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Hazardous Chemical Pollution of the Pearl River

Investigation of chemicals discharged with wastewaters from five industrial facilities in China, 2009

Technical Note 08/2009

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OCTOBER 2009

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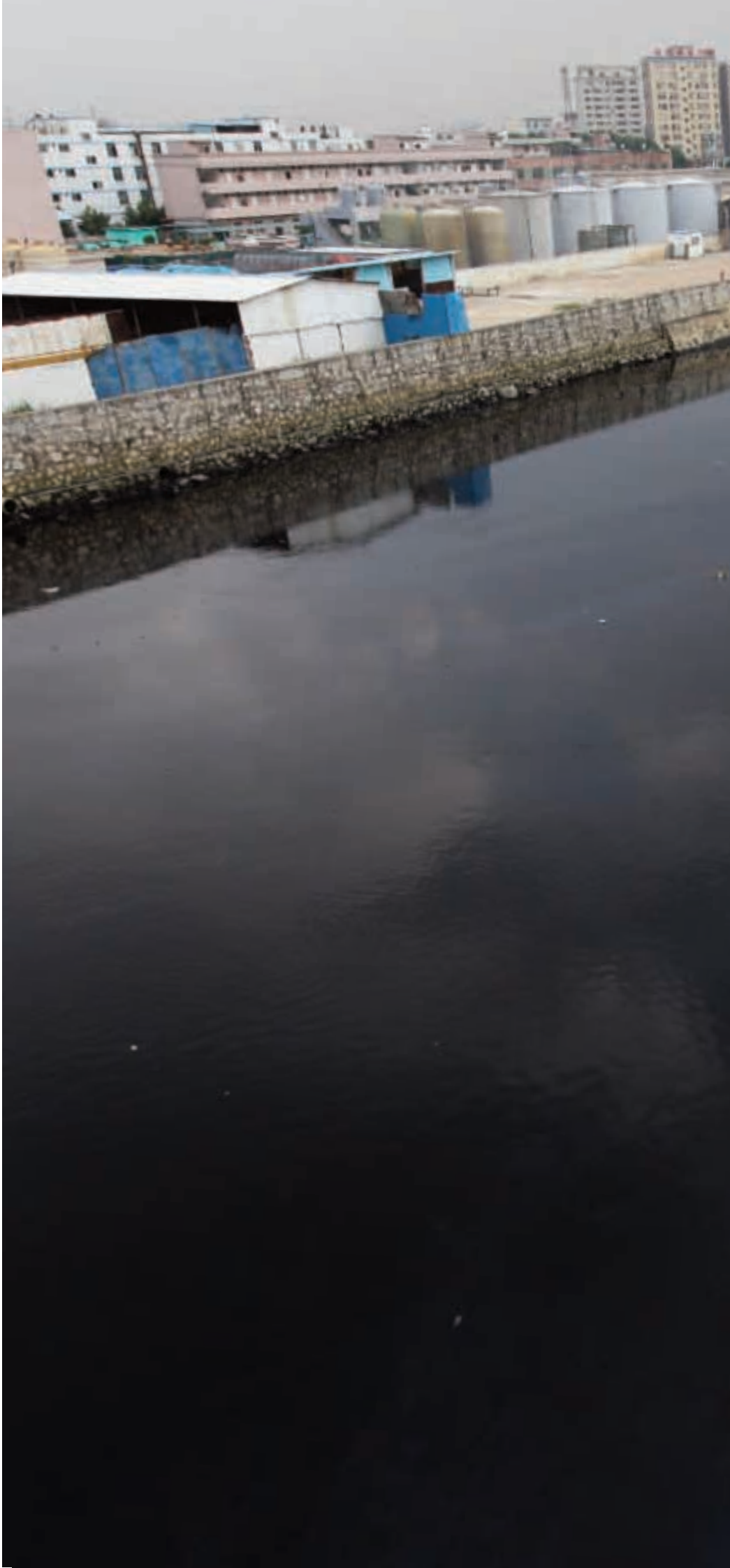
image A tributary flowing through the city of Shenzhen, higly contaminated by industral discharge along the river shows no sign of life.



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Executive Summary

The Pearl River, China's third longest river, flows into the South China Sea via a large and complex delta. This area, known as the Pearl River Delta (PRD), has undergone rapid urbanisation over recent years and emerged as one of the world's most dynamic industrial zones, accounting for more than 10% of China's total Gross Domestic Product (GDP). This rapid growth has contributed to increasing environmental degradation within the PRD and impacts on communities within the area, in part due to the release of hazardous chemicals from industrial sources.

Governmental monitoring and control measures that address industrial chemicals within China, including those released to the Pearl River system, have tended to focus on general measurements of chemical load alongside only a very limited number of individual chemicals. Numerous studies have demonstrated contamination of the Pearl River basin with a range of hazardous chemicals, including heavy metals and persistent organic pollutants. To date, however, such studies have tended to highlight the presence of industrial pollutants within the waterways of the Pearl River basin, rather than attempting to characterise industrial point sources of pollutants themselves. Furthermore, studies that have investigated persistent organic pollutants have tended to focus on a relatively limited range of widely recognised substances.

These facilities clearly represent only a small fraction of the total industrial activity and, therefore, wastewater inputs arising within the various industrial zones of the Pearl River system, but nonetheless illustrate the nature of what is likely to be a much wider problem.

This study was undertaken to provide data on the direct discharge of hazardous chemicals from a selection of industrial point sources to the Pearl River System, including the identification of diverse classes of chemicals in discharged wastewaters. Five separate facilities were investigated, two situated within industrial areas and three being individual factories. These industrial areas and facilities and the type of manufacturing activities undertaken at each are summarised below. Their locations within Guangdong Province, and with respect to the Pearl River Delta area, are shown in Figure 1 of the main report.

