Toxic chemical pollutants released from the Thai Plastic & Chemicals PVC facility to the Chao-Phraya River, Samut Prakan, Thailand

Kevin Brigden, Iryna Labunska & David Santillo

Greenpeace Research Laboratories
Technical Note 05/2004

June 2004

Table of contents

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

Executive summary

The Thai Plastic & Chemicals (TPC) PVC facility is located on the banks of the Chao-Phraya River in the Samut Prakan province of Thailand, close to the river estuary into the Gulf of Thailand. Polyvinyl chloride (PVC) is produced at this facility from vinyl chloride monomer (VCM), which is brought into the facility as a raw material. The plant commenced production in 1971, and was the first TPC operated PVC producing facility in Thailand. The environmental policy of TPC includes guidelines for the monitoring of chemicals within and around the factory site to prevent contamination of the environment.

The facility discharges wastewaters to a small channel, a side branch of the Chao-Phraya River. Greenpeace collected three samples in the vicinity of the TPC facility in May 2003; effluent from the main outfall, and two channel sediments from below TPC discharge pipes. All were analysed for a range of organic chemicals and heavy metals.

Effluent from the main TPC outfall contained a diversity of organic chemicals typical of waste streams from processes linked to PVC production. Most significant of these was a relatively high level of VCM (338 µg/l), a highly toxic organochlorine chemical and a known human carcinogen. This level would not be acceptable in discharges from an equivalent plant in the USA. Trace levels of other volatile organic compounds (VOCs) were also found, as well as derivatives of antioxidants often used in plastics.

The sediment samples contained numerous compounds used as additives in PVC formulations. These included a benzotriazole phenol derivative; a chemical used as a PVC stabiliser, as well as numerous phthalates; relatively persistent and bio-accumulative compounds that are commonly used as plasticising (softening) additives in PVC, including two that are toxic to reproduction. Also identified were chemicals related to phthalates, which may have been present in commercial phthalate formulations used by TPC.

Analysis of the effluent for heavy metals revealed little of interest. Nevertheless, there was evidence of lead and possibly cadmium contamination of the sediments from the channel, particularly at a location below pipes that were not discharging at the time the samples were collected. While the source of these toxic metals cannot be confirmed, particularly as the lead and cadmium contamination of the Chao-Phraya River is a long recognised phenomenon, the documented use of lead stabilisers by TPC may well have been a significant local and regional contributor.

TPC claim to employ monitoring and control programs to prevent contamination of the environment. Even on the basis of this limited investigation, adherence to these aims is questionable. TPC effluent is clearly a significant point source of toxic VOCs to the surrounding environment. Emissions of VOCs to the atmosphere are also likely to occur from within the TPC facility.

Thai legislation that sets standards for industrial effluents only address organic chemicals under very general parameters. It does not specifically address many of the toxic and hazardous chemicals identified in this study, despite the inclusion of organochlorine compounds as 'specific chemicals creating concern' within the National Chemicals Management Profile for Thailand.

Stringent national legislation addressing the production, use and releases of such chemicals from industrial facilities would offer greater protection for the environment and human health. However, given that the production of chlorinated chemicals, including PVC, inevitably generates complex chlorinated waste streams, the ultimate solution for addressing releases of such hazardous chemicals is through the progressive substitution of chlorine based processes and products with non-chlorinated and non-hazardous alternatives.

1 Introduction

1.1 PVC production

Polyvinyl chloride (PVC) is one of the mostly widely used thermoplastics in the world, with an annual global production of about 25 million tonnes (CIN 2003). PVC can be produced through a number of different processes. Currently, the majority of facilities employ processes that proceed via the ethylene dichloride (EDC) intermediate (Matthews 1996).

Ethylene dichloride (EDC) is manufactured by the chlorination of ethene, either directly with chlorine or through an oxychlorination process using hydrogen chloride and oxygen. Vinyl chloride, also called vinyl chloride monomer (VCM), is then produced from EDC (Stringer & Johnston 2001). Subsequently VCM is polymerised to produce PVC. The production of VCM and its polymerisation into PVC are not always carried out at the same facility.

The manufacture of EDC and VCM results in the generation of toxic chlorinated wastes containing dozens of hazardous chemicals, including chlorinated dioxins. The environs of many VCM production facilities are often contaminated with many of these chemicals (Labunska *et al.* 2002, Stringer & Johnston 2001, Stringer *et al.* 1995).

PVC formulations typically contain a range of additional chemicals that are incorporated to modify the properties of the plastic (Ehrig 1992). These additives include plasticisers to soften the PVC for non-rigid applications, stabilisers to combat UV and heat-induced degradation, and pigments to colour the plastic. A wide range of synthetic organic chemicals and heavy metal compounds are employed as such additives (Stringer & Johnston 2001).

1.2 Thai Plastic & Chemicals PVC facility

The Thai Plastic & Chemicals (TPC) PVC facility is located in Bangyaphraek, Amphoe Phrapradaeng, in the Samut Prakan Province of Thailand. The plant is situated on the banks of the Chao-Phraya River, south of Bangkok and close to the river estuary into the Gulf of Thailand. This plant was the first TPC operated PVC producing facility in Thailand, commencing production in 1971.

PVC is produced in powder and pellet form through the polymerization of VCM, which is brought into the facility as a raw material (TPC 2002a). As the VCM used by TPC is not produced at this facility, contamination of the local environment by the wastes associated with its production is not anticipated, though it may occur at the site or sites where it is manufactured (EC 1999, Stringer & Johnston 2001).

According to their website, TPC has an environmental policy which aims to ensure that its operations are carried out in an environmentally sound manner, through adhering to certain defined principles. Essential guidelines provided by the policy cover many operational aspects, and include the regular monitoring of wastewater, air and soil samples collected in and around the factory with the aim of preventing contamination of the environment (TPC 2002b).

To investigate the activities at the TPC facility, their impact on the Chao-Phraya River, and whether TPC are operating under appropriate controls including their own environmental policy, Greenpeace visited the site in May 2003 to collect samples for scientific analysis.

2 Materials and methods

2.1 Sample collection

Three samples were collected from the vicinity of the Thai Plastic & Chemicals (TPC) PVC facility in Samut Prakan Province on the 13th May 2003; one sample of discharged effluent and two river sediment samples. Details of the samples collected are given in Table 1.

Adjacent to the TPC facility, a small shallow channel approximately 100 metres in length branches off from the Chao-Phraya River and runs immediately alongside the TPC boundary wall. Being close to its estuary, the Chao-Phraya River is tidal at this location.

A number of discharge pipes exit the TPC facility through its boundary wall that runs along the edge of the side channel. The largest pipe discharges into the channel very close to where it branches from the Chao-Phraya River. A sample of effluent was collected from this outfall (AT03067). A sample of sediment (AT03068) was also collected from the channel directly below this outfall.

A number of smaller discharge pipes exit the TPC facility approximately 100m along the side channel, away from the Chao-Phraya River. At the time of sample collection, these pipes were not discharging to the channel. A sample of sediment (AT03069) was collected from the channel directly below these pipes.

Sample no.	Sample type	Sample location
AT03067	Effluent	Side channel to the Chao-Phraya River, main discharge pipe
AT03068	Sediment	Side channel to the Chao-Phraya River, below main outfall (AT03067)
AT03069	Sediment	Side channel to the Chao-Phraya River below non-discharging pipes, up-channel from the Chao-Phraya River

Table 1. Description of the samples collected from the TPC PVC facility, Samut Prakan, Thailand, 2003

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. The wastewater sample was collected in a fully filled 1-litre screw-cap bottle. The sediment samples were collected in 100ml bottles. All samples were kept cool and returned to the Greenpeace Research Laboratories for analysis. Detailed description of sample preparation and analytical procedures are presented in Appendix 1.

