Investigation of chemicals released by the Vinythai and Thai Plastic & Chemicals (TPC) PVC manufacturing facilities, Map Ta Phut Industrial Estate, Rayong Province, Thailand

Kevin Brigden, Iryna Labunska & David Santillo

Greenpeace Research Laboratories
Technical Note 09/2004

November 2004

Table of contents

Publ: Greenpeace Research Laboratories, Department of Biological Sciences, University of Exeter, Exeter EX4 4PS, UK

Executive summary

Vinythai and Thai Plastic & Chemicals (TPC) operate separate polyvinyl chloride (PVC) manufacturing facilities within the Map Ta Phut Industrial Estate, located in Rayong Province on the Eastern Seaboard of Thailand. Canals flow through the estate and receive discharged wastewaters from many facilities prior to discharging into the Gulf of Thailand. Both PVC manufacturing facilities discharge wastewaters to one of these canals herein referred to as the east canal. Within the Vinythai and TPC facilities, PVC is produced as well as the raw materials used in its manufacture, namely chlorine, ethylene dichloride (EDC) and vinyl chloride monomer (VCM).

In May 2003 Greenpeace collected samples of wastewaters from Vinythai and TPC at their point of discharge to the east canal, as well as sediments from this canal. All were analysed for a range of heavy metals and organic chemicals.

Discharged effluents from both Vinythai and TPC contained a diversity of chlorinated volatile organic compounds (VOCs) that possess a range of toxic characteristics. Many VOCs were common to discharges from both facilities, though all VOCs in Vinythai effluents were present only at low concentrations. The main TPC discharge (AT03032) contained more chlorinated compounds than all other discharges from either facility. Most significant was the presence of 1,2-dichloroethane (EDC) at 250 ug/l, a level that, if representative of continuous discharges, would be unacceptable for an equivalent plant in the USA. EDC is not highly persistent in the environment but is, however, toxic to humans and animals. The main TPC discharge also contained other organic chemicals including 2,4,6-trichlorophenol, a less volatile organochlorine, and DEHP, a phthalate ester widely used as a PVC additive and which is relatively persistent and toxic to reproduction.

VOCs may be readily lost to the air during production, storage, transfer and use, or from wastewaters during their treatment or discharge. Emissions to atmosphere *via* these additional release routes may be very significant for such volatile compounds but determination of such releases was not feasible in the current study.

The effluents from both facilities also contained some heavy metals at concentrations above background levels expected for uncontaminated surface waters, though the levels in Vinythai discharges were only slightly elevated above these levels. In contrast, two of the discharges from TPC contained high levels of zinc, with a concentration of 1590 ug/l in the main discharge (AT03032) and even higher in one other discharge (AT03030; 3020 ug/l). Zinc compounds are widely used as stabilisers in PVC formulations, and such use by TPC is a possible source of zinc to these wastewaters.

Analysis of sediments collected from the east canal yielded evidence for the discharge of heavy metals and organic chemicals over longer timeframes. Neither chlorinated compounds nor high concentrations of metals were found in sediment collected from the east canal upstream of both PVC manufacturing facilities. However, sediment collected by Vinythai's middle discharge (AT03026) contained metals at somewhat higher concentrations than those found upstream. Moreover, sediments collected adjacent to the TPC discharges contained far higher concentrations, particularly for zinc, which was present at levels more than 80 times higher than background near the most contaminated discharge (AT03031), and over 8 times background concentrations by the main TPC discharge (AT03033).

The sediment samples associated with TPC discharges also contained the phthalate ester DEHP. Furthermore, a number of highly chlorinated compounds (octachlorostyrene and chlorinated benzenes) were also identified in these sediments, though at trace levels. These chlorinated compounds, though not identified in TPC effluents at the time of sampling, can be formed as by-products of industrial processes involving chlorine compounds. They are highly persistent in the environment and many are able to accumulate in the bodies of animals and humans, particularly the higher chlorinated pentachlorobenzene and hexachlorobenzene (HCB). These chlorinated compounds exhibit a range of toxic effects in humans and animals.

The presence within canal sediments of organic pollutants and elevated concentrations metals that were also found in discharged wastewaters indicates their environmental accumulation as a result of ongoing discharges. The identification of additional organochlorines in sediments associated with TPC suggests these have been released from this facility at other times. As many of these contaminants are environmentally persistent, their presence in the east canal suggests ongoing inputs to the Gulf of Thailand as waters and associated sediments are discharged.

Both Vinythai and TPC have policies intended to address environmental impacts resulting from manufacturing within their facilities, and TPC claim to employ monitoring and control programs to prevent contamination of the environment. On the basis of this study, it appears that the practical effect of these policies may be somewhat limited. PVC manufacturing, particularly at the TPC facility, is clearly a significant source of toxic VOCs to the surrounding environment.

The discharge of the organochlorines identified in the effluents is not specifically addressed under legislation addressing industrial effluents in Thailand, despite the Thai National Chemicals Management Profile listing organochlorine compounds as ‘specific chemicals creating concern’.

Greater controls are clearly needed to address the production of hazardous and toxic chemicals, be they intentionally or unintentionally produced, as well as their use and release. Stringent legislation addressing discharges and releases could be a first step, though protecting the environment and human health from such chemicals in complex waste streams will only be fully addressed through the progressive substitution of hazardous chemicals with non-hazardous alternatives. These measures are particularly needed for industries involved in the production and use of chlorinated chemicals, which use process that are widely associated with the formation of toxic and persistent chlorinated by-products.

1 Introduction

The Map Ta Phut Industrial Estate is located in Muang District, Rayong Province, on the Eastern Seaboard of Thailand edging the Gulf of Thailand. This large estate is managed by the Industrial Estate Authority of Thailand (IEAT) and has been in operation since 1982. Over fifty separate facilities operate within the estate, including many involved in large volume chemical manufacture, primarily based upon the use of natural gas as a raw material (GTZ 2001). The IEAT is a state enterprise that operates under the Ministry of Industry. It has responsibility for the management and planning of the estate, including the control and monitoring of industrial pollution (Homchean 1998).

Three main canals flow through the industrial estate. These receive discharged wastewaters from many facilities within the estate and ultimately discharge into the Gulf of Thailand at the estates southern edge. One of the canals enters the estate in the north-western sector, flows through the centre of the estate *via* a concrete-lined channel and ultimately discharges on the estate's eastern edge to the Gulf of Thailand. Hereinafter this canal is referred to as the east canal.

Two facilities located within the industrial estate manufacture the thermoplastic polymer polyvinyl chloride (PVC). These two facilities are separately operated by Vinythai and Thai Plastic & Chemicals (TPC). Both facilities discharge wastewaters to the east canal as it passes through a concrete lined channel that runs between the two facilities. Both Vinythai and TPC produce the raw materials used in PVC manufacture, as well as producing finished PVC formulations (GTZ 2001).

TPC state that their facilities adhere to an environment policy which includes certain principles designed to ensure that operations are carried out in an environmentally sound manner. These policies include guidelines that aim to prevent contamination of the environment through the monitoring of wastewater, air and soil samples collected in and around the factory on a regular basis (TPC 2002).

Vinythai has also established policies designed to address environmental impacts resulting from manufacturing at their facilities. These include taking action to reduce any impacts on the environment on a continuous basis, and assuring that their products do not have any negative impacts on the environment and human health (GTZ 2001).

1.1 PVC production

Polyvinyl chloride (PVC) is one of the most widely used thermoplastics in the world. Global annual production of this plastic is about 25 million tonnes (CIN 2003). PVC is manufactured by the polymerisation of vinyl chloride, also called vinyl chloride monomer (VCM). A number of different processes are used for the production of VCM, though in most cases VCM is manufactured *via* a chemical intermediate called ethylene dichloride (EDC) (Matthews 1996).

The ethylene dichloride (EDC) intermediate is manufactured through chlorination of ethene, a natural gas. This process is carried out either directly with chlorine or using hydrogen chloride and oxygen in the oxychlorination process. EDC is converted into VCM, which is subsequently polymerised to produce PVC (Stringer & Johnston 2001).

The manufacture of EDC and VCM for use in PVC production results in the generation of wastes containing highly toxic chlorinated chemicals, including chlorinated dioxins. In many cases, releases from VCM manufacturing facilities have resulted in the contamination of the local environment with many chlorinated chemicals (Labunska *et al.* 2002, Stringer & Johnston 2001, Stringer *et al.* 1995).

A wide range of additional chemicals are commonly added to PVC formulations to modify the properties of the final plastic product (Ehrig 1992). Chemical pigments are added to colour the products, stabiliser chemicals are added to reduce degradation of the plastic that can result from exposure to heat and UV light, and for non-rigid products plasticisers are incorporated to soften the PVC. A wide range of heavy metal compounds and synthetic organic chemicals are employed in these different additive categories (Stringer & Johnston 2001).

2 Sampling program

Greenpeace visited the Map Ta Phut Industrial Estate in May 2003 to collect samples of wastewaters at their points of discharge to the east canal from the Vinythai and TPC facilities, as well as associated samples of sediment from the receiving canal. A map of the Map Ta Phut Industrial Estate showing the two PVC manufacturing facilities and the east canal is presented in Figure 1.

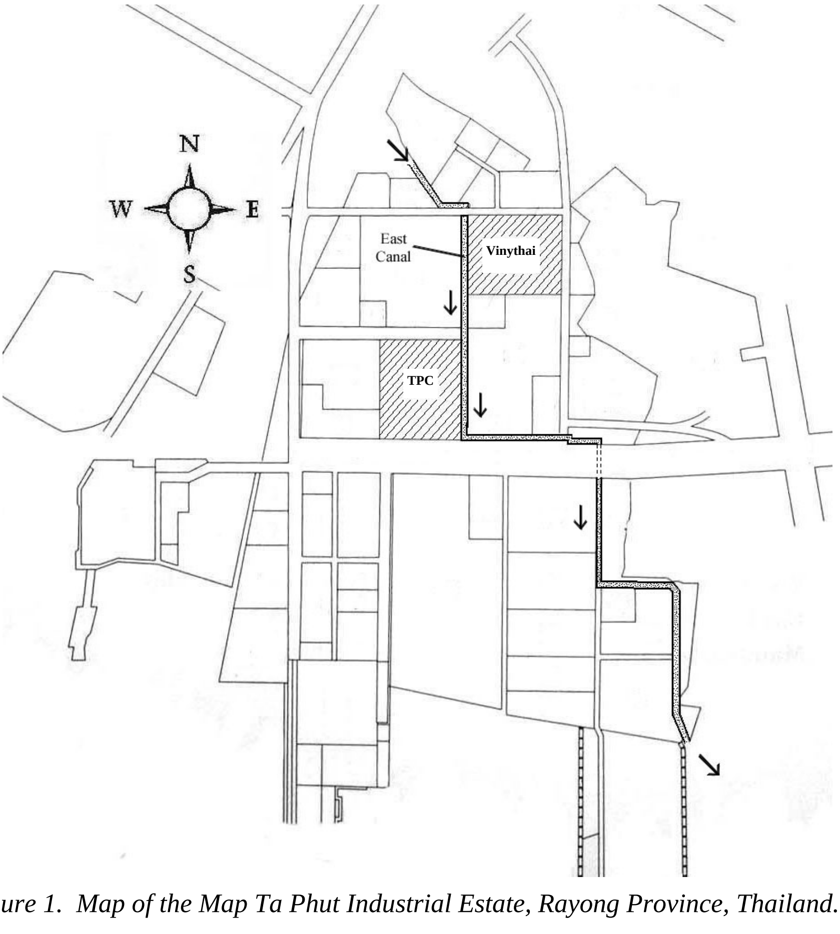

Figure 1. Map of the Map Ta Phut Industrial Estate, Rayong Province, Thailand.

An expanded map showing the locations of wastewater samples collected from the outfalls of both facilities and of sediments collected from within the east canal is presented in Figure 2.

Samples of discharged wastewater were collected from five separate outfalls that were observed discharging wastewaters to the east canal from the Vinythai and TPC facilities. Six sediment samples were collected from the east canal to gain an understanding of the nature of pollutants received by the canal over a longer timeframe. At the time of sampling there was little sediment in parts of the concrete lined section of the east canal that receives discharges from the Vinythai and TPC facilities.

All samples were collected and stored in pre-cleaned glass bottles that had been rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metal and organic residues. Each wastewater samples was collected in a 1-litre screw-cap bottle. For those water samples analysed for volatile organic compounds (VOCs), duplicate samples were collected in 125 ml amber bottles fitted with ground-glass stoppers to prevent the loss of volatile chemicals prior to sample analysis. Sediment samples were collected in 100ml glass bottles. All samples were kept cool and returned to the Greenpeace Research Laboratories for analysis. Detailed descriptions of sample preparation and analytical procedures are presented in Appendix 1.

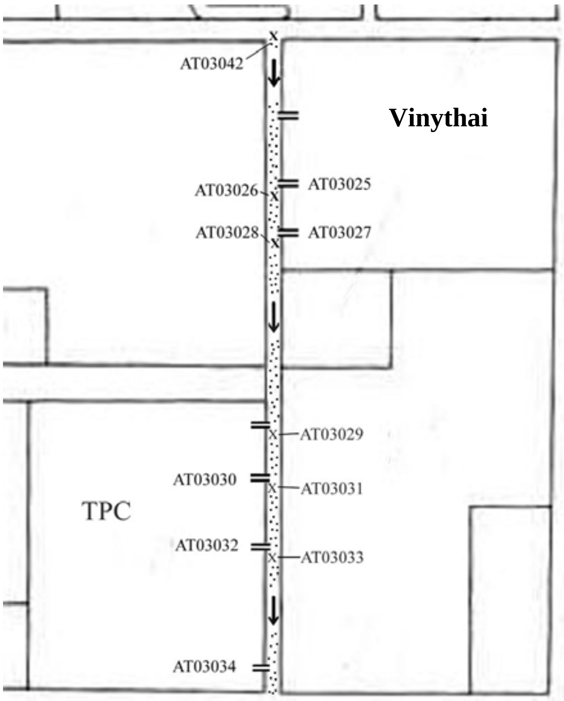

Figure 2. Map of the Vinythai and TPC facilities within the Map Ta Phut Industrial Estate showing the locations of wastewater discharges and sediment samples collected. 'X' denotes the position of sediment samples within the east canal.

2.1 Vinythai

The Vinythai facility is located on the eastern side of the east canal, which flows through the centre of the estate. Three potential discharge points from Vinythai to the canal were observed, though on the day the samples were collected no wastewaters were being discharge *via* the northern-most (upper) discharge point. Details of the samples associated with Vinythai are summarised in Table 2.1, and their locations presented on a map of the area in Figure 2.

At the middle of the three discharge points, wastewaters are discharged to the east canal *via* a concrete lined channel flowing underground from within the Vinythai facility. A sample of wastewater (AT03025) was collected from this concrete side channel at its point of discharge. A sample of sediment (AT03026) was collected from the east canal, approximately five meters downstream from this discharge point.