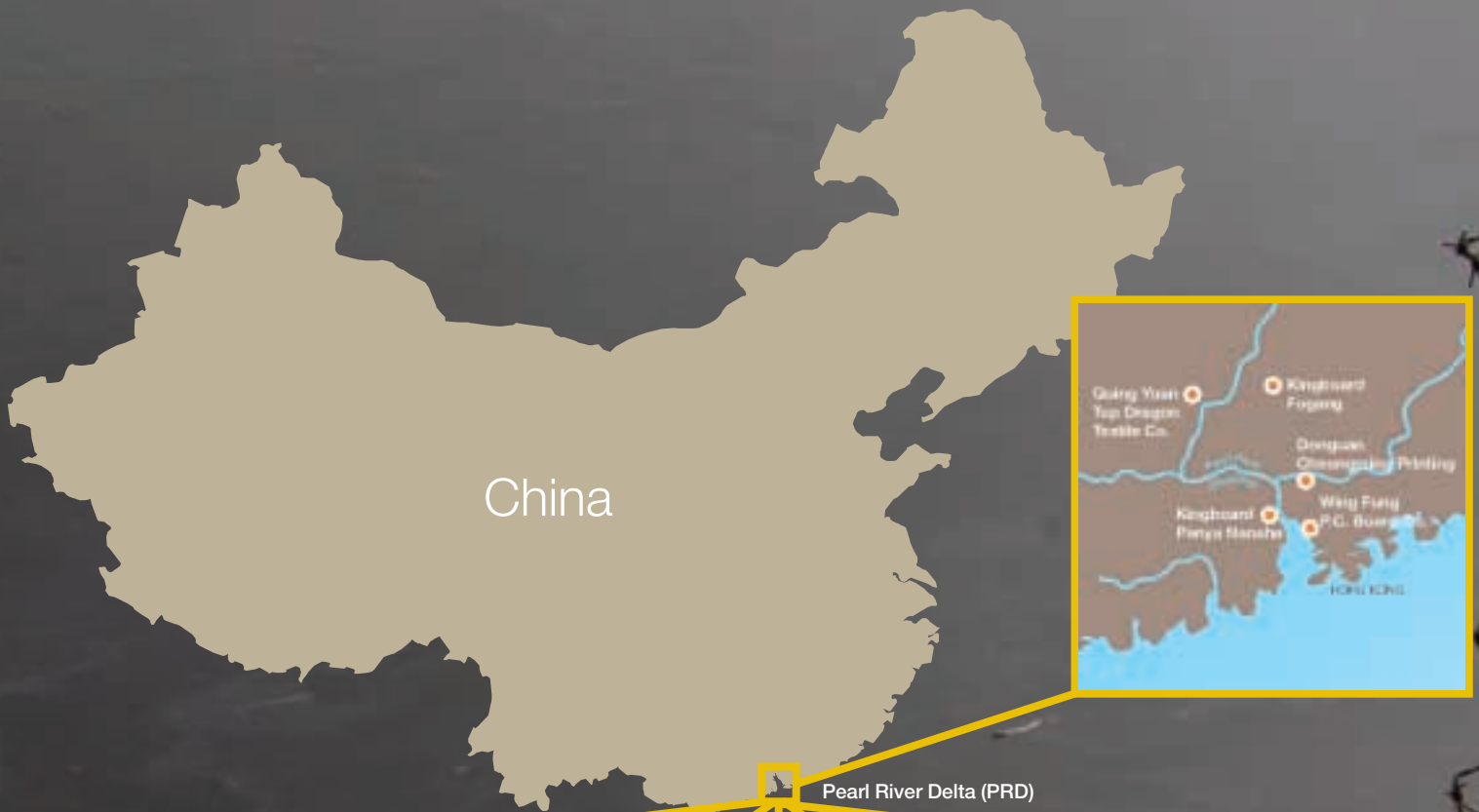
- **Kingboard (Fogang) Industrial Area:**- printed circuit board manufacture*
- **Kingboard (Panyu Nansha) Industrial Area**:- printed circuit board manufacture*
- **Wing Fung P.C. Board Co., Ltd.**:- printed circuit board manufacture*
- **QingYuan Top Dragon Textile Co., Ltd.**:- textiles manufacture
- **Dongguan Cheongming Printing Co. Ltd.**:- printing

A total of 25 samples were collected in June 2009, including wastewater samples from all identifiable and accessible discharge points emanating from these sites, as well as sediment samples from discharge channels and receiving water bodies. All samples were returned to the Greenpeace Research Laboratories (University of Exeter, UK) for analysis, including quantitative analysis for metals and for a range of volatile organic compounds (VOCs), and qualitative analysis of other, semi-volatile (solvent-extractable) organic compounds.

This study has demonstrated that, taken together, wastewater discharges from the five individual facilities are acting as significant point sources of heavy metals and potentially hazardous organic substances to the receiving freshwater environment of the Pearl River basin. These facilities clearly represent only a small fraction of the total industrial activity and, therefore, wastewater inputs arising within the various industrial zones of the Pearl River system, but nonetheless illustrate the nature of what is likely to be a much wider problem.

As might be expected, some similarities were found in the nature and extent of chemical discharges from the three printed circuit board manufacturing facilities. However, certain similarities were also found between discharges from these three facilities and those from the two other facilities involved in seemingly unrelated activities (textiles and printed products), most noticeably in the release of certain metals as well as organic chemicals commonly associated with the use of photoinitiator based processes.

* Through field investigation, interviews and desktop research, Greenpeace identified a cluster of Kingboard's industrial facilities in this area. For more detailed information, please refer to Section 2 and the Appendix.



Kingboard (Fogang) Industrial Area

Printed circuit board manufacturer

Kingboard (Panyu Nansha) Industrial Area

Printed circuit board manufacturer

Wing Fung P.C. Board Co., Ltd.

Printed circuit board manufacturer

QingYuan Top Dragon Textile Co., Ltd.

Textiles manufacturer

Dongguan Cheongming Printing Co. Ltd.

Printers

Key findings from this study can be summarised as follows:-

Metals:

Many of the wastewater discharges contained various toxic or potentially toxic heavy metals at high concentrations. At three sites, the levels of individual metals in wastewater samples exceeded maximum allowable discharge concentrations set under the Guangdong effluent standard (even noting that, for some metals, this standard sets different limits depending on how the receiving water body is used). These were:-

- Kingboard (Fogang) Industrial Area (CN09005); concentrations of beryllium (123 µg/l) and manganese (17100 µg/l) were 25 times and 3 times the respective upper allowable levels respectively, and the concentration of zinc (3240 µg/l) exceeded the lower and middle allowable levels.
- Wing Fung P.C. Board Co. Ltd. (CN09028); the concentration of copper (25600 µg/l) exceeded the lower limit by 50 times and the upper limit by 12 times.
- QingYuan Top Dragon Textile Co. Ltd. (CN09008); the concentration of manganese (5390 µg/l) exceeded the upper limit of 5000 µg/l.

The results also provide many other examples of wastewaters containing high concentrations of toxic metals, which although below regulatory limits still indicate that these effluent discharges are acting as significant point sources of pollution to the river system.

pH:

Wastewaters from two sites were highly acidic, far outside the permissible pH range (6-9) for discharges under the Guangdong effluent standard:-

- Kingboard (Fogang) Industrial Area (CN09005); pH=1
- Dongguan Cheongming Printing Co. Ltd (CN09021); pH=2

Organic chemicals:

Numerous organic chemicals, representing many different chemical classes, were identified in various wastewaters from the five sites, many with known hazardous properties. Foremost amongst these (and the sites at which one or more example of each class was identified) were the following hazardous chemicals:-

- brominated compounds, including the brominated flame retardant tetrabromobisphenol-A (TBBPA): Kingboard Fogang & Kingboard Panyu Nasha Industrial Areas
- alkyl phenols (octyl phenol and nonyl phenol): Kingboard Fogang Industrial Area & QingYuan Top Dragon Textile Co. Ltd.
- phthalate esters (DEHP, DnBP & DiBP): Kingboard Panyu Nansha Industrial Area, Wing Fung P.C. Board Co. Ltd. & Dongguan Cheongming Printing Co. Ltd.
- bisphenol-A: Kingboard Panyu Nansha Industrial Area
- dichloromethane: Dongguan Cheongming Printing Co. Ltd.

Other than for two phthalate esters (DEHP and DnBP), the discharge of wastewaters containing these hazardous substances are not specifically regulated under the Guangdong effluent standard. However, most are specifically listed as priority substances in one or more regulations or conventions that address their use and release in certain regions outside of China, as a result of concerns about environmental and/or human health impacts associated with them. The one exception, bisphenol-A, is widely recognised as a hazardous pollutant, particularly for the aquatic environment and is being subjected to increasing scrutiny and control in certain countries.