3 Results and discussion

The results of the qualitative organic screen and quantitative heavy metals analyses are presented below. Table 2 provides heavy metal concentrations, the number of organic compounds isolated from each sample, and a breakdown of the groups of organic compounds reliably identified using a GC/MS screening method, as described in Appendix 1. The concentrations of the organic compounds identified using this method were not determined. Volatile organic compounds (VOCs) in the effluent sample (AT03067) were identified separately, and the concentrations of a range of VOCs in this sample were determined. The quantitative results of the VOC analysis are presented in Table 3.

3.1 Organic pollutants

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 volatile organic compounds quantified in sample AT03067 is provided in Appendix 3. Detailed information on certain key pollutants detected during this study is presented in Appendix 4.

The sample of effluent from TPC (AT03067) contained a wide range of organic compounds including chlorinated compounds (organochlorines). Of the 77 individual compounds that were isolated from the effluent, only 20% could be reliably identified. The identity and, therefore, properties and potential impacts of the remaining compounds present in the effluent are unknown. Similarly, many of the compounds isolated from the two sediment samples could not be reliably identified.

Four organochlorines were identified in the effluent sample; vinyl chloride, chloroform, 1,1-dichloroethane and 1,2-dichloroethane. These contaminants are typical of waste streams from processes linked to PVC production (Johnston *et al.* 1994).

The effluent contained vinyl chloride at a concentration of 338 µg/l. Quantification of the remaining volatile organic compounds (VOCs) identified in the effluent sample showed them to be present at very low concentrations. Chloroform was present at a concentration below 1 µg/l, too low to be accurately quantified. Similarly, 1,1-dichloroethane and 1,2-dichloroethane were identified in the effluent at concentrations below their quantifiable levels; below 5 µg/l for 1,1-dichloroethane and below 10 µg/l for 1,2-dichloroethane.

Given the highly volatile nature of the organochlorines identified in the effluent, emissions and losses of these chemicals to atmosphere are also likely to occur from the TPC facility and its production waste streams. Such releases may occur from storage, handling and processing of chlorinated chemicals on the site, as well as by volatilisation from effluent streams, treatment plants and settling lagoons. Emissions to atmosphere were not quantified in the current study.

Vinyl chloride (VCM) was by far the most abundant organochlorine in the effluent. VCM is not a persistent chemical; it readily evaporates from surface waters, and is rapidly degraded in the atmosphere. VCM is far more persistent in groundwater, with an estimated degradation half-life of up to eight years (Howard *et al.* 1991). VCM is, however, an extremely hazardous chemical. It is highly toxic to both humans and animals, it is a known human carcinogen and can be explosive if mixed with air. Due to its volatility, the usual route of exposure to vinyl chloride is through inhalation (ATSDR 2000, IPCS 1999).

Sample number	AT03067	AT03068	AT03069
Description	Effluent	Sediment	Sediment
Location	main discharge	below main discharge	below non-discharging pipes
Metal	**µg/l**	**mg/kg dw**	**mg/kg dw**
Arsenic (As)	<400	<40	<40
Cadmium (Cd)	<10	<1	1.6
Chromium (Cr)	<20	62	179
Cobalt (Co)	<20	15	11
Copper (Cu)	40	36	31
Lead (Pb)	26	64	138
Manganese (Mn)	41	1330	1710
Mercury (Hg)	<2	<0.2	<0.2
Nickel (Ni)	<20	38	82
Zinc (Zn)	86	183	167
Number of organic compounds isolated	77	33	104
Number of organic compounds reliably identified	15 (19%)	26 (79%)	54 (52%)
Chlorinated compounds			
Chloroform	1*		
Dichloroethanes	2*		
Vinyl chloride	1*		
Benzene, 1,4-dichloro-			1*
Phthalate esters and related compounds			
DnBP		1	1
DEHP		1	1
DiNP		mix of isomers	mix of isomers
Phthalic anhydride			1
Phenols			
Phenol, 2,6-bis-tert-butyl-4-methyl- (Butylated hydroxytoluene, BHT)			1
2,6-Di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (BHT-quinol)	1		1
Phenol, 2-(2H-benzotriazol-2-yl)-4-methyl-			1
Other oxygenated compounds			
2-Ethylhexyl esters			2
Benzenemethanol			1
Aliphatic hydrocarbons			
Linear	7		7
Branched	3		

*Table 2. Organic chemicals and heavy metals identified in samples collected around the TPC PVC facility, Samut Prakan, Thailand, 2003. 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 using the more sensitive selective ion monitoring (SIM) method. Metal concentrations are given in mg/kg dry weight for solid samples and µg/l for liquid samples*

VCM has been classified by the International Agency for Research on Cancer (IARC) as carcinogenic to humans (IARC 1987), and has been classified as a known human carcinogen by the US government since 1980 (DHHS 2002). The cancer most strongly associated with VCM exposure in humans is angiosarcoma of the liver in occupationally exposed workers.

Vinyl chloride is narcotic, and inhalation can cause neurological effects that can culminate in damage to the nervous system. Also seen are toxic effects on the immune system, liver, spleen, thyroid function, eyes and skin of workers. Furthermore, there are also indications that VCM can affect both male and female reproductive systems (ATSDR 2000, IPCS 1999). Additional information on VCM is presented in Appendix 4.

Compound	AT03067 Concentration, µg/l
Methane, trichloro- (chloroform)	<1
Ethene, chloro- (vinyl chloride)	338
Ethane, 1,1-dichloro-	<5
Ethane, 1,2-dichloro-	<10

Table 3. Volatile organochlorine compounds (VOCs) quantified in the effluent sample AT03067 from the TPC PVC facility, Samut Prakan, Thailand, 2003; <# indicates compound detected, but at a concentration below the quantifiable level

Despite the hazardous nature of the organochlorine compounds identified in PVC effluents, few regulatory limits apply to releases from PVC manufacturing facilities anywhere in the world. In many instances legislation only addresses releases to air (IPCS 1999). Legislation addressing the discharge of industrial effluents in Thailand does not specify limits for vinyl chloride (PCD 2002).

In the US, maximum discharge limits are set for vinyl chloride in discharged wastewaters from plastics manufacture. The legislation specifies a range of limits depending on the type of discharge and measurement period, as summarised in Table 4 (USGPO 2000). While these regulatory limits do not apply to the TPC facility, they serve as a useful basis for comparison given the absence of applicable Thai legislation.

The effluent sample from TPC (AT03067) contained vinyl chloride at a concentration of 338 µg/l. The methods of treatment used at the TPC facility for vinyl chloride containing wastewaters are not known. Comparison of this concentration to the least stringent US limits (for facilities where end-of-pipe biological treatment is employed) shows that the vinyl chloride concentration in the TPC effluent was 1.26 times the maximum daily concentration and 3.25 times the maximum monthly average concentration.

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

Table 4. Discharge limits in US for vinyl chloride in wastewaters from plastics manufacture (USGPO 2000)

1,1-dichloroethane and 1,2-dichloroethane are chemical isomers, related compounds with similar chemical structures. 1,2-dichloroethane (also known as ethylene dichloride or EDC) is primarily employed in the manufacture of VCM (ATSDR 2000, IPCS 1995). 1,1-dichloroethane (also known as ethylidene dichloride) is used industrially but can also be produced from the reaction of vinyl chloride (VCM) and hydrochloric acid and therefore may be a side product of VCM production and purification (ATSDR 2000).

There are two possible sources of the dichloroethane isomers in the effluent from TPC. Both dichloroethane isomers have been found in process wastewaters from VCM production (Myszkowski & Milchert 2003) and, therefore, these chemicals may be present as trace components in the VCM used at the TPC facility in the production of PVC. An alternate source may the purification of VCM by distillation carried out at TPC (Setthamanit *et al.* 1985). This process can result in the formation of dichloroethane (ATSDR 2000).