At the Vinythai discharge furthest downstream (lower discharge point), it was observed that wastewaters are carried in an open channel for a considerable distance within the facility before discharging *via* a wide concrete-lined opening into the east canal. A sample of wastewater (AT03027) was collected at the point of discharge to the east canal. At the time of sampling, wastewater was being discharged at a low flow rate. A second sample of sediment (AT03028) was collected from the east canal approximately five meters downstream of this lower discharge point.

An additional sample of sediment (AT03042) was collected from the east canal immediately upstream of all discharges from the Vinythai facility. This control sample was collected to determine the nature and extent of chemical inputs to the east canal prior to receiving wastewaters from Vinythai.

Sample no.	Sample type	Sample location
AT03042	Sediment	East canal, upstream of the Vinythai discharges (control)
AT03025	Effluent	Concrete channel; middle discharge point to the east canal
AT03026	Sediment	East canal immediately downstream of the middle discharge (AT03025)
AT03027	Effluent	Concrete channel; lower discharge point to the east canal
AT03028	Sediment	East canal immediately downstream of the lower discharge point (AT03027)

Table 2.1. Description of the samples collected from the vicinity of the Vinythai PVC manufacturing facility, Map Ta Phut Industrial Estate, Rayong Province, Thailand, 2003

2.2 TPC

The TPC manufacturing facility is located on the western edge of the east canal, immediately downstream from the Vinythai facility (see Figures 1 and 2). All observed wastewaters discharge points from TPC therefore enter the east canal downstream of those from Vinythai. Details of the samples associated with Vinythai are summarised in Table 2.2, and their locations presented on a map of the area in Figure 2.

Four potential discharge points from the TPC facility to the east canal were observed. The most upstream (northern-most) of these was not flowing at the time of sample collection, though it appeared that wastewaters may be discharged *via* this outfall at other times. A sample of sediment (AT03029) was collected from the east canal below this outfall.

Sample no.	Sample type	Sample location
AT03029	Sediment	East canal, immediately downstream of the 1st (most upstream) discharge point (not discharging at time of sampling)
AT03030	Effluent	Discharge pipe; 2nd discharge point from TPC to the east canal
AT03031	Sediment	East canal, immediately downstream of 2nd discharge point (AT03030)
AT03032	Effluent	Main discharge pipe; 3rd discharge point from TPC to the east canal
AT03033	Sediment	East canal, immediately downstream of 3rd discharge point (AT03032)
AT03034	Effluent	Discharge pipe; 4th (most downstream) discharge point to the east canal

Table 2.2. Description of the samples collected from the vicinity of the TPC PVC manufacturing facility, Map Ta Phut Industrial Estate, Rayong Province, Thailand, 2003

Samples of wastewaters were collected from each of the three TPC outfalls which were discharging at the time of the visit (identified hereafter as 2nd, 3rd and 4th discharge points). One sample (AT03030) was collected from the 2nd discharge point (furthest upstream), a pipe releasing a low flow rate at the time of sample collection. A second sample (AT03032) was collected from the 3rd discharge point, comprised of two closely adjacent pipes releasing a considerably higher flow of effluent. Samples of sediment were collected from the east canal approximately five meters downstream of both the 2nd and 3rd discharge points (AT03031 and AT03033 respectively).

At the southern end of the TPC facility was a 4th discharge point, where wastewaters are carried *via* a large underground pipe. A sample of effluent was collected from this discharge point (AT03034). Immediately downstream of this point, the east canal receives wastewaters from a separate facility *via* a large and rapidly flowing discharge. As a result it was not possible to collect sediment from the east canal downstream of the southern-most (4th) TPC discharge point.

3 Results and discussion

The results of the qualitative organic screen and quantitative heavy metals analyses for samples associated with both Vinythai and TPC are presented in Tables 3.1 and 3.3 respectively, providing the data for each facility on heavy metal concentrations, the number of organic compounds isolated from each sample, and a breakdown of the groups of organic compounds reliably identified. Volatile organic compounds (VOCs) in effluent samples (AT03025, AT03027, AT03030, and AT03032) were separately quantified, and the concentrations of the VOCs identified in these samples are presented in Table 3.2.

A full list of all organic compounds both reliably and tentatively identified in all samples is provided in Appendix 2. A full list of the VOCs quantified in the effluent samples is provided in Appendix 3. Additional information on certain key pollutants detected during this study is presented in Appendix 4.

In many cases a large proportion of the compounds isolated from the samples could not be identified. The properties and potential impacts of the unidentified compounds remain unknown.

3.1 Vinythai

The two samples of effluent collected at their point of discharge from Vinythai to the east canal contained a range of volatile organic compounds, though all were present at very low concentrations.

Five compounds were identified in the effluent discharged *via* an underground concrete channel at the middle discharge point (AT03025); 1,1- and 1,2-dichloroethane, chloroform, trichloroethene and bromodichloromethane. The effluent discharged to the east canal further downstream *via* an open channel (AT03027) contained two of these compounds; chloroform, and 1,2-dichloroethane. In all but one case these compound were present at concentrations too low to be accurately quantified, the exception being sample AT03025 that contained chloroform at approximately 5 ug/l, close to the limit of quantification for the method. Quantification data including the method detection limits for the VOC compounds identified in the effluent samples are present in Table 3.2.

Sample number	AT03025	AT03027	AT03042	AT03026	AT03028
Description	Effluent	Effluent	Sediment	Sediment	Sediment
Location	Middle discharge	Lower (downstream) discharge	Upstream of Vinythai	East canal, by middle discharge (AT03025)	East canal, by lower discharge (AT03027)
Metals	ug/L	ug/L	mg/kg dw	mg/kg dw	mg/kg dw
Arsenic	<400	<400	<40	<40	<40
Cadmium	<10	<10	<1	<1	<1
Chromium	<20	<20	41	35	9
Cobalt	<20	<20	<2	5	<2
Copper	24	59	5	33	3
Lead	39	89	16	47	8
Manganese	22	<10	155	506	135
Mercury	<2	<2	<0.2	0.4	<0.2
Nickel	30	<20	23	45	2
Zinc	117	22	167	937	66
No. of organic compounds isolated	4	2	17	2	0
No. reliably identified (% of total)	4 (100%)	2 (100%)	9 (53%)	0	0
Chlorinated compounds					
Chloroform	1*	1*			
1,1-Dichloroethene					
1,1-Dichloroethane	1*				
1,2-Dichloroethane (EDC)	1*	1*			
Trichloroethene	1*				
Bromodichloromethane	1*				
Oxygenated compounds					
Benzenemethanol			1		
DEHP (ester of di(2-ethylhexyl) phthalate)			1		
Hydrocarbons					
Linear aliphatic hydrocarbons			7		

*Table 3.1. Organic chemicals and heavy metal concentrations identified in samples from around the Vinythai PVC manufacturing facility, MapTa Phut Industrial Estate, Rayong Province, Thailand, 2003. For both effluent and solid sample sets, the samples are arranged from left to right representing upstream to downstream along the east canal. For the groups of organic compounds reliably identified, the number of compounds identified using general GC/MS screening method is presented for each group; * signifies those compounds identified only at trace levels using a selective ion monitoring (SIM) method. Metal concentrations are given in mg/kg dry weight for solid samples and µg/l for liquid samples.*

The metals quantified in this study are naturally present in environmental samples, though generally at low concentrations. Significant anthropogenic inputs can result in elevated concentrations above these natural background levels. The concentrations of zinc in the sample from the middle discharge (AT03025) and those of copper and lead in the downstream wastewater discharge (AT03027) were 2-3 times higher than the maximum typically found in background surface waters (ATSDR 2000, Salomons & Forstner 1984).

The sediment collected by the middle discharge (AT03026) contained relatively high concentrations of some metals, the most significant being the concentrations of copper and zinc (approximately 6 times higher than their respective concentrations in the sediment sample collected upstream of Vinythai). The concentrations of all metals in the sediment collected by the downstream discharge (AT03028) were lower than those in the sediment upstream of Vinythai (AT03042).

Mercury was not detected in either effluent sample (AT03025 & AT03027), nor in the upstream and downstream sediment samples (AT03042 & AT03028). The sediment collected by the middle discharge (AT03026) did contain mercury at 0.4 mg/kg, though this is within the range of mercury concentrations typically found in background sediments (Salomons & Forstner 1984).

A number of organic compounds were identified in the sediment collected immediately upstream of Vinythai (AT03042), namely benzenemethanol, the phthalate ester DEHP and linear aliphatic hydrocarbons. None of these compounds were identified in the sediments collected adjacent to the Vinythai discharge points (AT03026 & AT03028). Two compounds were isolated from the sediment collected below the middle discharge (AT03026), though it was not possible to identify either one of these compounds. No organic compounds were isolated from the sediment collected adjacent to the lower (most downstream) discharge (AT03028).

Compound	**AT03025 (µg/l)**	**AT03027 (µg/l)**	**AT03030 (µg/l)**	**AT03032 (µg/l)**
Vinyl chloride, VCM	ND	ND	ND	<5
Ethene, 1,1-dichloro-	ND	ND	ND	6
Ethane, 1,1-dichloro-	<5	ND	ND	ND
Chloroform	5	<1	<1	11
Ethane, 1,2-dichloro-, EDC	<10	<10	<10	250
Ethene, trichloro-	<5	ND	ND	<5
Methane, bromodichloro-	<5	ND	<5	ND

Table 3.2. Volatile organic compounds (VOCs) quantified in effluent samples collected from the Vinythai and TPC facilities, MapTa Phut Industrial Estate, Rayong Province, Thailand, 2003; ND-not detected, <# indicates compound detected but at a concentration below the quantifiable level for that chemical. A full list of VOC compounds quantified is given in Appendix 3.

3.2 TPC

Sediment collected by the most upstream discharge (1st discharge point), which was not flowing at the time of sampling, contained few organic chemicals. The only compounds identified in this sample were two aliphatic hydrocarbons. Furthermore, all of the metals quantified in this sample were present at very similar concentrations to those found in the sediments collected upstream of both Vinythai and TPC (AT03042), and generally

Sample number	AT03030	AT03032	AT03034	AT03029	AT03031	AT03033
Description	Effluent	Effluent	Effluent	Sediment	Sediment	Sediment
Location	2nd discharge point	3rd (main) discharge point	4th (most downstream) discharge point	East canal, adjacent to 1st discharge (not flowing)	East canal, by 2nd discharge (AT03030)	East canal, by 3rd discharge (AT03032)
Metals	ug/L	ug/L	ug/L	mg/kg dw	mg/kg dw	mg/kg dw
Arsenic	<400	<400	<400	<40	<40	<40
Cadmium	<10	<10	<10	<1	<1	<1
Chromium	<20	<20	<20	14	77	20
Cobalt	<20	<20	<20	<2	4	<2
Copper	<20	<20	<20	4	146	36
Lead	<30	<30	<30	12	100	26
Manganese	163	83	<10	131	886	194
Mercury	2.7	<2	<2	<0.2	0.4	<0.2
Nickel	<20	<20	<20	10	41	14
Zinc	3020	1590	17	146	8800	833
No. of organic compounds isolated	3	22	18	5	24	26
No. reliably identified (% of total)	3 (100%)	8 (36%)	3 (17%)	2 (40%)	16 (67%)	15 (58%)
Chlorinated compounds						
Chloroform	1*	1*				
1,1-Dichloroeth**ene**		1*				
1,1-Dichloroeth**ane**						
1,2-Dichloroeth**ane**	1*	1*				
Vinyl chloride (VCM)		1*				
Trichloroethene		1*				
1,4-Dichlorobenzene						1*
1,2,4-Trichlorobenzene					1*	
1,2,3,4-Tetrachlorobenzene					1*	1*
Pentachlorobenzenes					1*	1*
Hexachlorobenzenes					1*	1*
2,4,6-Trichlorophenol		1				
Bromodichloromethane	1*					
Octachlorostyrene					1*	1*
Phenols						
Alkyl phenols					1	
Phthalate esters						
DEHP			1		1	1
Others						
Benzenemethanol derivatives		1			1	1
1H-indole					1	
Aliphatic alcohols			1			
Acetophenone						1
Hydrocarbons						
Alkyl benzenes					1	
Linear aliphatic hydrocarbons		1	1	2	6	7

*Table 3.3. Organic chemicals and heavy metals identified in samples from around the TPC PVC manufacturing facility, MapTa Phut Industrial Estate, Rayong Province, Thailand, 2003. For both effluent and solid sample sets, the samples are arranged from left to right representing upstream to downstream along the east canal. For the groups of organic compounds reliably identified, the number of compounds identified using general GC/MS screening method is presented for each group; * signifies those compounds identified only at trace levels using a selective ion monitoring (SIM) method. Metal concentrations are given in mg/kg dry weight for solid samples and μg/l for liquid samples.*

within the ranges expected for these metals in uncontaminated sediments (ATSDR 2000, Salomons & Forstner 1984).

A range of organic compounds were identified in the samples of effluent collected from the TPC discharges, including many chlorinated compounds. It was not possible, however, to identify the majority of the compounds isolated from the samples collected from the two downstream discharge points (AT03032 & AT03034).

Volatile organic compounds (VOCs) were quantified in the effluents collected from the two most upstream flowing discharges (AT03030 & AT03032), though not in the effluent sample collected from a discharge at the southern edge of the TPC facility (AT03034) and therefore the occurrence of VOCs in the wastewaters discharged at this location is unknown. The concentrations of VOCs quantified in the effluent samples are presented in Table 3.2.

Wastewaters from the 2nd (most upstream) discharge (AT03030) contained three chlorinated VOCs, namely chloroform, 1,2-dichloroethane (EDC) and bromodichloromethane. These were all present in the sample at low concentrations, similar to those found in the effluent samples collected from Vinythai.

The sample from the 3rd (what appeared to be the main) discharge (AT03032) contained more VOC compounds and these were present at higher concentrations in all but one case. Two compounds were present at concentrations below the limit of quantification, namely vinyl chloride (<5 ug/l) and trichloroethene (<5 ug/l). A further two compounds were present at concentrations that enabled quantification; 1,1-dichloroethene (6 ug/l) and chloroform (11 ug/l), though these concentrations are still relatively low. Of greater significance, however, was the presence in this sample of 1,2-dichloroethane (also known as ethylene dichloride or EDC) at a concentration of 250 ug/l, significantly higher than the other VOCs identified. This concentration of this compound in the upstream discharge (AT03030) was much lower, at <10 ug/l.

Additional organic chemicals were identified, though not quantified, in the 3rd (main, AT03032) and 4th (furthest downstream, AT03034) discharges. Significant within these was the presence of 2,4,6-trichlorophenol, an organochlorine, at the 3rd discharge point (AT03032) and di(2-ethylhexyl)-phthalate (DEHP), a phthalate ester, in the 4th (most downstream) discharge (AT03034).