Many of the metals present in the various discharged wastewaters can have toxic effects, particularly at high concentrations. One particular concern was the presence of dissolved copper, in some cases at extremely high levels, a metal to which many aquatic organisms are extremely sensitive. Highly acidic discharges, in addition to being hazardous to aquatic life in themselves, can also greatly increase the water solubility, mobility and therefore toxicity of metals present in the wastewater.

As noted above, many of the organic chemicals found to be present in one or more of the discharged wastewaters have known hazardous properties. For example, alkyl phenols are persistent, bioaccumulative and toxic to aquatic life, including through hormone disrupting effects. Some phthalates are toxic to reproductive development in mammals. There is evidence that TBBPA may interfere with endocrine (hormone) systems, amongst other toxic effects; Bisphenol A is a well known endocrine disrupter, in aquatic invertebrates as well as vertebrates, and can also be produced by the degradation of TBBPA in the environment. Furthermore, this study demonstrated that discharged wastewaters commonly contain many other substances about which little is known in terms of their toxicology or potential impacts following release to the environment. Additional detailed information on certain key pollutants which were detected during this study and which could be reliably identified is presented in the main report in Boxes A-G.

This study also identified instances where wastewaters discharged from facilities via the larger and most visible outfalls, or which are discharged during the daytime, may differ greatly from other discharges arising from the same sites but which are less visible because of their location or the time of their release. This situation raises additional difficulties and concerns regarding the monitoring of discharges from industrial facilities.

Many of the heavy metals and hazardous organic chemicals identified in the discharged wastewaters are able to accumulate in the environment following their release, either within sediments or in some cases in biota as a result of bioaccumulation. This study found that sediment samples collected in the vicinity of many of the discharge points contained certain hazardous chemicals present in the discharged wastewater. For these substances, ongoing releases are likely to lead to ever increasing levels in the receiving environment, which in many cases will not significantly decrease for long periods of time, even after any controls on their release have been introduced. This situation highlights the limitations of regulations that seek to address impacts of industrial waste discharges by setting either acceptable levels of discharge or acceptable levels in the receiving environment, especially as such limits are, other than for a very limited number of individual chemicals, largely based on general measurements of chemical load such as biological and chemical oxygen demand (BOD and COD). Such permitted discharge approaches are unable to address the serious and potentially irreversible consequences arising from ongoing releases to the environment of persistent organic and inorganic pollutants as components of industrial wastes.

Moreover, for many of these most hazardous substances, their presence in waste streams cannot be addressed effectively through the use of ‘end-of-pipe’ measures, including conventional wastewater treatment plants. Many persistent organic pollutants, for example, will either pass through the treatment process unchanged, be converted through partial degradation into other hazardous substances, or accumulate in treatment plant ‘sludges’ that then become hazardous wastes in themselves. The most effective measures to address hazardous substances are those that seek alternatives to the use of such hazardous substances in manufacturing processes, progressively replacing them with less hazardous, and preferably non-hazardous, alternatives in order to bring about rapid reductions and ultimate cessation in their discharges, emissions and losses (the principle of substitution).

This can be achieved by focusing ‘upstream’ in industrial terms, systematically rethinking and redesigning products and processes in order to progressively reduce industry’s reliance on hazardous chemicals, to build a more sustainable global industry and to eliminate both the waste of resources and the pervasive threats to the environment and human health that the ongoing use and release of hazardous chemicals entails.

A wide range of industrial activities take place within the PRD, which **covers over 40,000 km²** *and houses a population of over* **45 million people**, *including the manufacture of electrical equipment, petroleum and chemical products, textiles and motor vehicles*

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image Kingboard (Panyu Nansha) Petrochemical Company Limited outflow waste discharge pipe

1: Introduction

The Pearl River Delta (PRD) has emerged as one of the world's most dynamic industrial zones, accounting for more than 10% of the total Gross Domestic Product (GDP) of China, and more than 80% of the total GDP of Guangdong Province in which it is situated (Enright *et al*. 2007). A wide range of industrial activities take place within the PRD, which covers over 40,000 km^2 and houses a population of over 45 million people, including the manufacture of electrical equipment, petroleum and chemical products, textiles and motor vehicles (Enright *et al*. 2007). The PRD has been referred to as the 'world's factory floor' because of its position as China's main export manufacturing hub.

The PRD is situated on the lower reaches of the Pearl River, where it flows into the South China Sea. The regions of Hong Kong and Macau border the PRD to the south. The Pearl River is the third largest river in China after the Yangtze and Yellow Rivers, with a catchment area of 453,000 km^2. It has three principal tributaries, the Xijiang River, Beijiang River and Dongjiang River, and it also receives inputs from several other smaller tributaries that flow within the PRD area (Chen *et al*. 2004).

The PRD has undergone rapid urbanisation, particularly since the late 1970s, which has contributed to significant impacts on river water quality as a result of inputs from numerous sources, principally domestic and industrial wastewater discharges, storm water runoff and non-point source pollution from agricultural activities (Ouyang *et al*. 2006). These multiple sources have contributed to a diverse range of pollutants entering the river system.

The monitoring of pollutants within, and being released to, the Pearl River system, as well as pollution prevention and control measures, has tended to focus on a limited range of pollutant criteria, which include levels of nutrients such as nitrogen and phosphorus, faecal bacteria, and general measurements of chemical load such as biological and chemical oxygen demand (BOD & COD) (MEP 1998, 2006). Although a small number of individual industrial chemicals and chemical groups are addressed, inputs to the river system remain unregulated for the majority of chemicals manufactured, used and released in the Pearl River basin.

Many man-made chemicals are known to have intrinsic hazardous properties that make their release to the environment of particular concern, and a far greater number have never been properly tested for their safety. Properties of hazardous chemicals include being persistent (do not readily breakdown in the environment), bioaccumulative (able to accumulate in organisms), and toxic, including carcinogenic (chemicals which can cause cancer), mutagenic (chemicals with capacity to induce mutations and gene-defects), toxic to reproduction (chemicals which can harm the reproductive system) or to the nervous system, or capable of disrupting endocrine (hormone) systems.

For many hazardous chemicals it is difficult, if not impossible, to remove them or control the risks they present once they have been released into the environment. The more environmentally persistent chemicals can cause harm over a long period of time and over wide areas, even far from their point of release and long after any controls have been introduced. Furthermore, many cannot be contained or destroyed effectively using traditional 'end-of-pipe' measures such as wastewater treatment plants.

Numerous studies have demonstrated contamination of the Pearl River Delta with hazardous chemicals, including heavy metals (Cheung *et al*. 2003, Ip *et al*. 2007, Wang *et al*. 2008) and persistent organic pollutants (Fu *et al*. 2003, Chau 2006), with examples including deca-BDE and other polybrominated diphenyl ethers (PBDEs) (Guan *et al*. 2009a) and nonyl phenols (Chen *et al*. 2006, Peng *et al*. 2007). It is highly likely that these chemicals or their derivatives are among the many thousands of chemicals currently used and released to the environment within the river basin. Furthermore, some persistent organic pollutants present in the Pearl River system are no longer manufactured or used, such that their presence is due to their historic uses (for example polychlorinated biphenyls, PCBs) (Guan *et al*. 2009b). The presence of chemicals that are no longer in use, as well as other highly persistent chemicals that remain in use, highlights the long term consequences of the use and release of persistent chemicals.