Being highly volatile, both 1,1-dichloroethane and 1,2-dichloroethane (EDC) readily evaporate from water and soil (ATSDR 2000, IPCS 1995). While these chemicals are not highly persistent in the environment, they are both highly flammable and toxic to humans and animals. Exposure to either isomer is generally via inhalation as a result of their volatility, though both can also be absorbed via ingestion or through the skin (IPCS 1995). As for vinyl chloride, legislation addressing the discharge of industrial effluents in Thailand does not specify limits for 1,1- or 1,2-dichloroethane (PCD 2002).

Chloroform, the forth organochlorine identified in the effluent, has a range of industrial uses including use as a solvent in chemical processes (ATSDR 2000). However, it can also be generated during water disinfection using chlorine or chlorine-containing compounds (Oxenford 1996). It is a volatile chemical that evaporates readily from water. While chloroform is both toxic and possibly carcinogenic (ATSDR 2000), the effluent sample (AT03067) contained chloroform at a very low concentration (<1 μg/l).

The organochlorine 1,4-dichlorbenzene (1,4-DCB) was also identified in one of the sediment samples (AT03069). This chemical is widely used in lavatory deodorant blocks and room deodorants (Bryant 1993), which is the probable source of 1,4-DCB at this location. This chemical exhibits some toxic effects to the liver and kidney (CEC 1986).

In addition to the organochlorines described above, the effluent sample contained further chemicals, including 2,6-di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one, also known as BHT-quinol. This chemical is a known metabolite of butylated hydroxytoluene (BHT), a chemical frequently employed as an antioxidant in a wide range of products including plastics (Jobling *et al.* 1995). Both BHT-quinol and BHT were also identified in the sample of sediment collected directly below the non-discharging pipes (AT03069).

BHT is generally considered to have very low toxicity (WHO 1999). The FAO/WHO (Food and Agriculture Organization/ World Health Organization) joint expert committee on food additives (JECFA) has set an acceptable daily intake (ADI) of 0-0.3 mg/kg body weight for BHT (WHO 1999). There is, however, some evidence that BHT can act, in combination with carcinogenic substances, as a promoter of liver cancer (Williams *et al.* 1986). Very little is known about the toxicity of BHT-quinol. The only available information shows no effects in certain tests for certain specific adverse toxicological effects (Taffe *et al.* 1989, Nagai *et al.* 1993).

A range of linear and branched aliphatic hydrocarbons were also identified in the effluent sample (AT03067), and in the sediment collected below the non-discharging pipes (AT03069). These compounds are common components of crude oil and petroleum products (Hsieh *et al.* 2000), which is their probable source in this instance.

Additional compounds were identified in the two samples of sediment from the side channel (AT03068 & AT03069) that were not found in the effluent sample (AT03067).

A benzotriazole phenol derivative was identified in the sediment sample collected below the non-discharging pipes (AT03069). This compound is known under a number of names including 2-(2H-benzotriazol-2-yl)-4-methyl-phenol or 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, and under many trade names including Drometrizole, Tinuvin P and Runsorb UV-P.

This compound is a highly efficient absorber of ultraviolet light and is widely used as an ultraviolet light stabilizer to reduce discoloration and degradation in plastics (including PVC) which can result from exposure to sunlight (Crawford 1999, Niklasson & Bjorkner 1989). It has low acute toxicity to mammals and aquatic organisms and has been incorporation into plastics used for food storage, being permitted as an indirect food additive resulting from this use in the United States (USFDA 2004). However, there are a number of reported cases of this benzotriazole derivative causing allergic contact dermatitis in humans as a result of skin contact with plastic materials in which it was incorporated (Niklasson & Bjorkner 1989, Arisu *et al.* 1992).

Both sediment samples (AT03068 & AT03069) also contained three types of phthalate esters; DnBP (di-n-butyl phthalate), DEHP (di(2-ethylhexyl) phthalate) also known as DOP (di-sec-octyl phthalate), and DiNP (di-iso-nonyl phthalate). DnBP and DEHP are single chemicals, while DiNP is a complex isomeric mixture of different compounds with similar structures and properties.

Phthalate esters are commonly referred to as phthalates. These chemicals are employed in a wide range of uses from inclusion in inks, dyes and cosmetics to use as a concrete additive (ATSDR 2000, Jobling *et al.* 1995). By far the largest use of phthalates, however, is as softening plasticisers in the production of non-rigid PVC (Bizarri 1996, ECPI 2003). The concentration of phthalates in some plasticised PVC products can reach up to 60% of the total mass (Moller *et al.* 1996). Phthalates are relatively persistent in the environment and, as a result of their widespread use, are some of the most abundant man-made chemicals in the environment (Jobling *et al.* 1995). Studies have recently demonstrated the presence of phthalates and their metabolites in the human body (Colon *et al.* 2000, Blount *et al.* 2000).

The phthalate DEHP (DOP) has recently been detected in river water collected from the Chao-Phraya River downstream of Samut Prakan, as well as in seawater from Samut Prakan coastal waters (Boonyatumanond *et al.* 2002).

TPC produce a range of PVC products, including softened PVC that require the use of plasticisers (TPC 2002c). TPC are known to have used many thousands of tonnes of both DiNP and DEHP (DOP) plasticisers at this facility (Setthamanit *et al.* 1985). The use of phthalates in PVC materials produced at the TPC facility is the most likely source of these chemicals in the sediment samples collected at this location.

The identified phthalates exhibit a range of toxic effects to mammals. Of particular concern is the potential of some phthalates to interfere with the developing reproductive system in males, particularly for DEHP and DnBP (Jobling *et al.* 1995, Mylchreest *et al.* 2002). The toxicity of DEHP (DOP) to the developing male reproductive system has been recognised for more than 50 years (Park *et al.* 2002). Within the European Union (EU), both DEHP and DnBP are classified as “toxic to reproduction” (EC 2003a). Furthermore, DEHP has 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).

Although the reproductive toxicity is of lower concern for DiNP, evidence of weak oestrogenicity and abnormal sexual development in exposed rats has been reported (Gray *et al.* 2000, Harris *et al.* 1997).

The sediment sample AT03069 contained additional compounds associated with the production of phthalates, particularly DEHP; Phthalic anhydride, and two esters (2-ethylhexyl acetate and 2-ethylhexyl 2-ethylhexanoate). Phthalates are manufactured from phthalic anhydride and various alcohols. The alcohol employed in the production of DEHP is 2-ethylhexyl alcohol (ATSDR 2000). Under the conditions used to produce DEHP, it is possible that the two identified esters could be formed from the 2-ethylhexyl alcohol raw material (Forestiere *et al.* 1981).

The two identified esters do have direct uses; 2-ethylhexyl acetate is employed as a solvent (BASF 2004) while 2-ethylhexyl 2-ethylhexanoate has been used in various cosmetic products (EC 1996). However, the identification of both these esters and phthalic anhydride in the one sediment sample (AT03069) strongly suggests that their source is the DEHP used at TPC; either through the use of DEHP contaminated with these compounds, or possibly from the production of DEHP at TPC. The degradation of DEHP would not produce this mixture of compounds (Lundberg *et al.* 1992).

Upon release to river systems, many organic compounds will bind to sediment particles and accumulate in the vicinity of the discharge point. The nature of the compounds found in the sediment samples indicates that the TPC facility is a likely source of these chemicals. Their absence from the TPC effluent at the time the samples were collected may be due to changeable effluent composition at different times, possibly as a result of batch process operations within the TPC facility. Furthermore, a number of smaller pipes, located approximately 100m along the side channel from the main discharge pipe, were not discharging at the time the samples were collected. At other times, these may carry effluents containing the compound identified in the sediment samples.

Benzenemethanol was also identified in this sediment sample (AT03069). This compound has a number of industrial uses, but is also a naturally occurring chemical, which may explain its presence at this location (SFC 2002).

3.2 Inorganic pollutants

In addition the organic chemicals identified, the concentrations of certain metals were also determined in the samples. The effluent sample (AT03067) did not contain elevated levels of any of the quantified metals above concentrations typically found in uncontaminated ground and surface waters (ATSDR 2000). Furthermore, the concentrations in the effluent sample were below Thai industrial effluent standards (PCD 2002).