In addition to the organic compounds identified, wastewaters from both the 2nd and 3rd discharge points (AT03030, and the main discharge AT03032) also contained high concentrations of zinc, present at 3020 ug/l and 1590 ug/l respectively. The 2nd discharge (AT03030) also contained mercury at a concentration of 2.7 ug/l. Zinc is generally present in surface waters at concentrations below 50 ug/l, while mercury is typically below 0.1 ug/l (ATSDR 2000, USEPA 1997). Other than these, levels of metals in all TPC effluents were either below detection limits or within the ranges typically found in uncontaminated freshwaters (Alessio & Lucchini 1996, ATSDR 2000).

The concentrations of most of the metals quantified in the sediments collected by the 2nd and 3rd discharges (AT03031 & AT03033) were higher than those found in the sediment collected further upstream (AT03029), particularly for sample AT03031. The concentrations of zinc (8800 mg/kg) and copper (146 mg/kg) were particularly elevated in this sample, with concentrations 60 and 37 times higher than those in the upstream sample (AT03029) respectively. The concentration of zinc in this sample was approximately 90 times higher than typical background sediment concentrations, while those of both copper and lead were approximately three times higher than typical background concentrations (ATSDR 2000, Salomons & Forstner 1984).

A similar pattern of concentrations, though with somewhat lower values, was found in the sediment collected by the 3rd (main) discharge (AT03033). Concentrations of copper (36 mg/kg) and zinc (833 mg/kg) were elevated above concentrations found in the most upstream sediment associated with TPC (AT03029), by factors of 9 and 6 times respectively. The concentration of copper in AT03033 is within the range of background concentrations, though that of zinc is approximately 8 times background levels (ATSDR 2000, Salomons & Forstner 1984).

These sediment samples also contained a number of organic chemicals. The phthalate DEHP found in TPC effluents was also identified in two of the associated sediments, those collected by the 2nd and 3rd discharge points (AT03031 & AT03033). These sediments also contained a range of highly chlorinated compounds, though at trace levels. These included octachlorostyrene, penta- and hexa-chlorobenzene as well as lesser-chlorinated benzenes; 1,4-dichloro-, 1,2,4-trichloro- and 1,2,3,4-tetrachlorobenzene. None of these chlorinated compounds were identified in the TPC effluents being discharged at the time of sampling.

4 Discussion

The effluent samples collected from Vinythai and TPC discharges contained a range of chlorinated volatile organic compounds (VOCs). Many of the VOCs were common to the discharges from both PVC production facilities. All samples quantified for VOCs contained chloroform and 1,2-dichloroethane, and one sample from each facility also contained trichloroethene and bromodichloromethane. Other VOCs were found in discharges from only one of the PVC facilities, namely 1,1-dichloroethane from Vinythai and 1,1-dichloroethene and vinyl chloride monomer (VCM) from TPC. Many of these compounds have been previously reported in waste streams from PVC production processes, including in a recent study of another PVC manufacturing facility operated by TPC in the Samut Prakan Province of Thailand (Brigden *et al.* 2004, Johnston *et al.* 1994).

However, the majority of the VOCs identified in the current study were present at relatively low concentrations in the effluents. More chlorinated compounds were identified in the TPC effluents than those discharged by Vinythai. The effluent from TPC's main discharge (AT03032) contained more chlorinated compounds than all other effluent samples including 1,2-dichloroethane (EDC), which was present at 250 ug/l, far higher than the other VOCs identified.

The VOC compounds quantified in the effluent samples are volatile and may readily evaporate from the wastewaters. Wastewaters discharged from Vinythai *via* the southern-most (lower) outfall (AT02027) are carried in an open channel for some distance prior to discharge to the east canal, which could enhance loss to air of a significant fraction of the VOCs from the wastewater. This may explain the fewer number and lower concentrations of VOCs found in this effluent sample (AT03027) compared to that collected from the middle discharge (AT03025), which appeared to carry wastewaters *via* an underground pipe (although differences in sources within the plant may be the primary influence). For example, 1,2-dichloroethane was identified at a concentration below 10 ug/l in both effluent samples, while the significantly more volatile 1,1-dichloroethane was identified only in the effluent from the middle (underground) discharge, at a concentration below 5 ug/l (Budavari *et al.* 2000). Higher concentrations of VOCs may possibly be present in the effluent carried in the open channel (AT03027) at the point at which effluent first enters the channel, though this cannot be verified from this study.

Furthermore, significant losses of VOCs from the wastewaters may also occur during their treatment prior to discharge, unless such treatment processes are designed to contain volatile compounds. The loss of chemicals from wastewaters to the atmosphere in this way does not reduce the quantities of such chemicals released to the environment overall, but merely diverts their release to a different route. Emissions to atmosphere were not quantified in the current study and the significance of such losses from either Vinythai or TPC are not currently known.

The chlorinated VOCs identified in the discharged effluents from both Vinythai and TPC possess a wide range of toxic characteristics. It is important to note, however, that in all but TPCs 3rd (main) discharge (AT03032), these compounds were present at trace levels only.

The presence of 1,2-dichloroethane in the 3rd (main) effluent discharge from TPC (AT03032) at a concentration of 250 ug/l is of greatest concern. 1,2-dichloroethane (also known as ethylene dichloride or EDC) is a chemical intermediate used in the manufacture of VCM (ATSDR 2000, IPCS 1995). This compound is not highly persistent in the environment but is, however, toxic to humans and animals. Due to its volatility, exposure to EDC is generally *via* inhalation, though it can also be absorbed by ingestion or through the skin (IPCS 1995). Upon exposure to EDC it becomes distributed to all tissues of the body. The main target organs for toxic effects in humans are the liver, kidneys and central nervous system, though other effects have also been observed, including reduced blood clotting and cardiac effects. Similar effects have been reported in animal studies. Exposure to very large amounts of EDC can be fatal for both humans and animals (ATSDR 2000, IPCS 1995, Nouchi *et al.* 1984, Yodaiken & Babcock 1973). 1,2-dichloroethane (EDC) can readily evaporate from water and soil increasing the potential for exposure (ATSDR 2000, IPCS 1995).

EDC was also present in effluent discharged from Vinythai along with a very similar chemical, 1,1-dichloroethane (also known as ethylidene dichloride), though both at far lower concentrations to that of EDC in the effluent discharged by TPC. 1,1-Dichloroethane may be formed as a side product during the production or purification of VCM (ATSDR 2000). Being chemically very similar to EDC, 1,1-dichloroethane has many similar properties. It is toxic to humans and animals, though not highly persistent in the environment (ATSDR 2000, IPCS 1995). Both 1,1- and 1,2-dichloroethane have previously been identified in process wastewaters arising from VCM production at other facilities (Brigden *et al.* 2004, Myszkowski & Milchert 2003).

Vinyl chloride (VCM), also identified in the main and most contaminated effluent discharge from TPC (AT03032), is an extremely hazardous chemical. As for EDC, VCM is generally not persistent in the environment as it is highly volatile and is rapidly degraded in the atmosphere, though VCM can be more persistent in groundwater, with an estimated half-life of up to eight years (Howard *et al.* 1991). However, VCM is highly toxic to both humans and animals and is a known human carcinogen (IARC 1987). However, VCM was present in the TPC effluent at a low concentration (<5 ug/l). Discharged effluent from a PVC manufacturing facility operated by TPC in the Samut Prakan Province of Thailand was recently found to contain VCM at the much higher concentration of 338 ug/l (Brigden *et al.* 2004).

The additional volatile chlorinated chemicals identified in the effluents from both facilities may not be intentionally produced or used in the production of PVC within the Vinythai and TPC facilities, but are more likely unintentionally produced as by-products during various processes.

Chloroform is a widely used solvent in industrial processes (ATSDR 2000), though it can also be generated from reaction between chlorine or certain chlorine-containing compounds with trace chemicals present in water. This is widely observed during water disinfection using chlorine or chlorinated chemicals, but could also occur in the industrial context (IPCS 2000, Oxenford 1996). Similar processes can result in the formation of bromodichloromethane, another VOC found in effluents discharged by Vinythai (AT03025) and TPC (AT03030) (IPCS 2000). Trichloroethene can be formed by the chlorination of EDC (ATSDR 2000, Hickman 1993), and could therefore be formed as a by-product during EDC/VCM manufacture. This chemical has also been used as a chain terminator in the production of PVC from VCM (CEC 1986), which could be an alternate source of this chemical to the effluents.

1,1-dichloroethene, also known as vinylidene chloride, is a highly volatile chemical. When present in water it is reasonably persistent though upon release to the atmosphere it is rapidly broken down (ATSDR 2000). Vinylidene chloride is used in the manufacture of plastics including copolymers with VCM, though it is not known if such products are manufactures at the TPC facility. The concentrations at which these various additional VOCs were found in this study are unlikely to result in direct adverse health effects (ATSDR 2000, Quast *et al.* 1983). Nevertheless they do indicate that VOC emissions to water and air from both plants deserve further investigation and quantification.

Legislation addressing the discharge of industrial effluents in Thailand does not specify limits for the toxic and volatile chlorinated chemicals identified in the effluents from Vinythai and TPC (MSTE 1996). Maximum discharge limits are set in the United States for the concentration of EDC in discharged wastewaters arising from the manufacture of PVC. Limits for facilities that use end-of-pipe biological treatment specify a maximum concentration for any one day of 211 ug/l, and a maximum monthly average concentration of 68 ug/l (USGPO 2000). Although these regulatory limits do not apply to equivalent facilities in Thailand, they offer a useful basis for comparison given the absence of applicable Thai legislation. The main discharge from TPC (AT03032) contained EDC at a concentration of 250 ug/l. This concentration is above the US maximum allowable discharge concentrations (1.2 times the maximum US daily concentration, and 3.7 times the maximum US monthly average concentration), though it must be noted that the value reported here relates to a single spot sample rather than concentrations integrated over a longer period.

Additional less volatile chemicals were identified in the effluents discharged by TPC, the concentrations of these chemicals were not quantified. The main effluent discharge (AT03032) contained 2,4,6-trichlorophenol. This organochlorine is not used or produced in the manufacture of PVC. It is a synthetic chemical with a wide range of uses, historically the most important being as a wood preservative (ATSDR 2000). Little information is available on the human health effects of 2,4,6-trichlorophenol. The source of this chemical to the TPC effluent is not clear.

Di-(2-ethylhexyl)-phthalate (DEHP), a phthalate ester widely used as a softening additive in some PVC formulations (Bizarri 1996, ECPI 2003), was found in a number of samples associated with TPC. DEHP was present in the 4th (most downstream) discharge (AT03034), and was also found in the sediments associated with the 2nd and 3rd most downstream (main) discharges (AT03031 & AT03033). The presence of DEHP in the sediments at these locations may indicate the discharge of DEHP in wastewaters at other times. However, sediment collected upstream of both Vinythai and TPC (AT03042) also contained DEHP, indicating additional sources of this chemical to the east canal.

DEHP is employed in a wide range of product categories other than PVC formulations (ATSDR 2000, Jobling *et al.* 1995), though its incorporation into softened PVC products is by far the largest usage (Bizarri 1996). DEHP is relatively persistent in the environment and is one of the most widely distributed and abundant man-made chemicals in the environment due to its widespread use (Jobling *et al.* 1995). Exposures to this chemical have resulted in widespread accumulation of DEHP in the human body (Colon *et al.* 2000).

DEHP exhibit a range of toxic effects in mammals, including the potential to interfere with the developing reproductive system in males (Jobling *et al.* 1995, Mylchreest *et al.* 2002), an effect recognised for nearly 60 years (Park *et al.* 2002, Shaffer *et al.* 1945). Within the European Union (EU) DEHP is classified as “toxic to reproduction” (EC 2003). It has also been classified by the International Agency for Research on Cancer (IARC) as possibly carcinogenic to humans, and by the US Department of Health and Human Services as reasonably anticipated to be a human carcinogen (DHHS 2002).

The effluents from both facilities also contained heavy metals at concentrations above typically background levels. As for organic pollutants, the effluents discharged by TPC were significantly more contaminated with heavy metals than those discharged by Vinythai.

The concentrations of zinc in the middle discharge from Vinythai and those of copper and lead in effluent from the lower discharge were only slightly elevated above typical background levels. In contrast, effluent from the 2nd and 3rd discharge points from TPC, which includes what appeared to be the main discharge (AT03032), contained high concentrations of zinc. The 2nd discharge (AT03030), with a far lower flow rate, also contained a low yet significant concentration of mercury. The concentrations of metals in all discharges were, however, below their maximum allowable concentrations specified in Thai Legislation addressing the quality of discharge wastewaters. Maximum discharge concentrations for metals specified in this legislation include copper (2000 μg/l), lead (200 μg/l), mercury (5 μg/l) and zinc (5000 μg/l) (MSTE 1996).

Metals cannot be broken down upon release to the environment. Therefore, although the highest concentrations recorded here fall below the rather permissive regulatory limits, the ongoing discharge of wastewaters containing these metals will continuously add to the total burden received by the local environment.

The data for the TPC effluents suggest that zinc or zinc compounds are used within this facility. Compounds of zinc are widely used as stabilisers in PVC (Matthews 1996, Summers 1997), though we cannot be certain that such uses are responsible for the high levels in effluents recorded in this case.

The concentrations of copper, lead and zinc in the Vinythai effluents were only slightly elevated above typical background levels and far lower than those of zinc in the TPC effluents. Copper compounds are generally not used in PVC formulations. Although lead and zinc compounds are widely used as additives in some PVC formulations (Matthews 1996), the moderate concentrations of these metals in the Vinythai effluents may indicate that Vinythai effluents are not receiving these metals as a result of the use of their compounds in the production of PVC within this facility.

Although zinc is an essential trace nutrient for plants, animals and humans, exposure to high concentrations of bioavailable zinc can result in significant bioaccumulation with possible toxic effects (ATSDR 2000). For humans and animals, high doses of zinc can induce a range of symptoms, including pancreatic damage, anaemia, gastrointestinal distress and diarrhoea (ATSDR 2000, Goyer 1996). For aquatic organisms, prolonged exposure to even moderate concentrations can also result in adverse effects (UNEP 1993).

The concentration of mercury in one of the TPC effluents (AT03030) was 2.7 µg/l, far lower than those of other metals. However, mercury is typically present in freshwaters at extremely low concentrations, generally below 0.1 µg/l (ATSDR 2000, USEPA 1997). Chlorine is produced using the chlor-alkali process within this facility, for use in the manufacture of VCM (GTZ 2001). A number of different technology options exist for this process, including an outdated mercury based process that results in emissions to air and water of mercury, a highly toxic metal (EC 2001). The presence of mercury in this discharge may be the result of current or historic use of mercury-based technology in the production of chlorine within the TPC facility. Mercury was not detected in wastewaters discharged from Vinythai. Mercury is an extremely toxic, non-essential trace metal, having no biochemical or nutritional function (WHO 1989), though the quantities released in the TPC effluent are very small.