Previous studies have focused on the presence and levels of certain industrial pollutants present within the waterways of the Pearl River basin, rather than attempting to characterise pollutants being directly discharged to this river system from industrial point sources. This study was undertaken to provide data in this area, focusing on types of manufacturing facilities with known uses of certain hazardous chemicals. Direct discharges from five facilities were investigated, two of which are situated in industrial parks, and the other three being individual factories. Three of these five facilities are involved in the manufacture of printed circuit boards, one produces textiles and one produces printed paper and board products. The identities of the industrial parks and individual facilities and the general type of manufacturing activities undertaken at each are summarised in Table 1, and their locations within Guangdong Province, and with respect to the Pearl River Delta area, are shown in Figure 1.

Figure 1. Location of the five facilities within the Guangdong Province, showing the boundary of the Pearl River Delta area

Table 1. The five sites (Industrial park or facility) investigated and the types of activities undertaken at each

Industrial parks / facility	Activities undertaken
Kingboard (Fogang) Industrial Area*	printed circuit board manufacture
Kingboard (Panyu Nansha) Industrial Area*	printed circuit board manufacture
Wing Fung P.C. Board Co., Ltd.	printed circuit board manufacture
QingYuan Top Dragon Textile Co., Ltd.	Textiles manufacture
Dongguan Cheongming Printing Co. Ltd.	Printing

* Through field investigation, interviews and desktop research, Greenpeace identified a cluster of Kingboard's industrial facilities in this area. For more detailed information, please refer to Section 2 and the Appendix.

main image Toxics camapigner, Chung Ping Wong Gp China takes a waste water sample directly from the discharge outflow pipe from the Qingyuan Top Dragon Textile company, Qingyuan, Guangdong, China.

2: Sampling programme

The five sites investigated in this study (two industrial parks and three individual factories) were visited in June 2009, and a total of 25 samples (of wastewaters and sediment) were collected. Wastewater samples were collected from all discharge points that could be identified and accessed on the perimeters of each of the sites. Where available, samples of sediment were also collected from discharge channels and water bodies that receive discharged wastewaters.

In all cases, 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. Wastewater samples were collected in 1 litre screw-cap bottles for use in the quantitative analysis of metals and qualitative analysis of solvent extractable (semi-volatile) organic compounds. A duplicate sample was collected in a separate 125 ml amber bottle with a ground-glass stopper (filled to leave no headspace), to be analysed for volatile organic chemicals. Sediment samples were collected in 100 ml screw-cap bottles. All samples were immediately chilled and kept cool and dark during transit to the Greenpeace Research Laboratories at the University of Exeter in the UK for analysis. Detailed description of sample preparation and analytical procedures are presented in the Appendix.

image A sample of waste water collected from the discharge outflow pipe belonging to the Qingyuan Top Dragon Textile company, Qingyuan, Guangdong, China.

image The outflow pipe located outside the Shenzhen Resources Environmental Technology Co. Ltd. discharging manufacturing waste water.

The company processes and extracts chemicals from hazardous waste and waste water collected from other manufacturers.

3: Methodology

A number of different analyses were carried out on the wastewater and sediment samples collected. Heavy metal concentrations were determined for all samples by ICP atomic emission spectrometry (AES), following acid digestion and using appropriate certified reference materials in addition to intra-laboratory standards. Many wastewater samples contained suspended solids and therefore, for all samples, both the total concentrations in the whole (unfiltered) sample and the concentrations of dissolved forms in a filtered sample were determined separately.

Extractable organic compounds were isolated from each sample and identified as far as possible using gas chromatography and mass spectrometry (GC/MS), following liquid:solid extraction into a mixture of pentane and acetone for solid samples or liquid:liquid extraction with pentane only for wastewater samples. Volatile organic chemicals (VOCs) were identified and quantified in wastewater samples as received (with no pre-treatment) using GC/MS with HeadSpace sample introduction technique. A full list of all VOCs that were used as standards for Selective Ion Monitoring (SIM) GC/MS organic analysis, and for quantification of VOCs detected in water samples, is provided in the Appendix.

image The Pulp and Paper industry is one of the biggest waste water discharge polluters in the China.

4: Results and discussion

Each of the five sites is discussed separately in the following sections, with each section including:

- a summary of the information available in the public domain on the activities that take place at each site;
- a description of the samples of wastewater and associated sediments that were collected from the vicinity of each site (Tables 2a-6a);
- a map of the facility and surrounding area for the more complex sites; and
- a discussion of the results from the analyses of the samples.

The data from the analyses are summarised in Tables 2b-6b. In some cases no VOCs were identified in wastewater samples, and therefore the tables of data only present VOC data where these chemicals were identified.

Some key chemicals were identified in samples collected from more than one site. For these, the common uses, properties and any associated hazards of the chemicals are briefly discussed in the section of the report relating to the first site at which they were identified. For all subsequent sites at which they were identified, the presence of the chemical is noted but its properties not discussed. In addition, further background information on certain key pollutants detected during this study is presented in Boxes A-G.

It should be noted that all metals quantified in this study are naturally found at some level in uncontaminated environmental samples, such as sediments and surface waters, though generally at low concentrations. Inputs from point sources such as industrial discharge can, however, result in levels that far exceed natural background concentrations. The following sections focus on those metals found at levels in the various samples that indicate levels above background due to inputs from industrial or other anthropogenic sources.

4.1) Kingboard (Fogang) Industrial Area

The Kingboard (Fogang) Industrial Area is located in Shijiao Town, Fogang County, Qingyuan City in Guangdong Province. This very large site is situated adjacent to Huang-wen-yuan Village, on the banks of the Pa River (Pajiang), a tributary of the North River (Beijiang River) in the Pearl River system.

Within the site are eight separate facilities owned by the Kingboard group, and these form a complete production and supply chain for the manufacture of printed circuit boards (Kingboard 2009, TECHWISE 2009). These facilities produce, among other products, formalin, polyvinyl butyral (PVB) resin, copper foil, paper laminates for printed circuit boards, glass epoxy laminates, copper-clad paper laminates, glass filament and finished printed circuit boards. The printed circuit boards are produced by TECHWISE Shirai (Fogang) Circuits Limited (herein referred to as TECHWISE), which is situated in the southern part of the Kingboard Industrial Area., A small wastewater treatment plant (WWTP) is situated at the south corner of the TECHWISE facility.

In addition to this, a large WWTP is situated adjacent to the southern perimeter of the Kingboard site (see Figure 2), but this is a separate facility and is reported to process only municipal sewage (People.cn 2008). It is not believed to receive industrial wastewater from facilities within the Kingboard site.

Samples of wastewater were collected from two discharge pipes that were observed in the vicinity of the TECHWISE facility:

- the main outfall from the small WWTP (CN09003) into a small channel that flows alongside a highway and into the Pa River; and
- a second smaller concealed pipe that passes under the perimeter wall adjacent to the TECHWISE facility (CN09005) that discharges into the upper section of the same small channel.

For each of these outfalls, a sample of sediment was collected from close to the point of discharge (CN09004 and CN09006 respectively). The sediment at the main outfall was collected from beneath the flow of wastewater, between the pipe and the open channel, while the sediment collected by the concealed pipe was from the channel itself. An additional sample of sediment (CN09001) was collected from the Pa River at a location approximately 1 km upstream from the Kingboard (Fogang) Industrial Area, in order to identify any contaminants which might have arisen from other sources upstream from the Kingboard site.