The metals determined in this study do exist naturally in the environment, though normally at very low concentrations. For most quantified metals (arsenic, chromium, cobalt, copper, mercury, nickel and manganese), the concentrations in the sediment samples are within the typical ranges found in uncontaminated sediments (ATSDR 2000, Hamilton

1998, Salomons & Forstner 1984). For the majority of metals, the concentrations in the sediment collected below the non-discharging pipes (AT03069) were higher than in the sediment collected below the main discharge (AT03068).

The higher concentration of chromium and nickel in sediment sample AT03069 compared to AT03068 may be a result of inputs containing chromium and/or nickel at this location, though the source of such inputs is not clear.

The concentrations of lead and zinc in both sediment samples, and that of cadmium in AT03069, were elevated compared to typical background concentrations in uncontaminated sediments (ATSDR 2000, Salomons & Forstner 1984). The concentration of cadmium in the sediment collected below the non-discharging pipes (AT03069) was 1.6 mg/kg, while the concentration in the sediment collected by the main outfall (AT03068) was below the method detection limit of 1 mg/kg. Uncontaminated estuarine and river sediments typically contain less than 1 mg/kg of cadmium (Salomons & Forstner 1984). Both samples contained similar concentrations of zinc, approximately twice typical uncontaminated sediment concentrations. Sample AT03069 contained lead at 138 mg/kg, more than twice the concentration found in the sample collected by the main outfall (AT03068, 64 mg/kg). Lead concentrations in uncontaminated sediments are typically only 20-30 mg/kg (ATSDR 2000, Salomons & Forstner 1984).

It should be noted, however, that there are many sources of these heavy metals to the Chao-Phraya River, which has resulted in elevated concentrations in the rivers sediments over many years (Cheevaporn & Menasveta 2003, Menasveta & Cheevaparanapiwat 1981, McLaren *et al.* 2004). Sediments collected from the mouth of the Chao-Phraya in 1979 contained average concentrations of cadmium and lead of 1.2 and 140 mg/kg respectively (Menasveta & Cheevaparanapiwat 1981). A recent study found cadmium concentrations up to 0.95 mg/kg in sediments collected from the Sum-Rong canal, a tributary that enters the Chao-Phraya upstream of the TPC facility (McLaren *et al.* 2004). The 1979 study reported average sedimentary zinc concentrations of 71 mg/kg, less than half the concentration in the samples collected for this study. More recent data for zinc concentrations in sediments from the Chao-Phraya River are not available. It is to be expected that zinc concentrations would have increased in recent years as a result of accumulation from ongoing multiple inputs to this river system.

Although the Chao-Phraya River is general contaminated with these metals, effluent discharges from the TPC facility may contribute to the elevated sediment concentrations at this location. Thai legislation addressing the discharge of industrial effluents specifies maximum concentrations of cadmium (30 μg/l), lead (200 μg/l) and zinc (5000 μg/l) (PCD 2002). The concentrations of these metals in the one sample of effluent collected from the main discharge (AT03067) were below discharge limits. However, the higher concentrations of metals, particularly lead, in the sediment sample AT03069 compared to AT03068 suggest there may be inputs at this location. The most likely source is the pipes that exit the TPC facility immediately above the collection location of sample AT03069. While these were not discharging at the time that the samples were collected, the sediment concentrations suggest accumulation of lead and possibly cadmium as a result of effluent discharges at other times.

Compounds of cadmium, lead, and zinc are widely used as stabilisers and pigments in PVC (Matthews 1996, Summers 1997). Such use of these types of compounds at the TPC facility would explain the elevated concentrations in the sediments below their discharge pipes. In the past this TPC facility is known to have used many hundreds of tonnes of lead compounds as stabilisers (Setthamanit *et al.* 1985).

Less toxic alternatives to lead and cadmium compounds are available as PVC stabilisers (OSPAR 2002, ENDS 2004). The use of these toxic metals as PVC stabilisers is already being addressed in many places. Within the EU virtually all uses of cadmium and its compounds as pigments or stabilisers is prohibited in a wide range of products, including PVC where the cadmium content exceeds 0.01% (EEC 1991). In Sweden, the use of lead stabilisers has already been phased out (ENDS 2003) while in the rest of Europe PVC manufacturers are committed to a total phase out of lead stabilisers by 2015 (ENDS 2002).

Both lead and cadmium are highly toxic to plants, animals and humans, and they have no known biochemical or nutritional function (ATSDR 2000, IPCS 1992). Exposure to lead has been associated with a wide range of effects in both humans and animals, including effects on the nervous and cardiovascular systems, bone metabolism, kidney function, reproduction, and haemoglobin synthesis. Of particular concern is the impact on cognitive and behavioural development in children that can result from relatively low level exposure (ATSDR 2000, Goyer 1993, Pirkle 1998). Lead is also toxic to all aquatic biota and effects have been reported at very low concentrations in aquatic organisms, including reduction in growth, fertility and reproduction as well as mortality (IPCS 1989). Lead has a long residence time in the environment compared with most pollutants, and tends to accumulate in soils and sediments. As many plants and animals can accumulate lead from water and sediment, lead can remain accessible to animal and human food chains for long periods following release to the environment (ATSDR 2000, Bryan & Langston 1992, Sauve *et al.* 1997). As a result of elevated environmental concentrations, accumulation of lead in aquatic biota living in the Chao-Phraya River has been seen over many years (Menasveta & Cheevaparanapiwat 1981).

In both humans and animals, the kidney is the main target organ of cadmium toxicity. Other effects include skeletal (bone) disorders, the development of hypertension (high blood pressure) and heart disease (ATSDR 2000, Elinder & Jarup 1996, Goyer 1996, Iwata *et al.* 1993, IPCS 1992). As for lead, some aquatic organisms are very sensitive to cadmium (Bryan & Langston 1992). Cadmium is relatively mobile in aquatic environments. It is able to bioaccumulate in some aquatic and terrestrial organisms, and thus able to enter human food chains (ATSDR 2000).

4 Conclusions

The TPC facility is clearly a source of hazardous chemicals to the Chao-Phraya River. These include highly toxic and carcinogenic chemicals, some of which can readily evaporate into the atmosphere. Some of the chemicals released by TPC are persistent in the environment and able to bioaccumulate, which may lead to their entering the aquatic and possibly human food chains.

In their environmental policy, TPC state that they regularly monitor wastewater, air and soil samples in and around the factory site to prevent contamination of the environment (TPC 2002b). Furthermore, TPC are a member of the Thai Responsible Care Program (Responsible Care 2000). The guiding principles of this organisation include the operating of facilities in a manner that protects the environment, health, and the safety of their employees and the public. This study has demonstrated that monitoring programs conducted by TPC are ineffective at preventing environmental contamination. This facility is not operating to the principles of its own environmental policy nor those of the Thai Responsible Care Program.

Thai legislation that sets standards for industrial effluents only addresses organic chemicals under very general parameters. It does not specifically address many of the hazardous chemicals identified in this study, such as the toxic, carcinogenic and volatile chemical, vinyl chloride (PCD 2002). This is despite the inclusion of organochlorine compounds in the National Chemicals Management Profile for Thailand as specific chemicals creating concern (SCSIN 1998).

Stringent legislation specifically addressing the production, use and releases of these types of hazardous and toxic chemicals from industrial facilities would offer greater protection for the environment and human health. Such approaches, however, will never fully address the problem of complex waste streams containing toxic and persistent chemicals. The only real solution is to work towards the cessation of discharges, emissions and losses of such hazardous substances through the progressive substitution of chlorine-chemistry and chlorinated products with non-chlorinated, non-hazardous alternatives.

5 References

Arisu, K., Hayakawa, R., Ogino, Y., Matsunaga, K., Kaniwa, M. (1992) Tinuvin P in a spandex tape as a cause of clothing dermatitis. Contact dermatitis, 26 (5): 311-316S

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.