Upon release to a water body, many heavy metals and organic chemicals bind to particles in the water and over time accumulate in bottom sediments. The presence of organic compounds and higher concentrations of metals in sediments within water bodies that receive wastewaters are, therefore, indicative of the ongoing discharge of these pollutants.

The east canal contained little sediment within the concrete-lined section by the Vinythai discharges, particularly in the vicinity of the lower (most downstream) discharge (AT03027). Nevertheless, the sediment collected by Vinythai's middle discharge point (AT03026) contained metals at concentrations above those in the upstream (control) sediment (AT03042), particularly for copper and zinc. Their concentrations could indicate the accumulation of these metals as a result of discharges from Vinythai. Zinc was present in effluent at only a moderately higher concentration than background levels. However, the concentration of zinc in the associated sediment (AT03026) was nearly ten times higher than the typical background concentrations (ATSDR 2000, Salomons & Forstner 1984). Other than for zinc, however, the sediment metal concentrations are within the background ranges typically found for these metals in freshwater sediments, and the evidence for the ongoing discharge and accumulation for these metals is not conclusive. No organic compounds were isolated from this sediment sample.

Accumulation resulting from the ongoing discharge of zinc in wastewaters by TPC is demonstrated by the high concentrations within associated sediments at other locations, up to 88 times higher in places compared to background concentrations of this metal. At both locations where discharged effluents contained high zinc concentrations, the sediments (AT03031 & AT03033) were also found to contain high zinc concentrations, and the sediment with the highest concentration (AT03031) was that associated with the discharge of effluent containing the highest zinc level (AT03030).

Freshwater sediments typically contain zinc at less than 100 mg/kg, copper at less than 50 mg/kg (ATSDR 2000, Salomons & Forstner 1984) and mercury at 0.2-0.35 mg/kg (Salomons & Forstner 1984, USEPA 1997). Sediment samples collected from the east canal upstream of the TPC discharges are generally within these background ranges. However, the concentration of zinc in the sediment sample AT03031 was 88 times typical background concentrations. The concentration of zinc in the sediment sample by the 3rd (main) outfall (AT03033) was over 8 times background concentrations.

The concentrations of copper and lead in the sediment by the 2nd discharge point (AT03031), and to a lesser degree by the 3rd (main) discharge point (AT03033), were elevated above levels found upstream. Effluents discharged at these locations did not contain high concentrations of either metal, but the elevated sediment levels may indicate accumulation as a result of their discharge at other times. One sediment (AT03031) also contained a detectable concentration of mercury (0.4 mg/kg), though this falls within typical background levels for this metal (Salomons & Forstner 1984). This suggests that, while mercury was present in the associated effluent at a low concentration, significant quantities of mercury are not accumulating at this location.

The sediment associated with the 2nd discharge point (AT03031) also contained other metals at higher levels than those found in upstream sediments from the east canal, though these metals were not present in TPC discharges. The sources of these metals to the sediments are not clear.

The highly chlorinated compounds identified in sediments associated with TPC discharges were not identified in any of the sediments collected from the east canal further upstream. These compounds were not identified in the TPC effluents, but their presence in the sediments suggests they have been present in discharges at other times. These compounds were present in the sediment samples at trace levels.

Octachlorostyrene is not an intentionally manufactured chemical (Stringer & Johnston 2001). It is formed as a by-product of certain industrial processes involving chlorine compounds, including the production of chlorine - a process carried out at TPC (GTZ 2001, Kaminsky & Hites 1984). Upon release to the environment, octachlorostyrene is highly persistent and is able to accumulate in the bodies of animals and humans (Ingebrigtsen *et al.* 1988, Lunde and Bjorseth 1977).

Data on the potential toxicity of octachlorostyrene in humans is very limited. Animal studies have found that exposure can cause toxicity to the liver, kidney and thyroid (Chu *et al.* 1986). There is also evidence that octachlorostyrene is able to disrupt endocrine (hormone) systems (Satoh *et al.* 2001).

Chlorinated benzenes are also highly persistent in the environment, being highly resistant to microbial degradation, particularly for the higher chlorinated compounds penta- and hexachlorobenzene (HCB) (Giddings *et al.* 1994b, 1994c, Pohl *et al.* 2001, To-Figueras *et al.* 1995). Chlorinated benzenes can be formed as unwanted by-products in the synthesis of other organochlorine compounds (Newhook & Meek 1994, Sala *et al.* 1999). High concentrations of HCB have previously been found in the air around a chlorine (chlor-alkali) and organochlorine manufacturing plant, as well as in the blood of workers and local residents (Sala *et al.* 1999, Grimalt *et al.* 1994).

All the chlorinated benzenes identified in this study are toxic to a wide range or organisms including humans, having effects primarily on the liver, kidneys, thyroid and nervous system (ATDSR 2000, Giddings *et al.* 1994a,b,c, Newhook & Meek 1994). Furthermore, hexachlorobenzene is listed by the IARC as possible carcinogen to humans, and is known to disrupt animal hormone systems (IARC 2001, Ralph *et al.* 2003).

Other than the wastewater collected from the upstream discharge (AT03030), all liquid and solid samples also contained linear aliphatic hydrocarbons. The sediment collected by the upstream discharge (AT03031) also contained an alkyl benzene compound. These chemicals are commonly found in petroleum-based chemicals, which is their probable source in this instance (Hsieh *et al.* 2000).

5 Conclusions

This study has demonstrated that the manufacturing of PVC, and the raw materials used in its production, at the Vinythai and TPC facilities within the Map Ta Phut Industrial Estate give rise to the discharge of heavy metals and organic chemicals to the environment. At the time of sampling, wastewaters discharged by TPC contained more organic pollutants and significantly higher concentrations of both organic and metal pollutants than those from Vinythai. Of particular significance was the presence in what appeared to be the main effluent discharge from TPC of EDC, a chemical intermediate in PVC manufacture, at a concentration above daily limits which would be allowed for equivalent facilities in the United States.

Many of the organic compounds identified in effluents discharged by both facilities are volatile chlorinated compounds that may readily be lost to the atmosphere during storage, handling, and/or waste treatment, constituting a likely additional pathway for their release from these facilities. The determination of such atmospheric releases was beyond the scope of this study. Some of the chemicals discharged in wastewaters from both facilities are toxic and/or carcinogenic, though most were present at trace concentrations. It was not possible to identify many of the organic chemicals present in discharged wastewaters from TPC, such that their properties and potential impacts on the environment remain unknown.

Sediments collected from the receiving east canal that discharges to the Gulf of Thailand show some evidence of environmental accumulation of organic and metal pollutants, which appears to be a result of their ongoing discharge in wastewaters. The presence in sediment samples of additional toxic and highly environmentally persistent chlorinated chemicals, not identified in wastewater discharges collected on the day of sampling, suggests their release from the TPC facility at other times.

In addition to those chemicals identified in this study, the production of EDC and VCM used in the manufacture of PVC is known to result in the formation of chlorinated dioxins, highly toxic and persistent chemicals (Stringer & Johnston 2001), accumulating primarily in solid or semisolid wastes which are not discharged to water. The Environmental Protection Agency (EPA) in the US has very recently recognised that the manufacture of EDC and VCM, as well as possibly that of PVC, are sources of dioxin discharges, with the most significant arisings being from facilities that include chlor-alkali plants (USEPA 2004).

Both Vinythai and TPC have policies that are intended to address environmental impacts that result from manufacturing within their facilities. TPC state that regular monitoring of wastewaters is conducted with the aim of preventing contamination of the environment. This study has demonstrated that the manufacture of PVC at both facilities does result in chemical releases that could well impact on the environment, and that monitoring and control programs in place have therefore not been effective at eliminating environmental contamination, particularly in the case of TPC.

Chlorinated organic chemicals are included in the National Chemicals Management Profile for Thailand as specific chemicals creating concern (SCSIN 1998). However, legislation in Thailand that addresses the discharge of organic chemicals in industrial effluents only specifies very general parameters for organic chemicals, which do not address many of the hazardous pollutants identified in this study (MSTE 1996).

The production of hazardous and toxic chemicals, be it intentional or unintentional, as well as their use and release clearly needs greater control. Stringent legislation addressing discharges and releases could be a first step in providing greater protection for the environment and human health, though the problem of complex waste streams containing such chemicals will only be fully addressed through the progressive substitution of hazardous chemicals with non-hazardous alternatives. The production and use of chlorinated chemicals is widely associated with the formation of toxic and persistent chlorinated products and by-products, and this will only be eliminated through the progressive substitution of chlorine-chemistry and chlorinated products with non-chlorinated, non-hazardous alternatives. This approach is essential for preventing the ongoing discharges, emissions and losses of hazardous chemicals, particularly those that are persistent in the environment.

6 References

Alessio L, Lucchini R (1996) Manganese and manganese compounds. In: Argentesi F, Roi R, Sevilla Marcos JM, eds. Data profiles for selected chemicals and pharmaceuticals 3, 4, 5. Ispra, Italy, European Commission, Joint Research Commission.

ATSDR (2000) ATSDR's toxicological profiles on CD-ROM, CRC Press, Boca Raton, FL.

Bizarri, S.N., Jaeckel, M. & Yoshida, Y. (1996) Plasticizers. CEH Marketing Research Report. Publ: SRI International.

Brigden, K., Labunska, I., Santillo, D. (2004) Toxic chemical pollutants released from the Thai Plastic & Chemicals PVC facility to the Chao-Phraya River, Samut Prakan, Thailand. TN 05/2004, Greenpeace Research Laboratories, University of Exeter, UK; http://www.greenpeace.to/html/commreps.htm

Bryant, J.G. (1993) Chlorinated benzenes. In: Kroschwitz, J.I. & Howe-Grant, [Eds.]. The Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition, Publ. Wiley-Interscience, N.Y. 6:87-100

Budavari, S., O'Neil, M., Smith, A., Heckleman, P. & Obenchain, J. [Eds] (2000) The Merck index. 12th Edition, on CD_ROM, Version 12:3. Merck & Co., Inc.

CEC (1986) Trichloroethylene. In: Organochlorine solvents: Health risk to workers. Publ: Commission of the European Communities. ISBN 0-85186-078-8: 93-130

Chu I., Villeneuve D.C., Secours V.E., Valli V.E., Leeson S. and Shen S.Y. (1986). Long-term toxicity of ocatchlorostyrene in the rat. Fundamental and Applied Toxicology 6: 69-77

CIN (2003) Chemical Industries Newsletter, SRI International, Issue 4 of 2003, www.sriconsulting.com/nl/ Public/2003issue4.pdf

Colon, I., Caro, D., Bourdony, C.J. & Rosario, O. (2000) Identification of phthalate esters in the serum of young Puerto Rican girls with premature breast development. Environmental Health Perspectives 108(9): 895-900

DHHS (2002) 10^{th} Report on carcinogens. US Department of Health and Human Services, 263pp.

EC (2001) Integrated Pollution Prevention and Control (IPPC) Reference document on best available techniques in the chlor-alkali industry. December 2001, 162pp

EC (2003) Directive 2003/36/EC of the European Parliament and of the Council of 26 May 2003 amending, for the 25th time, Council Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (substances classified as carcinogens, mutagens or substances toxic to reproduction - c/m/r), Official Journal of the European Union L 156: pp. 26-30. http://europa.eu.int/eur-lex/pri/en/oj/dat/2003/l_156/l_15620030625en00260030.pdf

ECPI (2003) Plasticiser Applications, European Council for Plasticisers and Intermediates (ECPI) http://www.plasticisers.org/plasticiser applications

Ehrig, R.J. (Ed.) (1992) Plastics recycling, products and processes. Publ: Hanser, Munich

ENDS (2002) PVC industry agrees to phase out lead stabilisers by 2015. ENDS Report issue 328, May 2002, pp 31-32

ENDS (2003) Hydro Polymers: Searching for a more sustainable PVC. ENDS Report issue 344, September 2003, pp 25-28

Giddings, M., Meek, M.E. & Gomes, R. (1994a) Trichlorobenzenes: Evaluation of risks to health from environment exposure in Canada. Environ. Carcin. Ecotox. Revs. C12(2): 517-525

Giddings, M., Meek, M.E. & Gomes, R. (1994b) Tetrachlorobenzenes: Evaluation of risks to health from environment exposure in Canada. Environ. Carcin. Ecotox. Revs. C12(2): 473-481

Giddings, M., Meek, M.E. & Gomes, R. (1994c) Pentachlorobenzene: Evaluation of risks to health from environment exposure in Canada. Environ. Carcin. Ecotox. Revs. C12(2): 435-441

Goyer, R.A. (1996) Toxic effects of metals. In Casarett & Doull's Toxicology. The Basic Science of Poisons, Fifth Edition, Klaassen, C.D. [Ed]. McGraw-Hill Health Professions Division, ISBN 0071054766

GTZ (2001) The Economic and Environmental Status of the Map Ta Phut Industrial Estate, Thailand. Deutsche Gesellschaft Techniche Zusammenarbeit (GTZ). Available at; http://www.gtzth.org/library/files/gtzth_1998_3506_3_1.pdf

Hickman, J.C. (1993) Tetrachloroehylene. Chlorocarbons, -hydrocarbons ($CHCl=CCl_2$). In: Kirk-Othmer Encyclopedia of Chemical Technology. [Eds] Jacqueline I. Kroschwits; Mary Howe-Grant. Fourth edition, Vol. 6. John Wiley & Sons, Inc. pp.50-59

Homchean, K. (1998) Industrial Estate Authority of Thailand strategy for environmental compliance, Proceedings of the fifth international conference on environmental compliance and enforcement, Monterey, California, pp101-112

Howard, P.H., Boethling, R.S., Jarvis, W.F., Meylan, W.M. & Michalenko, E.M. (1991) Handbook of environmental degradation rates. Publ: Lewis Publishers, ISBN 0873713583, 725pp

Hsieh, M., Philp P. & J. C. del Rio (2000) Characterisation of high molecular weight biomarkers in crude oils. Organic Geochemistry 31(12): 1581-1588

IARC (1987) International Agency for Research on Cancer (IARC) monograph on the evaluation of carcinogenic risks to humans. Overall evaluation of carcinogenicity. Supplement 7. 440pp. ISBN 9283214110

IARC (2001) Hexachlorobenzene. In International Agency for Research on Cancer (IARC) monograph; Some thyrotropic agents, Vol. 79

IARC (1995) Trichloroethylene. In International Agency for Research on Cancer (IARC) monograph; Dry cleaning, some chlorinated solvents and other industrial chemicals, Vol. 63

Ingebrigsten K., Solbakken J.E., Norheim G. and Nafstad I. (1988). Distribution and elimination of carbon 14 octachlorostyrene in cod (*Gadus morhua*), rainbow trout (*Salmo Gairdneri*) and blue mussel (*Mytilus Edulis*). Journal of Toxicology and Environmental Health 25: 361-372

IPCS (1995) 1,2-Dichloroethane (second edition). International Programme on Chemical Safety Environmental Health Criteria 176, Publ: World Health Organisation, ISBN 924157176 4, 148pp.

