthalene, tri-sec-butyl-
Nonadecane
Tridecane

Compounds tentatively identified:

1-Propene, 1,1,2,3-tetrachloro-
Benzene, 1,3,5-trimethyl-2-propyl-
Benzene, 1,4-dimethyl-2-(2-methylethyl)-
Benzene, 1-(1-ethylpropyl)-4-methyl-
Benzene, 1-methyl-4-(1-methylpropyl)-
Cyclohexene, 3,4,5,6-tetrachloro-
Decane, 3,6-dimethyl-
Hexadecane, 2,6,10,14-tetramethyl-
Pentacosane
Undecane, 5-methyl-

NOTE: Five compounds have no match with library spectra, they are polychlorinated and have similar fragmentation patterns as would be expected of an isomeric mixture.

ANALYTICAL RESULTS

Sample Number: **IT02029**

Sample Type: **Soil**

Location: **Site of solar evaporation pond, north-east of Union Carbide plant, Bhopal, India**

Sampling Date: **14.10.2002**

Sample Information: **Sample collected from underneath broken/exposed plastic liner. Children were observed digging at this location.**

INORGANIC ANALYTICAL RESULTS

Analysis method: ICP-AES

Prepared by Kevin Brigden

METAL	CONCENTRATION (mg/kg dry weight)
Cadmium	<1
Chromium	96
Cobalt	37
Copper	57
Lead	8
Manganese	1461
Mercury	0.10
Nickel	74
Zinc	69

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen

Prepared by Iryna Labunska

Number of compounds isolated: 82

Compounds identified to better than 90%:

1,2-Benzenedicarboxylic acid, diisobutyl ester
1,2-Benzenedicarboxylic acid, di-n-butyl ester
1-Octadecene
Benzene, (1-butylheptyl)-
Benzene, (1-butyloctyl)-
Benzene, (1-ethyldecyl)-
Benzene, (1-ethylnonyl)-
Benzene, (1-methylundecyl)-
Benzene, (1-pentylheptyl)-
Benzene, (1-propylnonyl)-
Benzene, (1-propyloctyl)-
Benzene, 1,4-dichloro- (SIM)
Benzene, hexachloro- (SIM)
Benzene, pentachloro- (SIM)
Decane
Decane, 4-methyl-
Docosane
Dodecane
Heneicosane
Heptadecane
Hexadecane
Nonadecane
Octadecane
Pentadecane
Tetradecane
Tridecane
Undecane

Compounds tentatively identified:

1-Decanol, 2-hexyl-
3-Tetradecanol
Benzene, (1-methyldecyl)-
Benzene, (1-methylnonyl)-
Benzene, (1-pentylhexyl)-
Benzene, (1-pentyloctyl)-
Benzene, (octyloxy)-
Cyclohexane, 1,2,4-trimethyl-
Cyclohexane, 1,2-dimethyl-, cis-

Cyclotridecane
Decane, 2-methyl-
Heptadecane, 2,6,10,14-tetramethyl-
Octacosane
Propanoic acid, phenyl ester

ANALYTICAL RESULTS

Sample Number: **IT02030**

Sample Type: **Soil**

Location: **Site of solar evaporation pond, north-east of Union Carbide plant, Bhopal, India**

Sampling Date: **14.10.2002**

Sample Information: **Sample collected from underneath broken/exposed plastic liner. Children were observed playing at this location.**

INORGANIC ANALYTICAL RESULTS

Analysis method: ICP-AES

Prepared by Kevin Brigden

METAL	CONCENTRATION (mg/kg dry weight)
Cadmium	<1
Chromium	93
Cobalt	20
Copper	41
Lead	9
Manganese	770
Mercury	<0.1
Nickel	71
Zinc	67

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen

Prepared by Iryna Labunska

Number of compounds isolated: 39

Compounds identified to better than 90%:

Benzene, 1,4-dichloro- (SIM)
Docosane
Eicosane
Heneicosane
Hexacosane
Phenol, 2,4-bis(1,1-dimethylethyl)-
Tetracosane
Tridecane

Compounds tentatively identified:

Decane, 2,4,6-trimethyl-
Decane, 3,6-dimethyl-
Decane, 3,8-dimethyl-
Docosane, 11-decyl-
Heptacosane
Hexadecane, 2,6,10,14-tetramethyl-
Hexadecane, 2-methyl-
Hexadecane, 7,9-dimethyl-
Octane, 2-methyl-
Undecane, 4,7-dimethyl-

ANALYTICAL RESULTS

Sample Number: **IT02031**

Sample Type: **Soil**

Location: **Site of solar evaporation pond, north-east of Union Carbide plant, Bhopal, India**

Sampling Date: **14.10.2002**

Sample Information: **Sample collected from the banks of a pond where children and domestic animals bathe.**

INORGANIC ANALYTICAL RESULTS

Analysis method: ICP-AES
Prepared by Kevin Brigden

METAL	CONCENTRATION (mg/kg dry weight)
Cadmium	<1
Chromium	61
Cobalt	20
Copper	40
Lead	5
Manganese	1036
Mercury	<0.1
Nickel	53
Zinc	61

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen

Prepared by Iryna Labunska

Number of compounds isolated: 68

Compounds identified to better than 90%:

1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester
1-Hexadecene
2-Pentadecanone, 6,10,14-trimethyl-
Benzene, 1,4-dichloro- (SIM)
Decane, 3,6-dimethyl-
Docosane
Dodecane
Eicosane
Heptacosane
Heptadecane
Hexacosane
Hexadecane
Hexadecane, 2-methyl-
Nonadecane
Octacosane
Octadecane
Pentadecane
Sulfur, mol. (S8)
Tetracosane
Tetradecane
Tetratriacontane
Tricosane
Tridecane

Compounds tentatively identified:

5-Octadecene, (e)-
Decane, 3,8-dimethyl-
Decane, 3-methyl-
Docosane, 11-decyl-
Dodecane, 2,7,10-trimethyl-
Dodecane, 4,9-dipropyl-
Hexane, 3,3-dimethyl-
Nonane, 5-(2-methylpropyl)-
Nonane, 5-butyl-
Pentadecane, 8-heptyl-
Sulfur, mol. (s8)
Undecane, 5,7-dimethyl-
Undecane, 5-methyl-

ANALYTICAL RESULTS

Sample Number: **IT02032**

Sample Type: **Soil**

Location: **Site of solar evaporation pond, north-east of Union Carbide plant, Bhopal, India**

Sampling Date: **14.10.2002**

Sample Information: **Sample collected below broken/exposed plastic liner along the banks of a pond where children and domestic animals bathe.**

INORGANIC ANALYTICAL RESULTS

Analysis method: ICP-AES
Prepared by Kevin Brigden

METAL	CONCENTRATION (mg/kg dry weight)
Cadmium	<1
Chromium	70
Cobalt	21
Copper	40
Lead	12
Manganese	997
Mercury	<0.1
Nickel	58
Zinc	64

ORGANIC ANALYTICAL RESULTS

Analysis method: GC/MS screen

Prepared by Iryna Labunska

Number of compounds isolated: 36

Compounds identified to better than 90%:

1-Octadecene
Benzene, 1,4-dichloro- (SIM)
Docosane
Eicosane
Heptadecane
Hexacosane
Octadecane
Pentacosane
Tetracosane
Tricosane
Tridecane

Compounds tentatively identified:

6-Tridecene, 7-methyl-
Cyclohexane, 1,2,4-trimethyl-
Cyclopentane, 1-ethyl-2-methyl-
Dodecane, 2,6,11-trimethyl-
Nonane, 3,7-dimethyl-