Blount, B.C., Silva, M.J., Caudill, S.P., Needham, L.L., Pirkle, J.L., Sampson, E.J., Lucier, G.W., Jackson, R.J. & Brock, J.W. (2000) Levels of seven urinary phthalate metabolites in a human reference population. Environmental Health Perspectives 108(10): 979-982

Boonyatumanond, R., Jaksakul, A., Boonchalermkit, S., Puncharoen P., Tabucanon M.S. (2002) Monitoring of endocrine disruptor compounds in the coastal hydrosphere of Thailand. United Nations University (UNU) International Symposium on endocrine disrupting chemicals (EDCs): 'Tracing Pollutants From Agrochemical Use: Focus on EDC Pollution' Hanoi, Vietnam. Also available at; http://landbase.hq.unu.edu/Monitoring/Countryreports/Thailand/final%20data%20report%20UNU.htm

Bruckner, J.V. (1989) Written communication (June 2). Peer review comments on the toxicological profile for 1,1-dichloroethane. In ATSDR's toxicological profiles on CD-ROM, CRC Press, Boca Raton, FL.

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

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

CEC (1986) p-dichlorobenzene. In: Organo-chlorine solvents: Health risks to workers. Publ: Commission of the European Communities, ISBN 0851860788, pp1-16

Cheevaporn, V. and Menasveta, P. (2003) Water pollution and habitat degradation in the Gulf of Thailand. Marine pollution Bulletin 47: 43-51

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

Crawford, J.C. (1999) 2(2-hydroxyphenyl)2H-benzotriazole ultraviolet stabilizers. Progress in polymer science, 24(1): 7-43

CSTEE (2001a) EC Scientific Committee on Toxicity, Ecotoxicity and the Environment, Opinion on the results of the Risk Assessment of: 1,2-Benzenedicarboxylic acid, di-C8-10-branched alkyl esters, C9-rich and di-"isononyl" phthalate – Report version (Human Health Effects): Final report, May 2001. Opinion expressed at the 27th CSTEE plenary meeting, Brussels, 30 October 2001: 7 pp. http://europa.eu.int/ comm/food/fs/sc/sct/out120_en.

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

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

EC (1996) Commission decision of 8 May 1996 establishing an inventory and a common nomenclature of ingredients employed in cosmetic products. Official Journal L 132, 01.06.1996: 1- 684 (Annex section 1); available at http://pharmacos.eudra.org/F3/inci/index.htm

EC (1999) Integrated Pollution Prevention and Control (IPPC) Draft best available techniques reference document on the chlor-alkali industry. February 1999, 160pp

EC (2003a) 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

EEC (1991) Council Directive 91/338/EEC of 18 June 1991 amending for the 10th time 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. Official Journal L 186, 12.07.1991: 59-63

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

Elinder, C.G. and Jarup, L. (1996) Cadmium exposure and health risks: recent findings. Ambio 25, 5: 370-373

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

ENDS (2004) Lead stabilisers withdrawn from PVC water pipes. ENDS Report issue 350, March 2004, p35.

Forestiere, A., Level, G., Sillion, B. (1981) Esters by catalytic dehydrogenation of primary alcohols. American Chemical Society, Chemical Abstracts 95, 95:97096h

Goyer, R.A. (1993) Lead toxicity: current concerns. Environmental Health Perspectives 100: 177-187

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

Gray, L.E., Ostby, J., Furr, J., Price, M., Veeramachaneni, D.N.R. & Parks, L. (2000) Perinatal exposure to the phthalates DEHP, BBP and DINP, but not DEP, DMP or DOTP, alters sexual differentiation of the male rat. Toxicological Sciences 58(2): 350-365

Hamilton, E.I. (1998) The geobiochemistry of cobalt. The Science of the Total Environment 150: 7-39

Harris C.A., Henttu, P., Parker, M.G. & Sumpter, J.P. (1997) The estrogenic activity of phthalate esters in vitro. Environmental Health Perspectives 105 (8): 802-811

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 (2000) International Agency for Research on Cancer (IARC) Monographs on the Evaluation of Carcinogenic Risks to Humans. Some Industrial Chemicals, Vol. 77, 564pp. ISBN 9283212770

IPCS (1992) Cadmium; Environmental aspects. International Programme on Chemical Safety Environmental Health Criteria 135. Publ: World Health Organisation, ISBN 9241571357, 156pp.

IPCS (1989) Lead; Environmental aspects. International Programme on Chemical Safety Environmental Health Criteria 85. Publ: World Health Organisation, ISBN 9241542853, 106pp

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.

Iwata, K., Saito, H., Moriyama, M. and Nakano, A. (1993) Renal tubular function after reduction of environmental cadmium exposure: a ten year follow-up. Archives of Environmental Health 48, 3: 157-163

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

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

Lundberg, P., Högberg, J., Garberg, P., Lundberg, I., Dobson, S. & Howe, P. (1992) Diethylhexyl phthalate. Environmental Health Criteria 131. Publ: WHO, 141pp

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

McLaren, R.G.,Kanjanapa, K.,Navasumrit, P., Gooneratne, S.R., Ruchirawat M. (2004) Cadmium in the water and sediments of the Chao-Phraya River and associated waterways, Bangkok, Thailand. Water, Air, and soil Pollution 154:385-398

Menasveta. P., Cheevaparanapiwat, V. (1981) Heavy metals, organochlorine pesticides and PCBs in green mussels, mullets and sediments of river mouths in Thailand. Marine Pollution Bulletin 12(1): 19-25

Mochida, K., Gomyoda, M., Fujita, T. (1995) Toxicity of 1,1-dichloroethane and 1,2-dichloroethylene determined using cultured human KB cells. Bulletin of Environmental Contamination and Toxicology, 55: 316-319

Moller S., Larsen, J., Jeines, J.E., Faergemann, H., Ottoson L.M. & Knudsen F.E. (1996) Environmental Aspects of PVC - second edition. Environmental Project no. 313, Danish Environmental Protection Agency, Copenhagen, Denmark, 110pp

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

Nagai F., Ushiyama K. & Kano I (1993) DNA cleavage by metabolites of butylated hydroxytoluene. Archives of Toxicology, 67(8), 552-557

Niklasson, B., Bjorkner, B. (1989) Contact allergy to the UV-absorber Tinuvin-P in plastics. Contact dermatitis, 21 (5): 330-333

Öman, C & Hynning, P.-Å. (1993) Identification of organic compounds in municipal landfill leachates. Environmental Pollution 80: 265-271

OSPAR (2002) OSPAR Background Document on Cadmium, OSPAR Commision. ISBN 6956 93 6. Available at www.ospar.org/eng/html/publications

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

PCD (2002) Industrial Effluent Standards, Pollution Control Department, Ministry of Natural Resources and Environment. www.pcd.go.th/Information/Regulations/WaterQuality/Effluents.htm

Pirkle, J.L., Kaufman, R.B., Brody, D.J., Hickman, T., Gunter, E.W. and Paschal, D.C. (1998). Exposure of the U.S. population to lead, 1991-1994. Environmental Health Perspectives 106, 11: 745-750

Qasim, S.R. & Chiang, W. (1994) Sanitary Landfill Leachates. Publ: Technomic, Lancaster, USA pp.129-149

Responsible Care (2000) Responsible Care in Thailand, available at; http://members.fortunecity.com/unclesun/responsiblecareinthailand/

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

SCSIN (1998) National chemicals management profile for Thailand. Subcommittee on chemical safety information network, Thailand national chemical safety committee. ISBN: 974-8071-67-7

Setthamanit, S., Thammikarak, S., Sucharitthanont, S., Khoathien, S., Limpaseni, W., Phanpeng, T., Rattanakomut, S., Peinlamlert, P. & Rotarayanan, S. (1985) Environmental impact assessment report of plastic industry for Thai Plastic and Chemicals Co. Ltd., Environmental Research Institute of Chulalongkorn University, Thailand