IPCS (1999) Vinyl Chloride. International Programme on Chemical Safety Environmental Health Criteria 215. Publ: World Health Organisation, ISBN 9241572159, 356pp.

IPCS (2000) Disinfectants and disinfectant by-products. International Programme on Chemical Safety Environmental Health Criteria 216, Publ: World Health Organisation, ISBN 9241572167, 499pp.

Jobling, S., Reynolds, T., White, R., Parker, M.G. & Sumpter, J.P. (1995) A variety of environmentally persistent chemicals, including some phthalate plasticizers, are weakly estrogenic. Environmental Health Perspectives 103(6): 582-587

Johnston, P.A., Stringer, R.L., Clayton, R. & Swindlehurst, R.L. (1994) Regulation of toxic chemicals in the North Sea: the need for an adequate control strategy. In: Proceedings of the Scientific Symposium on the North Sea Quality Status Report 1993, 18-21 April 1994, Ebeltoft, Denmark. Publ: Danish Environmental Protection Agency, ISBN 87-7810-699-0, pp 269-274

Kaminsky, R. & Hites, R.A. (1984) Octachlorostyrene in Lake Ontario: sources and fates. Environmental Science and Technology 18(4): 275-279

Labunska, I., Brigden, K., Santillo, D. & Stringer, R. (2002) The Nováky Chemical Plant (Novácke chemické závody) as a source of mercury and organochlorine contaminants to the Nitra River, Slovakia. Greenpeace Research Laboratories Technical Note 01/2002: 44 pp. www.greenpeace.to/html/commreps.htm

Lunde G. and Bjorseth A. (1977). Human blood samples as indicators of occupational exposure to persistent chlorinated hydrocarbons. The Science of the Total Environment 8: 241-246

Matthews, G. (1996) PVC: production, properties and uses. Publ: The Institute of Materials, London.

Mayer, F.L., Stalling, D.L. & Johnson, J.L. (1972) Phthalate esters as environmental contaminants. Nature 238: 411-413

MSTE (1996) Industrial Effluent Standards, notification of the Ministry of Science, Technology and Environment, No. 3, B.E. 2539. Presented by the Pollution Control Department, Ministry of Natural Resources and Environment; http://www.pcd.go.th/info_serv/en_reg_std_water04.html#s1

Mylchreest, E., Sar, M., Wallace, D.G. & Foster, P.M.D. (2002) Fetal testosterone insufficiency and abnormal proliferation of Leydig cells and gonocytes in rats exposed to di(n-butyl) phthalate. Reproductive Toxicology, 16: 19-28

Myszkowski, J., Milchert, E. (2003) Recovery of organochlorine derivatives from waste waters in the stripper-adsorber system. Przemysl Chemiczny, 82(8-9): 1048-1050

Newhook, R. & Meek, M.E. (1994) Hexachlorobenzene: Evaluation of risks to health from Environmental Exposure in Canada. Environ. Carcin. Ecotox. Revs. C12(2): 345-360

Nouchi, T., Miura, H., Kanayama, M., Mizuguchi, O., Takano, T. (1984) Fatal intoxication by 1,2-dichloroethane - a case report. International archives of occupational and environmental health 54(2): 111-113

Oxenford, J.L. (1996) Disinfection by-products: current practices and future directions. In: Disinfection by-products in water treatment: the chemistry of their formation and control. Minear, R.A. & Amy G.A. [Ed] CRC Press, Inc. ISBN 1-56670-136-8: 3-16

Park, J.D., Habeebu, S.S.M. & Klaassen, C.D. (2002) Testicular toxicity of di-(2-ethylhexyl) phthalate in young Sprague-Dawley rats. Toxicology 171: 105-115

Pohl H.R., McClure P.R., Fay M., Holler J. and DE Rosa C.T. (2001). Public health assessment of hexachlorobenzene 43 (4-7): 903-908

Quast, J.F., Humiston, C.G., Wade, C.E., Ballard, J., Beyer, J.E., Schwetz, R.W., Norris, J.M. (1983). A chronic toxicity and oncogenicity study in rats and subchronic toxicity study in dogs on ingested vinylidene chloride. Fundamental and Applied Toxicology, 3(1): 55-62

Ralph J.L., Orgebin-Crist M-C., Lareyre J-J. and Nelson C.C. (2003). Disruption of androgen regulation in the prostate by the environmental contaminant hexachlorobenzene. Environmental Health Perspectives

111 (4): 461-466

Rontani, J.F., Volkman, J.K. (2003) Phytol degradation products as biogeochemical tracers in aquatic environments. Organic Geochemistry 34: 1–35

Salomons, W. & Forstner, U. (1984) Metals in the hydrocycle. Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, ISBN 3540127550

Sala, M., Sunyer, O., Otero, R., Santiago-Silva, M., Ozalla, D., Herrero, C., To-Figueras, J., Kogevinas, M., Anto, J., Camps, C. & Grimalt, J. (1999) Health effects of chronic high exposure to hexachlorobenzene in a general population sample. Arch. Environ. Health 54(2): 102-109

Satoh K., Nagai F. and Aoki N. (2001). Several environmental pollutants have binding affinities for both androgen receptor and estrogen receptor α. Journal of Health Science 47 (5): 495-501

SFC (2002) Report of the Scientific Committee on Food (SFC) on benzyl alcohol. Opinion expressed on 24 September 2002. Commission of the European Communities. Available at; http://europa.eu.int/comm/food/fs/sc/scf/out138_en.pdf

Stringer, R.L., Costner, P. & Johnston, P.A. (1995) PVC manufacture as a source of PCDD/Fs. Organohalogen Compounds 24: 119-123

Stringer, R.L. & Johnston, P.A. (2001) Chlorine and the Environment: An Overview of the Chlorine Industry. Publ. Kluwer Academic Publishers, Dordrecht, Netherlands. ISBN 0-7923-6797-9, 429pp

Summers, G.W. (1997) Vinyl chloride polymers. In: Kroschwitz, J.I. & Howe-Grant M., (Eds). The Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition. Publ. Wiley-Interscience, N.Y. Volume 27: 1017-1053

To-Figueras J., Barrot C., Rodamilans M., Gomez-Catalan J., Torra M., Brunet M., Sabater F. and Corbella J. (1995). Accumulation of hexachlorobenzene in humans: a long-standing risk. Human and Experimental Toxicology 14: 20-23.

TPC (2002b) Thai Plastic & Chemicals (TPC); www.thaiplastic.co.th/tpc/health/html/envir.html

UNEP (1993) Preliminary assessment of the state of pollution of the Mediterranean Sea by zinc, copper and their compounds and proposed measures. Mediterranean Action Plan UNEP (OCA)/MED/WG.66/Inf.3, Athens 3-7 May 1993

USEPA (1997) Mercury study report to congress, volume III: Fate and transport of mercury in the environment. Office of air quality planning and standards & office of research and development, United States Environmental Protection Agency (USPEA). www.epa.gov/oar/mercury.html

USEPA (2004) Technical support document for the 2004 Effluent Guidelines Program Plan, EPA-821-R-04-014. Engineering and analysis division, office of science and technology, United States Environmental Protection Agency (USEPA); http://www.epa.gov/guide/304m/tsd.pdf

USGPO (2000) Title 40- Protection of the Environment. Chapter 1, Part 414- Organic chemicals, plastics and synthetic fibers. Publ: US Government Printing Office; www.access.gpo.gov/nara/cfr/waisidx_00/40cfr414_00.html

WHO (2004) Guidelines for drinking-water quality. Vol.1: Recommendations. Third Edition, ISBN 92 4 154638 7, 515p.

Yodaiken, R.E., Babcock, J.R. (1973.) 1,2-dichloroethane poisoning. Archives of Environmental Health 26:281-284

Appendix 1; Analytical methodology

A1.1 Organic analysis

A1.1.1 Preparation of samples for standard organic screen analysis

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

A1.1.1.1 Solid Samples

In preparation for analysis of extractable organic compounds, approximately 30g (wet weight) of each 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. 15ml of pentane was added, followed by 5ml of acetone. The samples were then sonicated for 2 hours.

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

A1.1.1.2 Aqueous Samples

Prior to the extraction, the samples were spiked with deuterated naphthalene (an internal standard) at a concentration of 10mg/l. 20ml of pentane was added, and the sample agitated for 2 hours on a bottle roller to maximise contact between solvent and sample.

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

A1.1.2 Chromatographic Analysis

Organic compounds were identified qualitatively using Gas Chromatography Mass Spectrometry (GC-MS). Instrumentation was an Agilent 6890 Series gas chromatograph, interfaced with a Agilent Enhanced Chem-Station data system and linked to a 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. Also all extracts were analysed using selective ion monitoring (SIM) method against two standard solutions. The lists of compounds containing in Standard I and Standard II are presented below. All individual standards were obtained from Sigma Aldrich Co. Ltd., Supelco, UK.

Compound	Ions to monitor
Benzene, 1,3-dichloro-	146, 148, 111, 75
Benzene, 1,4-dichloro-	146, 148, 111, 75
Benzene, 1,2-dichloro-	146, 148, 111, 75
Benzene, 1,3,5-trichloro-	180, 182, 145, 74
Phenol, 2,4-dichloro-	162, 164, 63, 98
Benzene, 1,2,4-trichloro-	180, 182, 145, 109
Benzene, 1,2,3-trichloro-	180, 182, 145, 109
Dichlorvos	109, 185, 79, 47
Benzene, 1,2,3,5-tetrachloro-	216, 214, 218, 179
Benzene, 1,2,4,5-tetrachloro-	216, 214, 218, 179
Benzene, 1,2,3,4-tetrachloro-	216, 214, 218, 179
Benzene, pentachloro-	250, 252, 248, 215
alpha-HCH	181, 183, 219, 217
Benzene, hexachloro-	284, 286, 282, 249
Atrazine	200, 215, 202, 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 A1.1. List of compounds in the Standard I used for SIM analysis

Results are reported as either reliably or tentatively identified. Match qualities of 90% or greater against 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 qualities between 51% and 90% against Agilent Wiley7N and Pesticides Libraries only. Analytes yielding match qualities of 50% or less are taken to be unidentified.

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
Butadiene, hexachloro-	225, 190, 260, 118
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
Dinoseb	211, 163, 147, 117
PCB-28	256, 258, 186, 150
Heptachlor	100, 272, 274, 137
PCB-52	292, 220, 290, 222
Aldrin	66, 263, 265, 261
Octachlorostyrene	308, 310, 380, 378
Chlordane I	373, 375, 272, 237
PCB-101	326, 324, 254, 328
Chlordane II	373, 375, 272, 237
PCB-81	292, 290, 294, 220
Dieldrin	79, 81, 263, 265
PCB-77	292, 290, 294, 220
Endrin	67, 317, 319, 345
PCB-123	326, 324, 254, 328
PCB-118	326, 324, 256, 328
PCB-114	326, 324, 256, 328
PCB-153	360, 362, 290, 358
PCB-105	326, 324, 254, 328
PCB-138	360, 362, 290, 358
PCB-126	326, 324, 254, 328
PCB-167	360, 362, 290, 358
PCB-156	360, 362, 290, 358
PCB-157	360, 362, 290, 358
PCB-180	396, 394, 324, 162
PCB-169	360, 362, 358, 145
PCB-170	396, 394, 324, 326
PCB-189	396, 394, 398, 324

Table A1.2. List of compounds in the Standard II used for SIM analysis

A1.2 Volatile Organic Compounds (VOCs) analysis

For volatile organic compound analysis, no sample preparation was required. The original sample was sub-sampled immediately after opening. Four portions of 10ml each were transferred into separate 20ml headspace vials and sealed with Teflon-lined vial caps. One sub-sample was used for the organic screen analysis to evaluate the whole range of volatile compounds in the sample. The second sub-sample was analysed using Selective Ion Monitoring (SIM) method to detect the VOCs listed in the Table below. The third and forth sub-samples were used for quantification of the detected compounds with an external standard using SIM method. All standard compounds were obtained from Sigma-Aldrich Co. Ltd./Supelco UK.

Compound	**Target ion**	**Qualifying ions**
Methane, chloro-	50	52, 15, 49
Methane, dichloro-	49	84, 86, 51
Methane, trichloro- (chloroform)	83	47, 35, 118
Methane, tetrachloro-	117	35, 47, 82
Ethane, chloro-	64	66, 49, 51
Ethane, 1,1-dichloro-	63	27, 83, 98
Ethane, 1,2-dichloro-	62	27, 64, 49
Ethane, 1,1,1-trichloro-	97	61, 26, 117
Ethane, 1,1,2-trichloro-	97	83, 85, 99
Ethane, 1,1,1,2-tetrachloro-	131	133,117, 119
Ethane, 1,1,2,2-tetrachloro-	83	85, 95, 131
Ethane, pentachloro-	167	165, 169, 117
Ethane, hexachloro-	117	201, 203, 199
Ethene, chloro- (vinyl chloride)	27	62, 37, 47
Ethene, 1,1-dichloro-	61	96, 26, 35
Ethene, 1,2-dichloro-, *cis-*	61	96, 26, 35
Ethene, 1,2-dichloro-, *trans-*	61	96, 26, 37
Ethene, trichloro-	95	130, 132, 97
Ethene, tetrachloro-	166	129, 94, 47
Propane, 1,2-dichloro-	63	62, 65, 64
Propane, 1,3-dichloro-	41	76, 78, 27
Propane, 2,2-dichloro-	41	77, 43, 27
Propane, 1,2,3-trichloro-	75	77, 110, 112
1-Propene, 1,1-dichloro-	110	112, 39, 77
1-Propene, 1,3-dichloro-, *cis-*	75	77, 110, 112
1-Propene, 1,3-dichloro-, *trans-*	75	77, 110, 112
Hexachlorobutadiene	225	260, 190, 118

Table A1.3. List of volatile organic compounds and appropriate ions that were monitored during GC/MS analysis using SIM method.

A1.3 Heavy Metal Analysis

A1.3.1 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 at 105°C.

A1.3.1.1 Solid Samples

Samples were air dried until weighing readings became constant (approx. 5 days). They were then crushed using a pestle and mortar until homogenous and sieved through a 2-mm mesh. Approximately 0.5 g of sample was accurately 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. To prepare samples for arsenic and mercury analysis, this procedure was repeated in an identical manner other than using a digest temperature of 90°C.

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. Two certified reference materials; GBW8301 (River Sediment, certified by the State Bureau of Metrology of The People's Republic of China) & 7004 (Loam with elevated analyte levels, certified by the Czech Metrological Institute) and a blank sample were separately prepared in an identical manner with the batch of samples.

A1.2.1.2 Aqueous sample

The sample was shaken to be thoroughly mixed, and a 100ml representative portion was transferred to a clean glass bottle and acidified with nitric acid (10% v/v). 50 ml of this solution was subsequently transferred to a 100ml boiling tube, placed onto the Gerhardt Kjeldatherm digestion block, and refluxed at 130°C for four hours. After cooling to ambient temperature, the digest was filtered into a volumetric flask, diluted with deionised water, made up to a volume of 50 ml and mixed. With the batch of samples, a mixed metal quality control solution of 8 mg/l and a blank sample were separately prepared in an identical manner.