A stagnant lagoon is situated between the Kingboard site and the Pa River. This lagoon is connected to the main river, and though no direct wastewater discharges into the lagoon were observed at the time of sampling, the presence of a distinct green colouration in the sediment does suggest that the lagoon may receive industrial wastes from time to time. A sample of sediment was collected from this lagoon (CN09002).

Details of all samples are presented in Table 2a, along with a map showing the locations from where samples were collected (Figure 2).

Table 2a. Description of samples collected from the vicinity of the Kingboard (Fogang) Industrial Area in Qingyuan City, Guangdong Province, China, 2009

Sample	Type	Description
CN09003	wastewater	Discharge pipe outside the wastewater treatment plant of TECHWISE, into an open channel (as CN09004)
CN09004	sediment	Sediment and plant material collected from below the discharge pipe outside the wastewater treatment plant of TECHWISE (as CN09003)
CN09005	wastewater	Milky white wastewater collected from a concealed pipe that passes underneath the perimeter wall of TECHWISE and discharges into the open channel upstream of the main outfall (as CN09006)
CN09006	sediment	Collected from the open channel 0.5 m downstream of the discharge via a concealed pipe that passes underneath the perimeter wall of TECHWISE (as CN09005)
CN09001	sediment	Collected from the Pa River, approximately 1 km upstream of the Kingboard (Fogang) Industrial Area
CN09002	sediment	Collected from a stagnant water lagoon adjacent to the Kingboard (Fogang) Industrial Area. The lagoon is upstream of the outfalls and is connected to the Pa River

4.1.1) Results

Analysis of the two samples of wastewater (CN09003 and CN09005) showed that they were of two very different compositions with regard to industrial chemicals. With regard to organic chemicals, the one notable similarity was the presence of tetrabromobisphenol A (TBBPA) in both samples, a brominated chemical widely used as a flame retardant precursor in the manufacture of some printed circuit boards. Other than TBBPA (and some simple hydrocarbons common to both), the two wastewaters were markedly different in their content of organic contaminants.

Many groups of organic chemicals with known uses in the manufacture of printed circuit boards were identified in the wastewater discharged via the pipe adjacent to the wastewater treatment plant of the TECHWISE facility (CN09003). Among these were:

- six photoinitiators, or closely-related chemicals:
- a thioxanthen-9-one derivative known as 'Quantacure ITX';
- a diphenylethanone derivative known as DMPA or 'Photocure 51';
- three phenylethanone derivatives; and
- a coumarin derivative
- alkyl phenol derivatives:
- two octyl phenol ethoxylates (OPEs); and
- octyl phenol (OP), a chemical known to be produced by the degradation of OPEs
- a long chain fatty acid and closely-related long chain aldehyde and thiol compounds.

Figure 2. Map of the Kingboard (Fogang) Industrial Area, including the TECHWISE facility, showing the locations from which samples of wastewater and sediment were collected

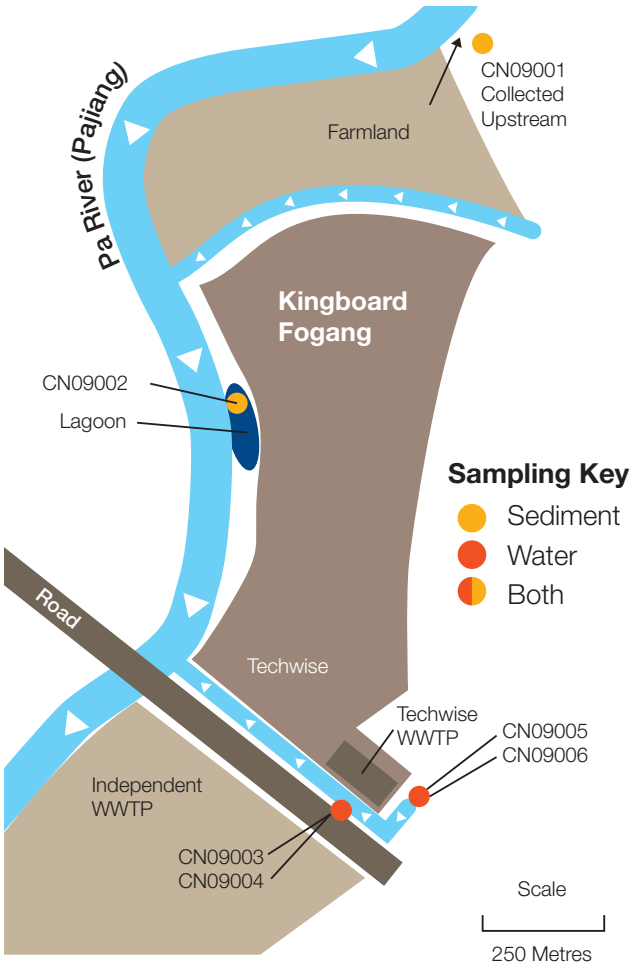

Table 2b. Organic chemicals identified, and concentrations of metals and metalloids, in samples of wastewater and sediment associated with the Kingboard (Fogang) Industrial Area in Qingyuan City, Guangdong Province, China, 2009. (..) signifies compounds identified at trace levels using a selective SIM method. For wastewater samples, concentrations are given for whole (unfiltered) samples, dissolved concentrations accounted for greater than 75% of the whole sample concentration unless otherwise indicated; 50-75%[a], 25-50%[b]

Sample	CN09003	CN09005	CN09004	CN09006	CN09002	CN09001
Type	Wastewater		Sediment			
Brief description	WWTP pipe	concealed pipe	WWTP pipe	concealed pipe	lagoon	upstream
pH	6	1	-	-	-	-
METAL	(µg/l)	(µg/l)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Antimony	<50	<50	<20	<20	<20	<20
Arsenic	<50	<50	<20	131	28	<20
Beryllium	<5	123[a]	<0.5	21.0	31.5	2.7
Cadmium	<5	21	3.0	1.7	2.3	3.3
Chromium	<20	1230	44	112	32	10
Chromium (VI)	<50	<50	-	-	-	-
Cobalt	<20	103	25	9	45	11
Copper	246	63[a]	30500	85	30300	82
Lead	<50	382[b]	97	698	78	109
Manganese	50	17100[a]	28	12	4	4
Mercury	<2	<2	<0.2	0.7	0.5	0.2
Nickel	39	31	328	4	33	16
Selenium	<200	<200	<30	<30	<30	<30
Thallium	<20	<20	<10	<10	<10	<10
Tin	<100	10100[a]	26300	716	<10	<10
Vanadium	<20	402	40	47	30	37
Zinc	30[a]	3240	160	202	523	743
Organic compound isolated	65	71	44	42	24	12
No. Reliably identified	24	17	11	16	22	10
(% of total)	(37%)	(24%)	(25%)	(38%)	(92%)	(83%)
Brominated compounds						
Tetrabromobisphenol A	1	1				
Deca-BDE (a PBDE)					1	1
Other PBDEs					5	
Other bromine compounds		2	1	2	1	
Chlorinated compounds						
Pentachloro benzene			(1)			
Dichloro benzenes		(2)				
Photoinitiators and related compounds						
Quantacure ITX	1					
Diphenylethanone derivative	1					
Phenylethanone derivative	3					
Coumarin deriv	1					
Alkylphenols and derivatives						
Octyl phenol	1					
Octyl phenol ethoxylates	2					
Other oxygen compounds						
Alkyl fatty acid	1					
Benzoic acid ester				1		
Benzoic acid derivatives				1		
Alkyl aldehyde	1					
Sulphur compounds						
Alkyl thiols	1					
Sulphur				1		
Hydrocarbons						
PAHs				3		
Alkyl benzenes	2			1		
Aliphatic hydrocarbons	9	12	9	7	15	9