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

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., 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

Sauve, S., McBride, M.B. & Hendershot, W.H. (1997) Speciation of lead in contaminated soils. Environmental Pollution 98(2): 149-155

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

Taffe, B.G., Zweier, J.L., Pannell, L.K. & Kensler, T.W. (1989) Generation of reactive intermediates from the tumour promoter butylated hydroxytoluene hydroperoxide in isolated murine keratinocytes or by hematin. Carcinogenesis, 10(7), 1261-1268

TPC (2002a) Thai Plastic & Chemicals (TPC); www.thaiplastic.co.th/tpc/main.html

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

TPC (2002c) Thai Plastic & Chemicals (TPC); www.thaiplastic.co.th/tpc/product/html/our_product.html

USEPA (1999) U.S. Environmental Protection Agency (EPA) Integrated Risk Information System (IRIS) on 1,1-dichloroethane. National Centre for Environmental Assessment, Office of Research and Development, Washington, DC. Available at; www.epa.gov/iris/subst/0409.htm

USFDA (2004) Food contact substance notification program's cumulative estimated daily intake/acceptable daily intake database. US Food and Drug administration, Office of Food Additive Safety. Available at; http://vm.cfsan.fda.gov/~dms/opa-tedi.html

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 (1999) Safety evaluation of certain food additives, food additives series 42**;** Evaluation of national intake assessments of butylated hydroxytoluene (BHT). International Programme on Chemical Safety, World Health Organization (WHO), Geneva, 1999

Williams G.M. & Weisburger J.H. (1986) Chemical carcinogens. In Toxicology: the basic science of poisons. Klaasen C.D., Ambur M.O. & Doull J. [Eds], MacMillan Publishing Co., New York: pp. 99-173

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

A1.1.2.1 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.

A1.2 Heavy Metal Analysis

A1.2.1 Preparation of samples for heavy metal analysis

All chemicals were of High Purity Aristar Grade. All glassware was cleaned in detergent, rinsed with tap water and deionised water, soaked in 10% nitric acid overnight, rinsed with deionised water and dried in an oven at 105°C.

A1.2.1.1 Solid Samples

Samples were air dried until weighing readings became constant (approx. 5 days). They were then crushed using a pestle and mortar until homogenous and sieved through a 2-mm mesh. 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 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. The certified reference material GBW8301 (River Sediment, certified by the State Bureau of Metrology of The People's Republic of China) and a blank sample were separately prepared in an identical manner with the batch of samples.

A1.2.1.2 Aqueous sample

On arrival, 100ml of the sample was transferred to a clean glass bottle and acidified with nitric acid (10% v/v). 50 ml of this solution was subsequently transferred to a 100ml boiling tube, placed onto the Gerhardt Kjeldatherm digestion block, and refluxed at 130°C for four hours. After cooling to ambient temperature, the 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 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 quality control solutions (80 µg/l mercury) and a blank sample were separately prepared in an identical manner.

A1.2.2 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.

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 µg/l and 100 µg/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 µg/l), prepared internally from different reagent stock. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Appendix 2; Compounds reliably identified and groups of compounds tentatively identified in all samples

Sample Number: AT03067	**Sample Number: AT03068**	**Sample Number: 03069**
Number of compounds isolated: 77	**Number of compounds isolated: 33**	**Number of compounds isolated: 104**
COMPOUNDS RELIABLY IDENTIFIED: 2,6-Di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (BHT-quinol) Chloroform * Decane, 3,6-dimethyl- Docosane Eicosane Eicosane, 2-methyl- Ethane, 1,1-dichloro- * Ethane, 1,2-dichloro- * Heptadecane, 3-methyl- Hexacosane Hexadecane Octadecane Pentadecane Tetradecane Vinyl chloride * **GROUPS OF COMPOUNDS TENTATIVELY IDENTIFIED:** Branched aliphatic hydrocarbons Branched aliphatic alcohols Alkyloxy benzene derivatives	**COMPOUNDS RELIABLY IDENTIFIED:** 1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP) 1,2-Benzenedicarboxylic acid, diisononyl esters (DiNP) 1,2-Benzenedicarboxylic acid, di-n-butyl ester (DnBP) **GROUPS OF COMPOUNDS TENTATIVELY IDENTIFIED:** None	**COMPOUNDS RELIABLY IDENTIFIED:** 1,2-Benzenedicarboxylic acid, diisononyl esters (DiNP) 1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP) 1,2-Benzenedicarboxylic acid, di-n-butyl ester (DnBP) 2-Ethylhexyl 2-ethylhexanoate 2-Ethylhexyl acetate Benzene, 1,4-dichloro- * Benzenemethanol Decane Docosane Eicosane Hexadecane Octadecane 2,6-Di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (BHT-quinol) Phenol, 2,6-bis-tert-butyl-4-methyl (Butylated hydroxytoluene, BHT) Phenol, 2-(2H-benzotriazol-2-yl)-4-methyl- Phthalic anhydride Tetradecane Undecane **GROUPS OF COMPOUNDS TENTATIVELY IDENTIFIED:** Linear aliphatic hydrocarbons Branched aliphatic hydrocarbons Branched aliphatic alcohols Oxygenated hydrocarbons

** - Compounds identified only at trace levels using selective ion monitoring (SIM) method*

Appendix 3; Volatile organic compounds identified and quantified in TPC effluent

Name of compound	**Concentration μg/l**
Methane, chloro-	ND
Methane, dichloro-	ND
Methane, trichloro- (chloroform)	<1
Methane, tetrachloro-	ND
Ethane, chloro-	ND
Ethane, 1,1-dichloro-	<5
Ethane, 1,2-dichloro-	<10
Ethane, 1,1,1-trichloro-	ND
Ethane, 1,1,2-trichloro-	ND
Ethane, 1,1,1,2-tetrachloro-	ND
Ethane, 1,1,2,2-tetrachloro-	ND
Ethane, pentachloro-	ND
Ethane, hexachloro-	ND
Ethene, chloro- (vinyl chloride)	338
Ethene, 1,1-dichloro-	ND
Ethene, 1,2-dichloro-, *cis*-	ND
Ethene, 1,2-dichloro-, *trans*-	ND
Ethene, trichloro-	ND
Ethene, tetrachloro-	ND
Propane, 1,2-dichloro-	ND
Propane, 1,3-dichloro-	ND
Propane, 2,2-dichloro-	ND
Propane, 1,2,3-trichloro-	ND
1-Propene, 1,1-dichloro-	ND
1-Propene, 1,3-dichloro-, *cis*-	ND
1-Propene, 1,3-dichloro-, *trans*-	ND
Hexachlorobutadiene	ND

ND indicates not detected, <# indicates compound detected, but at a concentration below the quantifiable level.

Appendix 4; Additional information for key organic compounds

A4.1 Vinyl chloride

Vinyl chloride, also known as chloroethene and vinyl chloride monomer (VCM), is a colourless, sweet smelling flammable gas.

Production and uses

VCM can be produced by the hydrochlorination of ethyne (acetylene), though over 90% of world production is currently carried out by the thermal cracking of 1,2-dichloroethane (EDC) (Cowfer & Gorensek 1997). Polymerisation to PVC can then carried out using either the suspension, emulsion or mass process.

Vinyl chloride manufacture accounts for 36% of global chlorine consumption (Chemical Week 1998). By far the major use of vinyl chloride is in the production of PVC; approximately 95% of the VCM produced globally has an end use in polymer or copolymer applications, of which by far the largest is for PVC production (ATSDR 2000). Non-polymeric uses include the manufacture of vinylidene chloride, trichloroethene, tetrachloroethene and other industrial compounds. Total world capacity of VCM in 1996 was approximately 25 500 kt per year, of which about 54% was concentrated in the United States and Western Europe (Cowfer & Gorensek 1997).