To prepare the sample for arsenic and mercury analysis, this procedure was repeated in an identical manner other than using 25 ml of each acidified sample solution and a digest temperature of 90°C. With the batch of samples, a blank sample and a quality control solution (80 ug/l mercury) was separately prepared in an identical manner.

A1.3.2 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Following preparation, samples were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), using a Varian Liberty-100 Sequential Spectrometer. The following metals were quantified directly: arsenic (As), cadmium (Cd), cobalt (Co), copper (Cu), chromium (Cr), lead (Pb), manganese (Mn), nickel (Ni) and zinc (Zn). 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.

Reference material	As (%)	Cd (%)	Cr (%)	Co (%)	Cu (%)	Hg (%)	Mn (%)	Ni (%)	Pb (%)	Zn (%)
GBW8301	91	70	56	86	86	90	84	85	78	92
CRM7004	76	104	58	102	90	95	80	95	85	89

Table A1.4 Percentage recovery data for the standard reference materials.

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

Appendix 2; Compounds identified in all samples

AT03025	AT03026	AT03027	AT03028	AT03029	AT03030	AT03031	AT03032	AT03033	AT03034	AT03042
No. isolated: 5	No. isolated: 2	No. isolated: 0	No. isolated: 0	No. isolated: 5	No. isolated: 3	No. isolated: 24	No. isolated: 22	No. isolated: 26	No. isolated: 18	No. isolated: 17
COMPOUNDS RELIABLY IDENTIFIED:										
Ethane, 1,1-dichloro- * Chloroform* Ethane, 1,2-dichloro-* Methane, bromodichloro-* Ethene, trichloro*	None	Chloroform* Ethane, 1,2-dichloro*	None	Heptadecane Pentadecane	Chloroform* Ethane, 1,2-dichloro-* Methane, bromodichloro*	Di(2-ethylhexyl) phthalate Benzene, (1-methylethenyl)- Benzene, 1,2,4-trichloro-* Benzene, 1,2,3,4-tetrachloro-* Benzene, pentachloro-* Benzene, hexachloro-* Benzenemethanol, .alpha.,.alpha.-dimethyl- Docosane Eicosane Heptadecane Hexadecane Indole Nonadecane Octachlorostyrene* Octadecane Phenol, 4-methyl-	Benzenemethanol, .alpha.,.alpha.-dimethyl- Chloroform* Ethene, 1,1-dichloro-* Ethane, 1,2-dichloro-* Ethene, trichloro-* Pentadecane Phenol, 2,4,6-trichloro- Vinyl chloride*	Di(2-ethylhexyl) phthalate Acetophenone Benzene, 1,4-dichloro-* Benzene, 1,2,3,4-tetrachloro-* Benzene, pentachloro-* Benzene, hexachloro-* Benzenemethanol, .alpha.,.alpha.-dimethyl- Docosane Eicosane Heptadecane Hexadecane Octachlorostyrene* Octadecane Tetracosane Tetradecane	Di(2-ethylhexyl) phthalate 1-Dodecanol, 2-methyl- 1-Tridecene	Di(2-ethylhexyl) phthalate Benzenemethanol Docosane Heptadecane Hexadecane Octadecane Tetracosane Tetradecane Tridecane
COMPOUND GROUPS TENTATIVELY IDENTIFIED:										
None	Aliphatic hydrocarbons	None	None	None	None	Aliphatic alcohol Aliphatic hydrocarbons Chlorinated hydrocarbons	Aliphatic hydrocarbons	Aliphatic alcohol Aliphatic hydrocarbons Phthalate ester	Aliphatic hydrocarbons Aliphatic aldehydes	Aliphatic hydrocarbons Aliphatic ketone

Appendix 3; Volatile organic compounds quantified in effluent samples

Name of compound	**Concentration, ug/l**			
	AT03025	**AT03027**	**AT03030**	**AT03032**
Methane, dichlorodifluoro-	ND	ND	ND	ND
Methane, chloro-	ND	ND	ND	ND
Vinyl chloride	ND	ND	ND	<5
Methane, bromo-	ND	ND	ND	ND
Ethane, chloro-	ND	ND	ND	ND
Methane, trichlorofluoro-	ND	ND	ND	ND
Ethene, 1,1-dichloro-	ND	ND	ND	6
Methane, dichloro-	ND	ND	ND	ND
Ethene, 1,2-dichloro-, trans-	ND	ND	ND	ND
Ethane, 1,1-dichloro-	<5	ND	ND	ND
Propane, 2,2-dichloro-	ND	ND	ND	ND
Ethene, 1,2-dichloro-, cis-	ND	ND	ND	ND
Methane, bromochloro-	ND	ND	ND	ND
Chloroform	5	<1	<1	11
Ethane, 1,1,1-trichloro-	ND	ND	ND	ND
Methane, tetrachloro-	ND	ND	ND	ND
1-Propene, 1,1-dichloro-	ND	ND	ND	ND
Ethane, 1,2-dichloro-	<10	<10	<10	250
Ethene, trichloro-	<5	ND	ND	<5
Propane, 1,2-dichloro-	ND	ND	ND	ND
Methane, dibromo-	ND	ND	ND	ND
Methane, bromodichloro-	<5	ND	<5	ND
1-Propene, 1,3-dichloro-, cis-	ND	ND	ND	ND
1-Propene, 1,3-dichloro-, trans-	ND	ND	ND	ND
Ethane, 1,1,2-trichloro-	ND	ND	ND	ND
Ethene, tetrachloro-	ND	ND	ND	ND
Propane, 1,3-dichloro-	ND	ND	ND	ND
Methane, dibromochloro-	ND	ND	ND	ND
Ethane, 1,2-dibromo-	ND	ND	ND	ND
Ethane, 1,1,1,2-tetrachloro-	ND	ND	ND	ND
Bromoform	ND	ND	ND	ND
Ethane, 1,1,2,2-tetrachloro-	ND	ND	ND	ND
Propane, 1,2,3-trichloro-	ND	ND	ND	ND
Ethane, pentachloro-	ND	ND	ND	ND
Ethane, hexachloro-	ND	ND	ND	ND
Propane, 1,2-dibromo-3-chloro-	ND	ND	ND	ND
Hexachlorobutadiene	ND	ND	ND	ND

Table A3.1. ND indicates the compound was not detected, <# indicates the compound was detected, but at a concentration below this quantifiable level.

Appendix 4; Additional information for key pollutants

A4.1 1,2-Dichloroethane (EDC)

1,2-Dichloroethane, which is also known as ethylene dichloride or EDC, is a colourless, volatile liquid. EDC does not naturally exist in the environment; it is highly flammable and in significant amounts may pose an explosion hazard (ATSDR 2000, IPCS 1995).

Production and use

1,2-Dichloroethane (EDC) is one of the leading bulk chemical products. It can be manufactured from ethene by direct chlorination, or by oxychlorination where ethene is reacted with dry hydrogen chloride and oxygen (Reed 1993).

The production of EDC results in the co-generation of many hazardous chlorinated chemicals. EDC is purified from the crude reaction mix by distillation, a process that generates “light ends” and “heavy ends” as waste. Light ends are the volatile compounds that distil off before EDC. Heavy ends, also known as EDC tars, are distillation residues of less volatile compounds that remain after the EDC has been separated. These are heavily contaminated with dioxin (EA 1997, ICI 1994) the concentrations of which can reach part per million levels (Stringer *et al.* 1995).

The primary use of EDC is in the manufacture of vinyl chloride (VCM), with over 90% of EDC produced in the US used in the production of VCM for use in the manufacture of PVC. Other applications of EDC include solvent manufacture, ethyleneamine preparation and as an additive to fuel anti-knock mixtures (ATSDR 2000, Snedecor 1993, Sulivan 1997).

To produce VCM, EDC is subjected to high pressures and temperatures. This causes the EDC to undergo pyrolysis (thermal cracking), yielding the vinyl chloride monomer and hydrogen chloride. The hydrogen chloride produced is often fed back into the oxychlorination process to manufacture further ethylene dichloride. The combination of direct chlorination with hydrogen chloride recycling through oxychlorination is referred to as the balanced process (OSPAR 1996, Snedecor 1993, Stringer & Johnston 2001).

Recognised methods for the removal of EDC from wastewaters include air stripping through aeration or boiling, or through treatment with granulated activated carbon. These processes, however, do not destroy EDC but either create an additional contaminated wastestreams (activated carbon) or simply transfer the EDC to the atmosphere (USEPA 1985, 1987).

Environmental Contamination

Releases of EDC to the environment can result from all aspects of its manufacture, use, storage, transport and disposal (ATSDR 2000). Due to its volatility EDC is releases from industrial processes, primarily to the atmosphere where EDC has an estimated residence time of 47-182 days, enabling it to be transported long distances before being precipitated or degraded. EDC is readily soluble in water where it is broken down slowly through microbial degradation, though when released to water bodies it can rapidly evaporate to the atmosphere. In soils EDC is highly mobile and generally either evaporates to the atmosphere or permeates through the soil into groundwater (ATSDR 2000, Brueggemann *et al.* 1991). The limited information available suggests that EDC does not bioconcentrate in aquatic organisms (Banerjee & Baughman 1991, Farrington 1991).

Toxicity

EDC is both hazardous and toxic. Because of its volatility, the most usual route of exposure is via inhalation, though it can also be absorbed through the skin or gastro-intestinal tract (IPCS 1995). Upon exposure to EDC it becomes distributed to all tissues of the body and can pass both the blood/brain barrier and the placenta. EDC can be toxic at concentrations too low to be detected by smell (ATSDR 2000, Snedecor 1993).

Information on the toxicity of 1,2-dichloroethane in humans is derived primarily from fatal cases following acute exposure to high levels by inhalation or ingestion. The main target organs in humans following exposure are the central nervous system, liver and kidney. Other acute effects include nausea, vomiting, as well as respiratory distress and cardiac arrhythmia. Effects on the blood system have also been observed including reduced blood clotting ability. Acute exposure to very large amounts of EDC can be fatal for both humans and animals, primarily through respiratory and cardiovascular effects (ATSDR 2000, IPCS 1995, Nouchi *et al.* 1984, Yodaiken & Babcock 1973). Very little information is available on health effects in humans following chronic exposures.

Effects in animals are similar to those in humans with the immune system, nervous system and kidneys being major target organs of toxicity. In animal experiments, however, respiratory effects were not been observed following exposure to sub-lethal levels by any route of exposure, suggesting that respiratory effects in fatal exposures result from general systemic stress (Cheever *et al.* 1990). The kidneys being target organs for EDC toxicity is further confirmed in animal experiments which found that long term exposure to significantly lower amounts of EDC than lethal levels, by any route of exposure, also resulted in kidney damage, with effects including tubular degeneration and increased kidney weight (ATSDR 2000).

Very little information is available relating to effects from dermal absorption of EDC in both humans and animals, although EDC is readily absorbed by this route and would be expected to produce similar effects as those observed following inhalation or ingestion (Morgan *et al.* 1991).

EDC is classified by the International Agency for Research on Cancer (IARC) as possibly carcinogenic to humans (IARC 1999) and the US Department of Health and Human Services classifies it as reasonably anticipated to be a human carcinogen (DHHS 2000).

Legislation

Legislation in the United States specifies maximum concentrations of EDC in discharged effluents from industrial facilities. Limits for facilities that use end-of-pipe biological treatment for wastewaters specify a maximum concentration for any one-day of 211 ug/l, and a maximum monthly average concentration of 68 ug/l. For facilities where end-of-pipe biological treatments are not used the equivalent maximum discharge limits are 574 ug/l for any one day and maximum monthly average concentration of 180 ug/l (USGPO 2000).

References

ATSDR (2000) ATSDR's toxicological profiles on CD-ROM, CRC Press, Boca Raton, FL.

Banerjee, S., Baughman, G.L. (1991) Bioconcentration factors and lipid solubility. Environmental Science and Technology 25: 536-539

Brueggemann, R., Trapp, S., Matthies, M. (1991) Behavior assessment of a volatile chemical in the Rhine River. Environmental Toxicology and Chemistry 10:1097-1104

Cheever, K.L., Cholakis, J.M., el-Hawari, A.M., Kovatch, R.M., Weisburger, E.K. (1990) Ethylene dichloride: The influence of disulfiram or ethanol on oncogenicity, metabolism, and DNA covalent binding in rats. Fundamental and Applied Toxicology 14(2): 243-261

DHHS (2002) 10th Report on carcinogens. US Department of Health and Human Services, 263pp.

EA (1997) Regulation of dioxin releases from the Runcorn operations of ICI and EVC. UK Environment Agency Information Report.

Farrington, J.W. (1991) Biogeochemical processes governing exposure of organic pollutant compounds in aquatic organisms. Environmental Health Perspectives 90: 75-84

IARC (1999) 1,2-Dichloroethane. In International Agency for Research on Cancer (IARC) monograph; Re-evaluation of Some Organic Chemicals, Hydrazine and Hydrogen Peroxide, Vol 71, 1589pp

ICI (1994) Report to the Chief Inspector HMIP authorisation AK6039 Improvement Condition part 8, Table 8.1, item 2: Formation of dioxins in oxychlorination, significance for human health and monitoring proposals. ICI Chemicals and Polymers report NWJP/BMTD, 27th April 1994, 16pp

IPCS (1995) 1,2-Dichloroethane (second edition). International Programme on Chemical Safety. Environmental Health Criteria 176, Publ: World Health Organisation, ISBN 92 4 157176 4, 148pp.

Morgan, D.L., Cooper, S.W., Carlock, D.L., Sykora J.J., Sutton, B., Mattie D.R., McDougal, J.N. (1991) Dermal absorption of neat and aqueous volatile organic chemicals in the Fischer 344 rat. Environmental Research 55(1): 51-63

Nouchi, T., Miura, H., Kanayama, M., Mizuguchi, O., Takano, T. (1984) Fatal intoxication by 1,2-dichloroethane - a case report. International archives of occupational and environmental health 54(2): 111-113

OSPAR (1996) Best available techniques for the vinyl chloride industry. Publ: Oslo and Paris Commissions.