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image A farm lady uses the river next to Kingboard Industrial park to water her crops. She unaware of the hazardous chemicals KB is manufacturing and discharging

TBBPA is a reactive flame retardant with the global consumption of 210,000 tonnes, making it the highest-volume brominated flame retardant (BFR) on the market (Alaee *et al*. 2003). TBBPA has a variety of uses such as in production of epoxy, vinyl esters and polycarbonate resins, including those that are used in electrical and electronic appliances (Lassen *et al*. 1999). The main application of TBBPA in epoxy resins is in printed circuit board laminates, where the bromine content may be 20% by weight (Alaee *et al*. 2003). It is also used as a flame retardant in polymers such as ABS, polystyrenes, phenolic resins, adhesives, paper products and textiles. Studies on toxicological properties of TBBPA showed that this chemical may interfere with endocrine (hormone) systems (Meerts *et al*. 1998 & 2001, Samuelsen *et al*. 2001, Olsen *et al*. 2003), raising the potential for diverse effects on growth and development. *In vitro* studies on TBBPA also indicate the potential for effects on other hormone systems, the immune system, liver and kidneys (Pullen *et al.* 2003, Fukuda *et al.* 2004, Ronisz *et al*. 2004, Tada *et al*. 2007). Furthermore, concerns have been raised over chemicals formed during the degradation of TBBPA in the environment, including the well known endocrine disrupter Bisphenol A (Liu *et al.* 2009, Arbeli & Ronen 2003, Ronen & Abeliovich 2000). More information on TBBPA can be found in Box A.

Box A. Brominated and phosphate flame retardants

Tetrabromobisphenol A (TBBPA) is used widely as a flame retardant in various industrial and consumer products, including electrical and electronic appliances (Lassen *et al*. 1999). This chemical is most frequently used in polymeric form, i.e. bound to the polymers in which it is incorporated, though a small percentage of total use is in additive uses (i.e. in a similar manner to the common additive flame retardants PBDEs and HBCD). Despite its primary use in reactive, polymeric forms, TBBPA has been found in the indoor environment, including in office dust samples (Leonards *et al*. 2001) as well as in environmental compartments (soils and sediments), fish and birds (Morris *et al*. 2004) . Studies on metabolism of TBBPA in rats and humans suggest its rapid conjugation with glucuronic acid and elimination in the bile (Kuester *et al*. 2007). However, TBBPA has been detected in cow and human milk (Thomsen *et al*. 2002a; Antignac *et al*. 2008), human serum (Hayama *et al*. 2004), human adipose tissue (Johnson-Restrepo *et al*. 2008) and umbilical cord serum (Antignac *et al*. 2008).

It has been reported that TBBPA may interfere with the binding of thyroid hormones (Meerts *et al*. 1998, 2001), raising the potential for diverse effects on growth and development. Concerns have also been raised that TBBPA can induce oestrogen-like properties (Meerts *et al*. 2001, Samuelsen *et al*. 2001, Olsen *et al*. 2003), neurotoxicity (Mariussen & Fonnum 2003), immunotoxicity (Pullen *et al*. 2003), nephrotoxicity (Fukuda *et al*. 2004) or hepatotoxicity (Ronisz *et al*. 2004, Tada *et al*. 2007). Environmentally relevant TBBPA concentrations have been shown to decrease reproductive success in zebra fish (Kuiper *et al*. 2007) and inhibition of oestradiol metabolism in lake trout (Jurgella *et al*. 2006). However, most of the studies are *in vitro* studies not specifically designed for the purpose of risk assessment. A more recent review of the toxic effects of some chemicals used in the plastic materials manufacture (Talsness *et al*. 2009) reported new studies on TBBPA toxicity confirming endocrine-disrupting potential of TBBPA in the rodent model; previous data on such effects were based on *in vitro* and *in vivo* studies performed in quail, fish and tadpoles. This review has also highlighted the need to decrease human exposure to TBBPA as one of the chemicals with significant body burden in young children, a group particularly sensitive to exogenous insults.

A risk assessment report published by the European Commission in 2006 (EC 2006) concluded that “No health effects of concern have been identified for TBBP-A”. This study has been prepared by the UK on behalf of the EU and was based on the scientific publications up to 2004. More recently, however, the UK revised the environmental risk assessment to take into account new test data and exposure information provided by Industry (DEFRA

2006). "The exposure section was updated with site-specific monitoring data. Initial results of studies of degradation in anaerobic sewage sludge and anaerobic sediment were added. These show de-bromination of TBBPA to form bisphenol A, another substance being assessed under the Existing Substances Regulation. Other recent studies in the published literature also found evidence for debromination of TBBPA in the environment. TC NES agreed that this source of bisphenol A to the environment should be considered further in an update to the bisphenol A risk assessment". However, in 2008, the European Commission officially concluded the Risk Assessment of TBBPA by publishing conclusions in the EU Official Journal (EC 2008a) which still said that no human health effect could be identified for TBBPA and that "competent authorities in the Member States concerned should lay down, in the permits issued under Directive 2008/1/EC, conditions, emission limit values or equivalent parameters or technical measures regarding TBBPA in order for the installations concerned to operate according to BAT taking into account the technical characteristic of the installations concerned, their geographical location and the local environmental conditions". The final statement, at the same time, highlighted the necessity for ensuring that "no risk to the environment is expected". As was mentioned above, the biggest concern in terms of TBBPA effects on the environment is the formation of TBBPA debromination products including well known endocrine disrupter bisphenol A (Liu *et al*. 2009, Arbeli & Ronen 2003, Ronen & Abeliovich 2000).

2,4,6-Tribromophenol (2,4,6-TBP) is produced as fungicide and flame retardant with high-volume worldwide production of 9500 t/year in 2001 (IUCLID 2003). 2,4,6-TBP may be also formed as one of the major degradation products of tetrabromobisphenol A in the presence of UV-light and hydroxyl radicals (Eriksson and Jakobsson 1998). In addition to its synthetic manufacture, it can occur naturally in certain marine organisms (Chung *et al*. 2003, Vetter and Janussen 2005).

Tribromophenols have been detected in various environmental compartments including in estuarine sediments (Tolosa *et al*. 1991), in river water (Schwarzbauer & Heim 2005), and in indoor air and dust (Takigami *et al*. 2009a, b). The toxicity of 2,4,6-TBP has been investigated in both in vivo and *in vitro* experiments. A study on pregnant Wistar rats (Lyubimov *et al*. 1998) reported that 2,4,6-TBP may cause development neurotoxicity, embryotoxicity and foetotoxicity. Another *in vitro* study on SH-SY5Y human neuroblastoma cells reported the induction of neuroblastoma cell differentiation in the presence of tribromophenol, as expressed by the inhibition of cell growth and the increase in acetylcholinesterase activity, and apoptosis at high concentrations (Rios *et al*. 2003). The findings of latter study have also suggested that tribromophenol is a potential embryotoxic and foetotoxic chemical. Furthermore, in a study on the Ca^{2+} homeostasis in endocrine cells (PC 12), it was shown that 2,4,6-TBP has a disruptive effect on endocrine system by reduction of depolarisation-induced Ca^{2+} elevations and increase of intracellular Ca^{2+} (Hassenklover *et al*. 2006). TBPs have been shown to be a strong competitor for thyroxin binding to transthyretin (Polo *et al*. 2006). In addition, pyrolysis of 2,4,6-TBP or its mixtures with trichlorinated phenols (e.g. during incineration of the materials containing brominated and chlorinated phenols) leads to a formation of toxic and carcinogenic compounds such as polyhalogenated dibenzo-p-dioxins, a potential by-product of the incineration of all organobromine compounds (Na *et al*. 2007).