Environmental distribution

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

Hazards

Vinyl chloride is an extremely hazardous chemical. It can cause a wide variety of toxic effects in both humans and animals, and can be explosive when mixed with air. It has been known for over 20 years that this chemical can cause cancer in humans, and it was first classified by the US government as known to be a human carcinogen in 1980 (DHHS 2002). The cancer most strongly associated with vinyl chloride is angiosarcoma of the liver in the occupationally exposed and, although the evidence is less strong, other studies have shown elevated levels of cancers of the brain and nervous system, lung and respiratory tract and the lymphatic/haemapoietic system (IARC 1987). There are further indications of cancers in other organs, though these are less well supported (ATSDR 2000). Retrospective analysis of the histories of individuals with angiosarcomas at different sites suggest that exposure to vinyl chloride, PVC and other polymeric materials may have been a factor (Rhomberg 1998).

The most common route of exposure to vinyl chloride is through inhalation. There is evidence that vinyl chloride can cause emphysema, dyspnea, pulmonary lesions and a number of other lung problems (ATSDR 2000). Exposure to high levels of vinyl chloride can cause Raynaud's phenomenon, a condition where the blood circulation in workers' fingers is damaged causing them to become white and painful in cold conditions. This illness is sometimes followed by resorption of the bones in the tips of the fingers or lesions on bones in other parts of the body (ATSDR 2000). Workers exposed to vinyl chloride have also been reported to die more frequently from cardiovascular and cerebrovascular disease (e.g. heart attacks and strokes). Furthermore, vinyl chloride can also reduce the blood's ability to clot normally (ATSDR 2000).

Vinyl chloride is narcotic and inhalation can cause dizziness, headaches, drowsiness or unconsciousness, euphoria, memory loss, visual and/or hearing disturbances, sleep disturbance, nausea, irritability and nervousness. Damage to the nervous system manifests itself in peripheral neuropathy with tingling, pain or numbness in the fingers (ATSDR 2000). Toxic effects are also seen on the immune systems, livers, spleens, thyroid function, eyes and skin of workers. Anorexia (weight loss) has been reported and there are some indications that vinyl chloride can affect the reproductive systems of both men and women (ATSDR 2000).

Existing controls

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

The high toxicity of vinyl chloride has lead to it being banned for domestic use in both the US and the European Union (EU). The US ban dates from 1974 (DHHS 2002). Within the EU, directive 76/769/EEC controls the sales and use of dangerous substances. When this directive came into force in 1976 it banned the use of vinyl chloride as an aerosol propellant on the basis of its hazards to human health (EEC 1976). Vinyl chloride was one of the first three substances controlled under this legislation, a measure of the hazard it represents.

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

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

References

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

Chemical Week (1998) Polyvinyl chloride. Chemical Week 160(42): 36

Cowfer, J.A. & Gorensek, M.B. (1997) Vinyl chloride. In: Kroschwitz, J.I. & Howe-Grant, M. (Eds). The Kirk-Othmer Encyclopedia of Chemical Technology, Fourth Edition. Publ. Wiley-Interscience, N.Y. Volume 24, pp 851-882

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

EC (1999) Proposal for a Council Decision concerning the approval, on behalf of the Community, of OSPAR Decision 98/4 on emission and discharge limit values for the manufacture of vinyl chloride monomer and of OSPAR Decision 98/5 on emission and discharge limit values for the vinyl chloride sector (1999/C 158/04) COM(1999) 190 final – 99/0098 (CNS). OJ C 158, 4.6.1999: 19-32

EEC (1976) Council Directive 76/769/EEC of 27 July 1976 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. OJ L 262, 27.9.76: 201-203

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 0-87371-358-3, 725pp

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

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

Rhomberg, W. (1998) Exposure to polymeric materials in vascular soft-tissue sarcomas. International Archives of Occupational and Environmental Health 71: 343-347

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

A4.2 Phthalate esters (phthalates)

Phthalates are non-halogenated ester derivatives of phthalic acid which are widely used in a range of industrial and consumer applications. Some are marketed as discreet chemical products (e.g. the well-known di(ethylhexyl) phthalate or DEHP; also known as di-sec-octyl phthalate or DOP), while others are complex isomeric mixtures comprising many individual compounds with similar chemical structures (e.g. di-iso-nonyl phthalate, DiNP, and di-iso-decyl phthalate, DiDP). As a result of their high volume uses in open applications, they are now among the most ubiquitous man-made chemicals found in the environment.

Production and uses

Phthalates have a range of applications, dependent on the precise chemical form, although by far their greatest use is as plasticising (softening) additives in flexible plastics, especially PVC. They are produced in very large quantities in Europe, almost 1 million tonnes per year, primarily for use within the EU. For example, estimated production volumes in the mid-1990s were 595 000 tonnes DEHP and around 185 000 tonnes DiNP and around 200 000 tonnes for DiDP (CSTEE 2001a, b, 2002).

Of these three main phthalates, over 90% of use is in PVC applications, including toys, flooring and other building/furnishing materials, car interiors, cables and medical equipment (see e.g. http://www.ecpi.org/plasticisers/index.html). Minor applications include use as components of inks, adhesives, paints, sealants and surface coatings. Other phthalates, including di-n-butyl phthalate (DnBP) and di(ethyl) phthalate (DEP), have also been used as PVC additives, but are also used as solvents and fixatives in perfumes and as ingredients in other cosmetics (Koo *et al.* 2002).

Environmental distribution

All uses of phthalates, especially the major use as PVC plasticisers, result in losses to the environment (both indoors and outdoors) during both the production and use of products, and again following disposal (amounting to thousands of tonnes per year across the EU, CSTEE 2001a). As a consequence, phthalates have long been recognised as one of the most abundant and widespread man-made environmental contaminants (Mayer *et al.* 1972) and our exposure to phthalates is therefore widespread and continuous.

Although some degradation is possible, phthalates are considered to be relatively persistent, especially in soils and sediments. They also have the inherent ability to accumulate in biological tissues, although continuous exposure undoubtedly also contributes to tissue levels. Risk assessments conducted under the EU system have documented the widespread distribution of phthalates in all environmental compartments (e.g. see CSTEE 2001c, d). A number of recent studies have reported the presence of phthalates and their primary metabolites in the human body (Colon *et al.* 2000, Blount *et al.* 2000).

Because of their extensive use in building materials and household products, phthalates are common contaminants in indoor air (Otake *et al.* 2001, Wilson *et al.* 2001). They have also been reported as substantial components of house dust, in some cases at more than 1 part per thousand (1g/kg) of the total mass of dust (Butte and Heinzow 2002).

Hazards

As noted above, phthalates are relatively persistent in the environment and can bioaccumulate. Substantial concerns also exist with regard to their toxicity to wildlife and to humans, although the precise mechanisms and levels of toxicity vary from one compound to another. In many cases, it is the metabolites of the phthalates which are responsible for the greatest toxicity (e.g. Dalgaard *et al.* 2001).

EU risk assessments for DEHP (DOP), DiNP and DiDP concluded that there were no significant risks to aquatic or terrestrial organisms. However, the EU's Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE 2001c, d) has disagreed with this conclusion for the terrestrial environment, noting that there is very little evidence to justify such a conclusion. The CSTEE has also highlighted concerns relating to secondary poisoning, i.e. the build up of phthalates through the food chain.

With respect to humans, although substantial exposure can occur through contaminated food, direct exposure to phthalates from consumer products and/or medical devices is likely to be very significant. Perhaps the best known example is the exposure of children to phthalates used in soft PVC teething toys (see e.g. Stringer *et al.* 2000), now subject to emergency controls within Europe (see below).