Reed D.J. (1993) Chlorocarbons, -hydrocarbons (survey). In: Kroschwitz, J.I. & Howe-Grant, M. (Eds). The Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition. Publ. Wiley-Interscience, N.Y. Volume 5, pp 1017-1028

Snedecor, G (1993) Other chloroethanes. In: Kroschwitz, J.I. & Howe-Grant, M. (Eds), The Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition. Publ: Wiley-Interscience, N.Y., Vol. 6, pp.11-36

Stringer, R.L. & Johnston, P.A. (2001) Chlorine and the Environment: An Overview of the Chlorine Industry. Publ. Kluwer Academic Publishers, Dordrecht, Netherlands. ISBN 0-7923-6797-9, 429pp

Sullivan, D.A. (1997) Solvents, industrial. In: Kroschwitz, J.I. & Howe-Grant, M. (Eds). The Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition. Publ. Wiley-Interscience, N.Y. Vol. 22, pp 529-571

USEPA (1985) Health assessment document for 1,2-dichloroethane final report 600/8-84- 006F. Office of Health and Environmental Assessment, United States Environmental Protection Agency (USEPA), Washington

USEPA (1987) Atmospheric persistence of eight air toxics project summary EPA600/83-87/004. Atmospheric Sciences Research Laboratory, United States Environmental Protection Agency (USEPA),

USGPO (2000) Title 40- Protection of the Environment. Chapter 1, Part 414- Organic chemicals, plastics and synthetic fibers. Publ: US Government Printing Office; www.access.gpo.gov/nara/cfr/waisidx_00/40cfr414_00.html

Yodaiken, R.E., Babcock, J.R. (1973) 1,2-dichloroethane poisoning. Archives of Environmental Health 26:281-284

A4.2 Chlorinated Benzenes

Production and major uses

1,4-Dichlorobenzene (p-dichlorobenzene) is used largely in the production of deodorant blocks and room deodorants. It is also used as a moth control agent, as an insecticide and an intermediate for production of insecticides and dyes. Trichlorobenzenes have no significant intentional uses (Bryant 1993, CEC 1986). Tetrachlorobenzenes have historically been used in dielectric fluids and 1,2,4,5-tetrachlorobenzene was used in the production of 2,4,5-trichlorophenol, but this use has now been discontinued (Giddings *et al.* 1994b).

Pentachlorobenzene is no longer produced in the UN-ECE and is not listed in the Chemicals Data Base of the European Chemicals Bureau (ECB). No data are available on production, recent or past, outside the UN-ECE region (van de Plassche *et al.* 2002). Hexachlorobenzene (HCB) has been used as a wood preservative, as a fungicide for treating seeds, as well as an intermediate in organic syntheses (Budavari *et al.* 2000). HCB is not currently manufactured in the US as a commercial end product (ATSDR 2000).

In addition to the intentional production of chlorinated benzenes, including HCB, these compounds may be also formed as unwanted by-products in the synthesis of other organochlorine compounds, and from high-temperature sources (Newhook & Meek 1994, Sala *et al.* 1999). Vogelgesang (1986) reported that HCB was formed as a waste product from the treatment of aluminium smelt with hexachloroethane and chlorine gas.

Identity

Chlorinated benzenes are manufactured by direct chlorination of benzene in the liquid phase with ferric chloride as a catalyst, with only limited control over the final product mix. Separation of the isomers by distillation has limited resolving power and the products are always mixtures of close boiling isomers, which can be further separated by crystallisation (Bryant 1993). This distillation process also gives rise to chlorinated tars.

Chlorobenzene, 1,2-dichlorobenzene and 1,3-dichlorobenzene are colourless liquids; 1,4-dichlorobenzene forms colourless crystals at room temperature (Ware 1988). 1,2,3- and 1,3,5-trichlorobenzene are solids and 1,2,4-trichlorobenzene is a liquid (Budavari *et al.* 2000). Tetrachlorobenzenes, pentachlorobenzene and hexachlorobenzene are white solids (van de Plassche *et al.* 2002, ATSDR 2000).

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

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

Dichlorobenzenes

1,4-Dichlorobenzene (DCB) is ubiquitous in the environment, having being measured in air, effluents, surface and ground water, sediments and biota. It is not persistent in air or surface water due to its volatility, but it does persist and accumulate in anaerobic sediments (McPherson *et al.* 2002). 1,4-DCB may be absorbed both through the inhalation of vapours, through the skin and though consumption of contaminated food. Human symptoms include damage to the liver, kidneys and lungs (Ware 1988). Animal experiments have recorded liver and kidney damage to be the most frequent effects, though high doses caused CNS perturbation and death through respiratory depression. 1,4-DCB also has estrogenic potency and may disrupt hormone systems, though effects have only been observed at far higher concentrations than those that typically occur in the environment (Versonnen *et al.* 2003). Dichlorobenzenes are bioaccumulative in algae, aquatic invertebrates and fish, and have also been reportedly found in blood samples (Ware 1988).

Trichlorobenzenes

Little research has been carried out in comparison with some other chlorobenzenes. For general human populations the greatest route of exposure is through inhalation. The toxicity of all isomers appears similar; they damage the liver, kidney and thyroid. There is some indication of slight fetotoxicity at high doses (Giddings *et al.* 1994a). All three isomers are also toxic to phytoplankton (Sicko-Goad & Andresen 1993a & b). 1,2,4-trichlorobenzene has been found in all environmental media, though there is insufficient analytical data to tell how widespread contamination is (Hermanson *et al.* 1997).

Tetrachlorobenzenes

There are not large differences between the toxicity of the different isomers. The greatest exposure of the general population is probably through food. All isomers affect the liver, kidney, thyroid and lungs, with 1,2,4,5-tatrachlorobenzene being the most toxic. Animal studies have also found that 1,2,4,5-tetrachlorobenzene causes changes in the spleen, thymus, lymph nodes and haematological parameters (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). Not enough information is available to classify the carcinogenicity of tetrachlorobenzenes (Giddings *et al.* 1994b). In previous studies, 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).

Pentachlorobenzene

Animal studies demonstrate weight loss and effects on the liver, thymus, kidney, adrenal glands and digestive tract following exposure. Anaemia and malformation of sperm also occurred. There is some indication of fetotoxicity and developmental toxicity and impacts on the thyroid have also been observed. Pentachlorobenzene cannot be assigned a carcinogenicity classification because of lack of data. Pentachlorbenzene accumulates in, and is toxic to algae (Sicko-Goad *et al.* 1989). Pentachlorobenzene has been detected in air, drinking water, food and human breast milk (Giddings *et al.* 1994b), and has been shown to accumulate in and be toxic to algae (Sicko-Goad *et al.* 1989).

Hexachlorobenzene (HCB)

Once introduced into environment, HCB strongly absorbs to soil materials and almost no desorption take place (Bahnick & Doucette 1988). It is bioaccumulative and biomagnifies in many organisms. It can be measured in ambient air, drinking water, soil, food and breast milk (Newhook & Meek 1994). The transfer of HCB across the placenta has also been demonstrated in humans (Sala *et al.* 2001).

HCB is toxic to aquatic life, land plants, land animals, and humans. It is listed by the IARC as possible carcinogen to humans and also appears to be a tumour promoter (IARC 2001). Hexachlorobenzene may damage the developing foetus, liver, immune system, thyroid and kidneys and nervous system, with the liver and nervous system being the most sensitive. 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. (ATSDR 2000, Newhook & Meek 1994, van Birgelen 1998). Recent research (van Birgelen 1998) suggests that HCB also has dioxin-like toxicity and inclusion of HCB in the dioxin TEF system has been proposed based on the toxicological point of view for assessing health hazards (Pohl *et al.* 2001). A study has found a higher detectable frequency and higher mean concentrations of DDE or HCB in women with breast cancer compared to control groups, which may indicate that exposure to these environmental endocrine disruptors is a factor in breast carcinogenesis (Charlier *et al.* 2004). HCB has been shown to be an endocrine disruptor in laboratory animal studies (Ralph *et al.* 2003, Verreault *et al.* 2004).

For the general population most human exposure to HCB occurs through food, though other routes exist. Inhabitants living near to a chlorinated solvent factory in Flix, Spain were found to have high serum levels of HCB (mean 36.7 mg/ml) and one case of subclinical porphyria cutanea tarda and five of coproporphyrinuria were reported (Ozalla *et al.* 2002). High concentrations of HCB were also 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).

Legislation

Hexachlorobenzene (HCB) is the most regulated chemical among all chlorinated benzenes, being addressed under many national, regional and global measures. For example HCB is one of twelve priority POPs addressed under the Stockholm Convention on Persistent Organic Pollutants, to which Thailand is a signatory, that requires the phase out and ultimately elimination of POPs and their sources, be they intentional production or practices that yield unwanted by-product POPs such as incineration and thermal processes involving chlorine (UNEP 2001). Furthermore the UNECE (1998) lists HCB alongside PCDD/Fs and PAHs as being the most important persistent organic pollutants (POPs) emitted from stationary sources and HCB is included on Annex I of the Draft UNECE POPs Protocol under the Convention on Long-Range Transboundary Air Pollution (LRTAP) (UNECE 1998).

The lesser chlorinated benzenes are also addressed under a range of national and regional legislations. For example; Pentachlorobenzene is one of the priority substances of the EU Water Framework Directive (EC 2000) and was recently proposed as a candidate for inclusion in the Protocol on POPs based on its potential for long-range atmospheric transport, persistence (in water, sediment and soil), bioaccumulation and (eco)toxicity (van de Plassche *et al.* 2002). Trichlorobenzenes are regulated in the EU under the Council Directive 90/415/EEC which sets limit values for discharges of all three isomers of trichlorobenzene.

References

ASTDR (2000) ATSDR's toxicological profiles on CD-ROM. U.S. Department of Health and Human Services, Public Health Service, CRC Press Inc

Bahnick, D.A. & Doucette, W.J. (1988) Use of molecular connectivity indices to estimate soil sorption coefficients for organic chemicals. Chemosphere 17: 1703-1715

Bryant, J.G. (1993) Chlorinated benzenes. IN: Kroschwitz, J.I. & Howe-Grant, (Eds). The Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition .Publ. Wiley-Interscience, N.Y. Volume 6: 87-100

Budavari, S., O'Neil, M., Smith, A., Heckleman, P. & Obenchain, J. [Eds] (2000) The Merck index. 12th Edition, on CD_ROM, Version 12:3. Merck & Co., Inc.

CEC (1986) p-dichlorobenzene. IN: Organo-chlorine solvents: Health risks to workers. Publ: Commission of the European Communities, ISBN 0-85186-078-8, pp1-16

Charlier C., Foidert J-M., Pitance F., Herman P., Gaspard U., Meurisse M. and Plomteux G. (2004). Environmental dichlorodiphenyltrichloroethane or hexachlorobenzene exposure and breast cancer: is there a risk? Clin Chem Lab Med 42 (2): 222-227

EC (2000) Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Official Journal L 327:1-73

Giddings, M., Meek, M.E. & Gomes, R. (1994a) Trichlorobenzenes: Evaluation of risks to health from environment exposure in Canada. Environ. Carcin. Ecotox. Revs. C12(2): 517-525

Giddings, M., Meek, M.E. & Gomes, R. (1994b) Tetrachlorobenzenes: Evaluation of risks to health from environment exposure in Canada. Environ. Carcin. Ecotox. Revs. C12(2): 473-481

Grimalt, J.O., Sunyer, J., Moreno, V., Amaral, O.C., Sala, M., Rosell, A., Anto, J.M. & Albaiges, J. (1994) Risk excess of soft-tissue sarcoma and thyroid cancer in a community exposed to airborne organochlorinated compounds with a high hexachlorobenzene content. International Journal of Cancer 56: 200-203

Hermanson, M.H., Monosmith, C.L. & Donnelly-Kelleher, M.T. (1997) Seasonal and spatial trends of certain chlorobenzene isomers in the Michigan atmosphere. Atmos. Environ. 31(4): 567-573

IARC (2001) Hexachlorobenzene. In International Agency for Research on Cancer (IARC) monograph; Some thyrotropic agents, Vol. 79

McPherson C.A., Tang A., Chapman P.M., Taylor L.A. and Gormican S.J. (2002). Toxicity of 1,4-dichlorobenzene in sediments to juvenile polychaete worms. Marine Pollution Bulletin 44 (12): 1405-1414

Newhook, R. & Meek, M.E. (1994) Hexachlorobenzene: Evaluation of risks to health from Environmental Exposure in Canada. Environ. Carcin. Ecotox. Revs. C12(2): 345-360

Ozalla D., Herrero C., Ribas-Fito N., To-Figueras J., Toll A., Sala M., Grimalt J., Basagana X., Lecha M. and Sunyer J. (2002). Evaluation of urinary porphyrin excretion in neonates born to mothers exposed to airborne hexachlorobenzene. Environmental Health Perspectives 110 (2): 205-209.

Pohl H.R., McClure P.R., Fay M., Holler J. and DE Rosa C.T. (2001). Public health assessment of hexachlorobenzene 43 (4-7): 903-908

Ralph J.L., Orgebin-Crist M-C., Lareyre J-J. and Nelson C.C. (2003). Disruption of androgen regulation in the prostate by the environmental contaminant hexachlorobenzene. Environmental Health Perspectives 111 (4): 461-466

Sala, M., Sunyer, O., Otero, R., Santiago-Silva, M., Ozalla, D., Herrero, C., To-Figueras, J., Kogevinas, M., Anto, J., Camps, C. & Grimalt, J. (1999) Health effects of chronic high exposure to hexachlorobenzene in a general population sample. Arch. Environ. Health 54(2): 102-109

Sala M., Ribas-Fito N., Cardo E., de Muga M.E., Marco E., Mazon C., Verdu A., Grimalt J.O. and Sunyer J. (2001). Levels of hexachlorobenzene and other organochlorine compounds in cord blood: exposure across placenta. Chemosphere 43 (4-7): 895-901

Sicko-Goad, L., Evans, M.S., Lazinsky, D., Hall, J. & Simmons, M.S. (1989) Effect of chlorinated benzenes on diatom fatty acid composition and quantitative morphology. IV. Pentachlorobenzene and comparison with trichlorobenzene isomers. Arch. Environ. Contam. Toxicol. 18: 656-668

Sicko-Goad, L. & Andersen, N.A. (1993a) Effect of lipid composition on the toxicity of trichlorobenzene isomers to diatoms. I. Short-term effects of 1,3,5-trichlorobenzene. Arch. Environ. Contam. Toxicol. 24: 236-242

Sicko-Goad, L. & Andersen, N.A. (1993b) Effect of lipid composition on the toxicity of trichlorobenzene isomers to diatoms. II. Long-term effects of 1,2,3-trichlorobenzene. Arch. Environ. Contam. Toxicol. 24: 243-248

UNECE (1998) Protocol to the 1979 Convention on long-range transboundary air pollution on persistent organic pollutants. Publ UNECE, 61pp.