Tris(2-ethylhexyl)phosphate or TEHP, belongs to a family of organophosphorus esters (OPs). TEHP has been extensively employed as a flame retardant, especially in PVC and cellulose acetate applications, and as a solvent (WHO 2000a). In general, OPs are normally not bound to the matrix into which they are added and, therefore, they can easily reach the surrounding environment due to volatilisation, leaching and/or abrasion processes. As a result, several OPs, including TEHP, have been detected in different environmental and domestic compartments, such as groundwater, river water, wastewater from WWTPs (Wensing *et al*. 2008), and in indoor environments (Takigami *et al*. 2009a, b, Wensing *et al*. 2005, Hartmann *et al*. 2005). TEHP expressed low acute toxicity for mammals, the oral LD 50 being >10g/kg body weight for rats (WHO 2000a). Tests for chronic toxicity and carcinogenicity of TEHP in rats and mice have shown some evidence of hepatocellular carcinomas in female mice at high dosesand equivocal evidence of carcinogenicity based on the increased incidence of adrenal phaeochromocytomas in male rats. However, considering the low incidence of this tumour, its occurrence in only one sex of one species, the lack of evidence of genetic toxicity, and the low exposure of humans to TEHP, it is thought unlikely that TEHP poses a significant carcinogenic risk to humans (WHO 2000a).

A number of the chemicals identified in sample CN09003 have known uses as photoinitiators (light-sensitive compounds used to induce polymerisation or to cure materials). Quantacure ITX has been widely used as a photoinitiator in inks in the flexographic printing industry (USEPA 2000). There is little information available on the properties of this chemical, though it has been shown that isopropylthioxanthone compounds of this type can cause long-term effects in aquatic organisms at relatively low concentrations (USEPA 2000). DMPA or 'Photocure 51', a diphenylethanone derivative (also known as a phenylacetophenone derivative), is one of the most widely used acetophenone-based photoinitiators despite the fact that so little information exists in the public domain concerning its toxicity.

Two isomeric methylated acetophenone derivatives, which are chemically related to DMPA, have also been detected in this sample; no reliable information is available on the toxicity of either of these chemicals. Quantacure ITX and DMPA have previously been identified in wastewater samples from other facilities manufacturing printed circuit boards (Brigden *et al*. 2007). Another chemical from the photoinitiator family, 1-propanone, 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-, is a high production volume photoinitiator with 99 global suppliers, 72 of which are located in China (ChemicalBook 2007). It is sold under various trade names including Acetocure 97, Photocure-907, Photoinitiator907 and Caccure 907. Very limited information on the toxicity of this chemical is available. However, it has been classified as 'Dangerous for the Environment' by the Nordic Council of Ministers (Pedersen & Falck 1997). A coumarin derivative detected in sample CN09003, 2H-1-benzopyran-2-one, 7-(diethylamino)-4-methyl-, is used as a fluorescent dye (Priyadarsini *et al*. 1990), giving bright light blue fluorescence in dilute solution. It is also used as an optical brightener, and as an invisible marking agent. It has a variety of trade names including Aclarat 8678, Blancophor AW, and Coumarin 47. There is no reliable information available on the toxicity of this compound. Some additional information on the photoinitiators mentioned above is presented in Box B.

Alkyl phenol ethoxylates (APEs) are non-ionic surfactants. The most widely-used APEs are ethoxylates of nonylphenol (NPEs) and, to a lesser extent, octylphenol (OPEs). Following release, APEs can degrade back to alkyl phenols (APs), including octyl phenol (OP) and nonyl phenol (NP), which are persistent, bioaccumulative and toxic to aquatic life, primarily through hormone disrupting effects (OSPAR 2001, Jobling *et al*. 1996). Exposure to OP has also been shown to cause adverse effects on reproductive systems in mammals (Blake *et al*. 2004). More information on alkylphenols and their ethoxylates is given in Box C.

Box B. Photoinitiators and related compounds

Photoinitiators are additives that use ultraviolet (UV) or visible light to induce polymerisation, or to cure materials, as in the case of coatings and inks. Photoinitiators have extensive applications in the manufacture of printed circuits, encapsulation of electronic components, decorative coating, surface coating, etc. The main advantage of polymerisation started by photoinitiators is temperature-independence and easy control. It can be conducted at very low temperatures and can be stopped simply by removing the light source.

Photoinitiators are sold under various trade names including Quantacure, Irgacure, Darocure, Photocure, Vicure and others. Many photoinitiators that have been traditionally used by the industry in the past and those that remain in use are derivatives of the chemicals benzophenone (Allen *et al*. 1988, 1990, 1997, Eustis *et al*. 2006) or acetophenone (Torbiero *et al*. 2006, Umarji *et al*. 2005, Mijangos *et al*. 2006). Industrial developments during the last two decades promoted fast growing research and synthesis of new chemicals that are used in the fields of photopolymerisation and photoimaging science and technology (Corrales *et al*. 2003, Yilmaz *et al*. 2004). As a result, new polymers bearing thioxanthone (Jiang *et al*. 2006), anthraquinone, camphorquinone or benzyl moieties (Seidl *et al.* 2006) have been synthesised. Publicly-available information on these photoinitiators is mainly in the form of numerous patents and, as a consequence, there is very little information on the toxicity of these new compounds. This is a major concern because it is unknown what effects they could cause on human health and the environment through use in, and release from, manufacturing processes.

Benzophenone and related compounds

Benzophenone itself and its derivatives are used as a photoinitiators during production of UV-cured resins, inks and coatings (Eustis *et al*. 2006). Apart from this application, benzophenone has many other uses, including as a fragrance enhancer, and, occasionally, as a flavour ingredient. It is also used in the manufacture of insecticides, agricultural chemicals and pharmaceuticals and is an additive for plastics and adhesives (US DHHS 2000). It has been shown in experimental animals that the liver is the primary target organ of benzophenone toxicity in rats and mice, based on increases in liver weights, hepatocellular hypertrophy, clinical chemistry changes, and induction of liver microsomal cytochrome P450 2B isomer. The kidney was also identified as a target organ of benzophenone toxicity in rats only, based on exposure concentration-related increases in kidney weights and microscopic changes (US DHHS 2000). Benzophenone and some of its derivatives displayed oestrogenic activity in the

MCF-7 cell proliferation assay (Matsumoto *et al*. 2005) and in the yeast two-hybrid assay (Kawamura *et al*. 2003). The studies on the chronic toxicity and carcinogenicity of benzophenone (Rhodes *et al*. 2007) when administered in the diet of rats and mice have revealed some evidence of carcinogenic activity of benzophenone, e.g. in male F344/N rats, based on increased incidences of renal tubule adenoma, in male $B6C3F_1$ mice, based on increased incidences of hepatocellular neoplasms, primarily adenoma, and in female $B6C3F_1$ mice, based on increased incidences of histiocytic sarcoma. The incidences of hepatocellular adenoma in female $B6C3F_1$ mice may also have been related to benzophenone exposure. There was equivocal evidence of carcinogenic activity of benzophenone in female F344/N rats based on the marginal increased incidences of mononuclear cell leukemia and histiocytic sarcoma.