DEHP (DOP), still the most widely used phthalate, is a known reproductive toxin, interfering with testes development in mammals, and is classified in the EU as "toxic to reproduction". Indeed, its toxicity to the developing male reproductive system has been recognised for more than 50 years (Park *et al.* 2002). Observed toxicity is due mainly to the compound MEHP, formed in the body as a metabolite of DEHP, and appears to impact on many aspects of development and liver function, including hormone metabolism and immune function (Dalgaard *et al.* 2001, Wong and Gill 2002). Other recent studies have reaffirmed the reproductive toxicity of several other commonly used phthalates, including butylbenzyl phthalate (BBP) and di-n-butyl phthalate (DnBP) (Ema and Miyawaki 2002, Mylchreest *et al.* 2002). As for DEHP, DnBP is classified in the EU as "toxic to reproduction".

Reproductive toxicity is generally thought to be of lower concern for the other widely used phthalates DiNP and DiDP, although Gray *et al.* (2000) did report evidence for abnormal sexual development in rats exposed to DiNP. Prior to this, Harris *et al.* (1997) reported the weak oestrogenicity of several phthalates, including DiNP. Other concerns for DiNP and DiDP relate primarily to toxic effects on the liver and kidney.

In the indoor environment, correlations have been reported between incidence of bronchial obstruction (asthma) in children and the abundance of phthalate-containing materials in the home (Oie et al 1997).

Existing controls

At present, there are few controls on the marketing and use of phthalates, despite their toxicity, the volumes used and their propensity to leach out of products throughout their lifetime. Of the controls which do exist, probably the best known is the EU-wide emergency ban on the use of six phthalates in children's toys designed to be chewed (first agreed in 1999 and recently renewed for the 13th time, EC 2003). While this ban addressed one important exposure route, exposures through other toys and, indeed, other consumer products, as well as though PVC medical devices, remain unaddressed.

In 1998, the Ministerial Meeting of OSPAR agreed on the target of cessation of discharges, emissions and losses of all hazardous substances to the marine environment of the Northe-East Atlantic by 2020 (the "one generation" cessation target) and included the phthalates DnBP and DEHP (DOP) on the first list of chemicals for priority action towards this target (OSPAR 1998). DEHP (DOP) is also proposed as a "priority hazardous substance" under the European Union Water Framework Directive (EC 2001), such that action to prevent releases to water within 20 years will be required throughout Europe, though a decision on this classification remains under consideration.

References

Blount, B.C., Silva, M.J., Caudill, S.P., Needham, L.L., Pirkle, J.L., Sampson, E.J., Lucier, G.W., Jackson, R.J. & Brock, J.W. (2000) Levels of seven urinary phthalate metabolites in a human reference population. Environmental Health Perspectives 108(10): 979-982

Butte, W. & Heinzow, B. (2002) Pollutants in house dust as indicators of indoor contamination. Reviews in Environmental Contamination and Toxicology 175: 1-46.

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

CSTEE (2001a) EC Scientific Committee on Toxicity, Ecotoxicity and the Environment, Opinion on the results of the Risk Assessment of: 1,2-Benzenedicarboxylic acid, di-C8-10-branched alkyl esters, C9-rich and di-"isononyl" phthalate - Report version (Human Health Effects): Final report, May 2001. Opinion expressed at the 27th CSTEE plenary meeting, Brussels, 30 October 2001: 7 pp. http://europa.eu.int/comm/food/fs/sc/sct/out120_en.pdf

CSTEE (2001b) Scientific Committee on Toxicity, Ecotoxicity and the Environment (European Commission), Opinion on the results of the Risk Assessment of: 1,2-Benzenedicarboxylic acid di-C9-11-branched alkyl esters, C10-rich and di-"isodecyl"phthalate - Report version (Human health effects): Final report, May 2001. Opinion expressed at the 24th CSTEE plenary meeting, Brussels, 12 June 2001, http://europa.eu.int/comm/food/fs/sc/sct/out103_en.html

CSTEE (2001c) EC Scientific Committee on Toxicity, Ecotoxicity and the Environment, Opinion on the results of the Risk Assessment of: 1,2-Benzenedicarboxylic acid, di-C8-10-branched alkyl esters, C9-rich and di-"isononyl" phthalate - Report version (Environment): Final report, May 2001. Opinion expressed at the 27th CSTEE plenary meeting, Brussels, 30 October 2001: 5 pp. http://europa.eu.int/comm/food/fs/sc/sct/out122_en.pdf

CSTEE (2001d) Scientific Committee on Toxicity, Ecotoxicity and the Environment (European Commission), Opinion on the results of the Risk Assessment of: 1,2-Benzenedicarboxylic acid di-C9-11-branched alkyl esters, C10-rich and di-"isodecyl"phthalate - Report version (Environment): Final report, May 2001. Opinion expressed at the 24th CSTEE plenary meeting, Brussels, 12 June 2001, 5 pp. http://europa.eu.int/comm/food/fs/sc/sct/out121_en.pdf

CSTEE (2002) EC Scientific Committee on Toxicity, Ecotoxicity and the Environment, Opinion on the results of the Risk Assessment of Bis (2-ethylhexyl) phthalate (DEHP). Report version: Human Health, September 2001. Opinion expressed at the 29th CSTEE plenary meeting, Brussels, 09 January 2002: 8 pp. http://europa.eu.int/comm/food/fs/sc/sct/out141_en.pdf

Dalgaard, M., Nellemann, C., Lam, H.R., Sorensen, I.K. & Ladefoged, O. (2001) The acute effects of mono(2-ethylhexyl)phthalate (MEHP) on testes of prepubertal Wistar rats. Toxicology Letters 122: 69-79

EC (2001) Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC, Official Journal L 249 , 17/09/2002: 27-30

EC (2003) Commission Decision 2003/113/EC amending Decision 1999/815/EC concerning measures prohibiting the placing on the market of toys and childcare articles intended to be placed in the mouth by children under three years of age made of soft PVC containing certain phthalates. Official Journal L 46, 20.2.2003: 27-28

Ema, M. & Miyawaki, E. (2002) Effects on development of the reproductive system in male offspring of rats given butyl benzyl phthalate during late pregnancy. Reproductive Toxicology 16: 71-76

Gray, L.E., Ostby, J., Furr, J., Price, M., Veeramachaneni, D.N.R. & Parks, L. (2000) Perinatal exposure to the phthalates DEHP, BBP and DINP, but not DEP, DMP or DOTP, alters sexual differentiation of the male rat. Toxicological Sciences 58(2): 350-365

Harris C.A., Henttu, P., Parker, M.G. & Sumpter, J.P. (1997) The estrogenic activity of phthalate esters in vitro Environmental Health Perspectives 105 (8): 802-811

Koo J-W, Parham F, Kohn MC, Masten SA, Brock JW, Needham LL, *et al.* 2002. The association between biomarker-based exposure estimates for phthalates and demographic factors in a human reference population. Environmental Health Perspectives 110:405-410

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

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

Oie, L., Hersoug, L.G. & Madsen, J.O. (1997) Residential exposure to plasticizers and its possible role in the pathogenesis of asthma. Environmental Health Perspectives 105 (9): 972-978

OSPAR (1998) OSPAR Strategy with Regard to Hazardous Substances, OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, OSPAR 98/14/1 Annex 34

Otake, T., Yoshinaga, J. & Yanagisawa, Y. (2001) Analysis of organic esters of plasticizer in indoor air by GC-MS and GC-FPD. Environmental Science and Technology 35(15): 3099-3102

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

Stringer, R., Labunska, I, Santillo, D., Johnston, P., Siddorn, J. & Stephenson, A. (2000) Concentrations of phthalate esters and identification of other additives in PVC children's toys. Environmental Science and Pollution Research 7(1): 27-36

Wilson, N.K., Chuang, J.C. & Lyu, C. (2001) Levelsof persistent organic pollutants in several child day care centres. Journal of Exposure Analysis and Environmental Epidemiology 11(6): 449-458

Wong, J.S. & Gill, S.S. (2002) Gene expression changes induced in mouse liver by di(2-ethylhexyl) phthalate. Toxicology and Applied Pharmacology 185(3): 180-196