UNEP (2001) Stockholm Convention on Persistent Organic Pollutants, United Nations Environment Program (UNEP); www.pops.int

van Birgelen, A.P.J.M. (1998) Hexachlorobenzene as a possible major contributor to the dioxin activity of human milk. Environ. Health Perspectives 106(11): 683-688

van de Plassche, E., Schwegler, A., Rasenberg, M. & Schouten G. (2002) Pentachlorobenzene. Report presented at the Third Meeting of the POPs Expert Group in Geneva, Switzerland, in June 2002, available at http://www.unece.org/env/popsxg/pentachloorbenzeen.pdf

Verreault J., Skarre J.U., Jenssen B.M. and Gabrielsen G.W. (2004). Effects of organochlorine contaminants on thyroid hormone levels in arctic glaucous gulls, *Larus hyperboreus*. Environmental Health Perspectives 112: 532-537

Versonnen B.J., Arijs K., Verslycke T., Lema W. and Janssen C.R. (2003). In vitro and in vivo estrogenicity and toxicity of *o*-, *m*-, and *p*-dichlorobenzene. Environmental Toxicology and Chemistry 22 (2): 329-335

Vogelgesang J. (1986). Hexachlorobenzene, octachlorostyrene and other organochlorine compounds in waste-water from industrial high-temperature processes involving chlorine. Journal for water and wastewater research 19 (4): 140-144

Ware, G.W. (Ed.) (1988) Ortho-, meta- and para- dichlorobenzene. Rev. Environ. Contam.Toxicol. 106: 51-56

A4.3 Octachlorostyrene

Sources

Octachlorostyrene is not an intentionally manufactured chemical (Stringer & Johnston 2001) but is formed as a by-product of certain industrial processes involving chlorine compounds, including chlorine production using graphite anodes (Kaminsky & Hites 1984), and various high temperature metal production processes (Kaminsky & Hites 1984, Deutscher & Cathro 2001, Doring *et al.* 1992)

Environmental Contamination

Octachlorostyrene is a persistent organic environmental pollutant that has been identified in environmental samples and in the tissues of both wildlife and humans in many different locations (Chu *et al.* 2003, Coelhan *et al.* 2000, Kaminsky & Hites 1984). It is lipophilic and has a high bioaccumulation factor (Ingebrigtsen *et al.* 1988). A study on a rice field ecosystem on the Ebro delta, Spain detected octachlorostyrene in sediments and biota and noted the presence of a chloroalkali factory 200km upstream which could be a source (Pastor *et al.* 2004). Studies show that environmental contamination with octachlorostyrene is widespread on a global basis as a result of its production in chemical processes, with reports of its presence in biota in remote regions such as the arctic (Sandau *et al.* 2000).

In humans, the first report of octachlorostyrene contamination in blood of the general population and of persons working in magnesium and PVC producing plants was from a study in Norway (Lunde and Bjorseth 1977). The study showed that the average level of octachlorostyrene in the blood of employees from a magnesium plant (1.24 ppb) was higher than the average level from employees with no exposure to chlorinated hydrocarbons (0.20 ppb).

Toxicity

Studies to investigate the toxicity of octachlorostyrene have been carried out on laboratory rats (Chu *et al.* 1982, Chu *et al.* 1986). In one study on acute toxicity octachlorostyrene was found to cause caused toxicity to the liver (hepatic changes), and histological changes were observed in the liver and thyroid (Chu *et al.* 1982). A study on the long-term toxicity of octachlorostyrene in exposed rats showed similar toxic effects to the acute study (Chu *et al.* 1986), with the liver, thyroid and kidney being the target organs, all showing histological changes.

Many chemicals that contaminate the environment have been designated to be endocrine (hormone system) disruptors. Octachlorostyrene has been tested in an *in vitro* study to screen chemicals for their endocrine-disrupting ability, specifically their estrogen receptor and androgen receptor binding affinities (Satoh *et al.* 2001). Octachlorostyrene was found to have a binding affinity for the estrogen and the androgen receptor. The results suggested that it had mimicking or blocking effects on the actions of androgen and estrogen.

In humans, data on the potential toxicity of octachlorostyrene is very limited. One study investigated porphyrin metabolism in workers who had previously been exposed to hexachlorobenzene and octachlorostyrene through the process of aluminium degassing with hexachloroethane (Seldén *et al.* 1999). Octachlorostyrene has been shown experimentally to be porphyrinogenic andthe study on foundry workers indicated that aluminium degassing with hexachloroethane may have affected porphyrin metabolism, presumably by exposure to hexachlorobenzene and octachlorostyrene. The metabolic alterations observed were subtle and clinically insignificant, but they were congruent with early secondary coproporphyrinuria, which is the first step in the development of chronic hepatic porphyria induced by polyhalogenated aromatics.

References

Chu I., Secours E. and Villeneuve D.C. (1982). Acute and subacute toxicity of ocatchlorostyrene in the rat. Journal of Toxicology and Environmental Health 10: 285-296

Chu I., Villeneuve D.C., Secours V.E., Valli V.E., Leeson S. and Shen S.Y. (1986). Long-term toxicity of ocatchlorostyrene in the rat. Fundamental and Applied Toxicology 6: 69-77

Chu S., Covaci A., Voorspoels S. and Schepens P. (2003). The distribution of octachlorostyrene (OCS) in environmental samples from Europe. Journal of Environmental Monitoring 5: 619-625.

Coelhan M., Reil I., Rimkus G. and Parlar H. (2000). Peak patterns of chlorostyrenes in fish and fish oils from the North Atlantic. Environmental Science and Technology 34 (22): 4695-4700

Deutscher, R.L. & Cathro, K.J. (2001) Organochlorine formation in magnesium electrowinning cells. Chemosphere 43(2):147-155

Doring, J., Damberg, M., Gamradt, A. & Oehme, M. (1992) Screening method based on the determination of perchlorinated aromatics for surface soil contaminated by copper slag containing high levels of polychlorinated dibenzofurans and dibenzo-p-dioxins. Chemosphere 25(6): 755-762

Ingebrigsten K., Solbakken J.E., Norheim G. and Nafstad I. (1988). Distribution and elimination of carbon 14 octachlorostyrene in cod (*Gadus morhua*), rainbow trout (*Salmo Gairdneri*) and blue mussel (*Mytilus Edulis*). Journal of Toxicology and Environmental Health 25: 361-372

Kaminsky, R. & Hites, R.A. (1984) Octachlorostyrene in Lake Ontario: sources and fates. Environmental Science and Technology 18(4): 275-279

Lunde G. and Bjorseth A. (1977). Human blood samples as indicators of occupational exposure to persistent chlorinated hydrocarbons. The Science of the Total Environment 8: 241-246

Pastor D., Sanpera C., Gonzalez-Solis J., Ruiz X. and Albaiges J. (2004). Factors affecting the organochlorine pollutant load in biota of a rice field ecosystem (Ebro Delta, NE Spain). Chemosphere 55 (4): 567-576

Sandau C.D., Meerts I.A.T.M., Letcher., R.J., McAlees A.J., Brouwer A. and Norstrom R.J. (2000). Identification of 4-hydroxyheptachlorostyrene in polar bear plasma and its binding affinity to transthyretin: A metabolite of octachlororstyrene? Environmental Science and Technology 34 (18): 3871-3877

Satoh K., Nagai F. and Aoki N. (2001). Several environmental pollutants have binding affinities for both androgen receptor and estrogen receptor α. Journal of Health Science 47 (5): 495-501

Selden A.I., Floderus Y., Bodin L.S., Westberg H.B. and Thunell S. (1999). Porphyrin status in aluminium foundary workers exposed to hexachlorobenzene and octachlorostyrene. Archives of Environmental Health 54 (4): 248-253

Stringer R. and Johnston P. (2001). Chlorine and the Environment: An overview of the chlorine industry. Kluwer Academic Publishers. ISBN 0-7923-6797-9

A4.4 Zinc (Zn)

Production and major uses

Zinc is primarily produced from ores through smelting or electrolyses, but can also be recovered from secondary sources such as recycled scrap (ATSDR 2000, Kroschwitz & Howe-Grant 1995).

Zinc is one of the most extensively used “trace” metals (Nriagu 1990). It is most commonly employed as a protective coating for other metals e.g. galvanised steel, or as a component of bronze, brass and die-casting alloys. In addition, zinc compounds or ‘salts’ are widely employed as wood preservatives, herbicides, catalysts, analytical reagents, vulcanisation accelerators for rubber, and stabilisers in PVC (ATSDR 2000, Matthews 1996). They can also be found in ceramics, textiles, fertilisers, paints, pigments, batteries and dental, medical, and household products (ATSDR 2000, Annema & Ros 1994, UNEP 1993, Budavari *et al.* 1989).

Identity

Zinc (Zn) is a metallic element that is naturally present in the environment, principally as ionic compounds. It is found in the Earth’s crust at an average concentration of 80 mg/kg, although some clay sediments and shales may contain higher concentrations (Alloway 1990, Salomons & Forstner 1984). In ionic forms, the divalent oxidation state Zn(II) predominates (ATSDR 2000).

Environmental Fate

Zinc is a relatively abundant metal, which is found at varying concentrations in nearly all uncontaminated aquatic and terrestrial ecosystems (see Table A3.1).

Environmental Matrix	Concentration	Reference
Seawater (open ocean) (coastal and estuarine)	<1 μg/l 0.3-70 μg/l	Bryan & Langston 1992, UNEP 1993
Freshwater	<50 μg/l	ATSDR 2000
Drinking water	0.02-1.2 mg/l	ATSDR 2000
Soil	50 mg/kg average (10-300 mg/kg)	Alloway 1990
Freshwater sediment	<100 mg/kg	ATSDR 2000, Salomons & Forstner 1984
Marine Sediment	<100 mg/kg	Bryan & Langston 1992, UNEP 1993

Table A3.1 Background concentrations of zinc found in water, sediments and soil.

In the environment zinc occurs primarily in the +2 oxidation state, either as the free (hydrated) zinc ion, or as dissolved and insoluble complexes and compounds (ATSDR 2000). In soils, zinc generally remains strongly sorbed, and in the aquatic environment it will predominantly bind to suspended material before finally accumulating in the sediment (ATSDR 2000, Bryan & Langston 1992, Alloway 1990). Re-solubilisation back into an aqueous, more bioavailable phase, is possible under certain physical-chemical conditions, e.g. the presence of soluble anions, the absence of organic matter, clay minerals and hydrous oxides of iron and manganese, low pH and increased salinity (ATSDR 2000). Zinc in a soluble form (e.g. sulphate or chloride, as present in incinerator ash, or ore processing wastestreams) is far more likely to migrate through the environment than if it is bound to organic matter or present as an insoluble precipitate (e.g. as in sewage sludge) (ATSDR 2000).

Toxicity and Essentiality

Zinc is an essential nutrient for plants and animals and humans. However, if exposed to high concentrations of bioavailable zinc, significant bioaccumulation can results, with possible toxic effects (ATSDR 2000).

Human toxicity

Zinc is a nutritionally essential metal in the human diet, playing a role in enzymatic, structural and regulatory systems (Goyer 1996, Aggett & Comerford 1995). Due to its essentiality, dietary allowances of zinc are recommended; 15 mg/day for men, and 12 mg/day for women (ATSDR 2000). Deficiency can result in severe health consequences including growth retardation, anorexia, dermatitis, depression and neuropsychiatric symptoms (Aggett & Comerford 1995).

High doses of zinc in the diet, however, can induce a range of symptoms in humans, including pancreatic damage, anaemia, gastrointestinal distress and diarrhoea (ATSDR 2000, Goyer 1996). For example, humans taking supplements at higher than recommended doses (400-500 mg/day) suffered severe gastro-enteritis (Abernathy & Poirier 1997); and humans who drank water from galvanised pipes over a prolonged period suffered irritability, muscular stiffness and pain, loss of appetite and nausea (UNEP

1993).

Exposure and toxic effects can also occur *via* inhalation of zinc fumes, primarily in an occupational situation. Inhalation of zinc oxide fumes presents the most significant effect, with symptoms including include chills and fever, profuse sweating and weakness. Attacks usually begin after 4-8 hours of exposure, and last between 24-48 hours (ATSDR 2000, Goyer 1996).

Environmental toxicity

Excessive oral exposure to zinc can cause a similar range of toxic effects in animals as described above for humans (ATSDR 2000, Goyer 1996). For example, animal studies involving doses 1,000 times higher than the RDA, taken over a period of a month, resulted in anaemia and injury to the pancreas and kidney. Furthermore, rats that ate very large amounts of zinc became infertile (ATSDR 2000).

In the aquatic environment, appreciable quantities of zinc can have a direct disrupting effect on the external cell membranes or cell walls of organisms, resulting in rapid mortality (UNEP 1993). Prolonged exposure to lower sub-lethal concentrations can also affect aquatic organisms. For example, studies have shown that at concentrations as low as 15 µg/l, carbon fixation rates in natural phytoplankton populations were depressed. Others observed that the growth of cultured diatoms was inhibited at 20 µg/l (Bryan & Langston 1992).

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

Legislation

Applicable standards set by the Ministry of Science, Technology and Environment of Thailand for zinc include ‘Effluent standards for industrial and industrial estate sources’ (No.3, BE 2539). These standards set limits for zinc in effluents of 5.0 mg/l (MSTE 1996).

References

Abernathy, C.O. & Poirier, K.A. (1997) Uncertainties in the risk assessment of essential trace elements: the case of zinc. Human and Ecological Risk Assessment 3(4): 627-633

Aggett, P.J. & Comerford, J.G. (1995) Zinc and human health. Nutrition Reviews 53(9): S16-S22

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

Annema, J.A. & Ros, J. (1994) Management of the zinc chain. Resources, Conservation and Recycling 12: 209-219

ATSDR (2000) Toxicological profile for zinc on CD-ROM. Agency for Toxic Substances and Disease Registry. U.S. Public Health Service

Bryan, G.W. & Langston, W.J. (1992) Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. Environmental Pollution 76: 89-131

Budavari, S.M., O'Neil, J., Smith, A. & Heckleman, P.E. [Eds] (1989) The Merck Index: an encyclopaedia of chemicals, drugs and biologicals. 11TH Edn Merck and Co, Inc., New Jersey, USA

Goyer, R.A. (1996) Toxic effects of metals. In Casarett & Doull's Toxicology. The Basic Science of Poisons, Fifth Edition, Klaassen, C.D. [Ed]. McGraw-Hill Health Professions Division, ISBN 0071054766

Kroschwitz, J.I & Howe-Grant, M. [Eds] (1995) Kirk-Othmer Encyclopaedia of Chemical Technology Volume 7.Fourth Edition. Zinc and zinc alloys. John Wiley and Sons, New York, Chichester, Brisbane, Toronto and Singapore

Matthews, G. (1996) PVC: production, properties and uses. Publ: The Institute of Materials, London.

MSTE (1996) Industrial Effluent Standards, notification of the Ministry of Science, Technology and Environment, No. 3, B.E. 2539. Presented by the Pollution Control Department, Ministry of Natural Resources and Environment; http://www.pcd.go.th/info_serv/en_reg_std_water04.html#s1

Nriagu, J.O. (1990) Global metal pollution. Poisoning the biosphere? Environment 32(7): 7-11;28-33

Salomons, W. & Forstner, U. (1984) Metals in the hydrocycle. Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, ISBN 3540127550

UNEP (1993) Preliminary assessment of the state of pollution of the Mediterranean Sea by zinc, copper and their compounds and proposed measures. Mediterranean Action Plan UNEP (OCA)/MED/WG.66/Inf.3, Athens 3-7 May 1993