Acetophenone and related compounds

One of the most widely-used acetophenone-based photoinitiators is 2,2-dimethoxy-1,2-diphenylethanone, also known as 2,2-Dimethoxy-2-phenylacetophenone (DMPA) or 'Photocure 51'. DMPA is a photoinitiator that is added to polysiloxanes to produce photosensitive polymers, which are widely used in silicon microelectronics (Torbiero *et al*. 2006, Umarji *et al*. 2005). Diphenylethanedione (also known simply as 'benzil') is a raw material used in the production of DMPA. Another acetophenone-based photoinitiator, 2,2-diethoxyacetophenone, is used in the synthesis of telechelic polyurethane methacrylates, which have widespread use in the coatings industry (Asha *et al*. 2005).

Despite the fact that acetophenone-based photoinitiators have been in use for over two decades, little information exists in the public domain concerning their toxicity. Acetophenone itself is a toxic chemical. Acute exposure of humans to acetophenone vapour may produce skin irritation and transient corneal injury. Acute oral exposure has been observed to cause hypnotic or sedative effects, hematological effects and a weakened pulse in humans. Congestion of the lungs, kidneys, and liver were reported in rats acutely exposed to high levels of acetophenone via inhalation (USEPA 2000a). DMPA has been found to be toxic to HepG2 cells, a human hepatoma cell line, in dose-dependent manner during photopolymerisation experiments in tissue engineering (Liu & Bhatia 2002).

Thioxanthone and related compounds

Thioxanthones are bimolecular photoinitiators widely used in vinyl polymerisations. They have been employed in processes such as UV-cured printing inks, surface coating, microelectronics, and photoresists (Corrales *et al*. 2003). The thioxanthones were also often used in conjunction with other photoinitiators to design cost effective synergistic photoinitiator blends (Cho *et al*. 2003, Segurola *et al*. 1999, Andersen *et al*. 1996). Recently thioxanthone-based photoinitiators have received a revitalised interest because of their absorption characteristics at near UV range (Temel *et al*. 2006). Isopropyl derivatives of thioxanthone are used as photoinitiators under the trade name Quantacure ITX in many applications, including production of UV-cured inks that comprise a comparatively new ink technology in the flexographic printing industry (USEPA 2000b). Little information is available on these compounds, though derivatives of thioxanthone including isomers of isopropylthioxanthone are known to be of high aquatic hazard and capable of causing long-term effects in aquatic organisms even at concentrations of less than 0.1 mg/l (USEPA 2000b).

Public and regulatory concerns arose around the proprietary product Quantacure ITX in September 2005, when a laboratory in Italy reported that traces of this photoinitiator had been found in some milk products for babies. Quantacure ITX, which was used as a curing agent for ink on Tetra Pak's packaging, had migrated through packaging into the milk. Followed by this discovery, millions of litres of the baby milk were recalled or confiscated by government authorities. Consequently, analytical methods have been developed for photoinitiator determination in milk products, including Quantacure ITX (Sanches-Silva *et al*. 2008), in order to control for the migration of these chemicals from food packaging. However, there are still insufficient studies conducted on the toxicity of thioxanthone derived photoinitiators. One study (Momo *et al*. 2007) conducted after the case with baby milk contamination reported that ITX can affect the mobility/rigidity status of biological membranes through strong interactions with the cellular lipid bilayer.

Quinine related compounds

Derivatives of *ortho*- and *para*- benzoquinones are used as intermediates in the organic synthesis involving photochemical reactions (Van der Graaf *et al*. 1991). Once again, very limited information is available on the toxicity and fate of these chemicals. Congeners of p-benzoquinone, including 2,6-di-tert-butyl-p-benzoquinone (DBQ), have been found to express cytotoxicity in primary rat hepatocyte and PC12 cell cultures tests (Siraki *et al*. 2004). DBQ has been found among the semi-volatile chemicals emitted during heating of nitrogen-containing plastic (Watanabe *et al*. 2007). Another compound identified, 1-ethyl-9,10-anthracenedione, is a derivative of anthraquinone. In general, anthraquinones are used in photoinitiation systems and exhibit a high reactivity when used in combination with tertiary amines as co-initiators (Corrales *et al*. 2003). There is no reliable information available on their toxicity.

Box C. Alkyl phenols and their ethoxylates

Alkylphenols (APs), which include **octyl phenol (OP)** and **noyl phenol (NP)**, are non-halogenated chemicals manufactured almost exclusively to produce alkylphenol ethoxylates (APEs), a group of non-ionic surfactants. The most widely-used APEs are ethoxylates of nonylphenol (NPEs) and, to a lesser extent, octylphenol (OPEs). Once released to the environment, APEs can degrade back to APs, which are persistent, bioaccumulative and toxic to aquatic life. NPEs have been used as surfactants, emulsifiers, dispersants and/or wetting agents in a variety of industrial and consumer applications, the largest share in industrial and institutional cleaning products (detergents), with smaller amounts used as emulsifiers, textile and leather finishers and as components of pesticides and other agricultural products and water-based paints (OSPAR 2001, Guenther *et al*. 2002). OPEs are reported to have had a similar range of uses to NPEs, although fewer reliable data are available for this group.

Both APEs and APs (especially nonylphenol and its derivatives) are widely distributed in fresh and marine waters and, in particular, sediments, in which these persistent compounds accumulate (see e.g. Fu *et al*. 2008, Shue *et al*. 2009, David *et al*. 2009). Because of their releases to water, APEs and APs are also common components of sewage effluents and sludge (Micic and Hofmann 2009, Ying *et al*. 2009, Yu *et al*. 2009), including that applied to land. NP has been detected in rain and snow in Europe (Fries & Püttmann 2004, Peters *et al*. 2008), while residues of both NP and OP have been reported as contaminants in house dust (Butte & Heinzow 2002, Rudel *et al*. 2003) and indoor air (Rudel *et al*. 2003, Saito *et al*. 2004). Research into levels in wildlife remains limited, although there have been reports of significant levels in both invertebrates and fish in the vicinity of sites of manufacture and/or use of APEs and close to sewer outfalls (Lye *et al*. 1999, Rice *et al*. 2003, Mayer *et al*. 2007). Both NP and OP are known to accumulate in the tissues of fish and other organisms, and to biomagnify through the food chain (OSPAR 2001). Basheer *et al*. (2004) identified alkylphenols as common contaminants of seafood from Singapore. More recently, the presence of alkylphenols as contaminants in human tissues has also been reported (Lopez-Espinosa *et al*. 2008)

The most widely recognised hazard associated with APs (both NP and OP) is undoubtedly their oestrogenic activity, i.e. their ability to mimic natural oestrogen hormones. This can lead to altered sexual development in some organisms, most notably the feminisation of fish (Jobling *et al*. 1995, 1996). Atienzar *et al*. (2002) described direct effects of NP on DNA structure and function in barnacle larvae, a mechanism that may be responsible for the hormone disruption effects seen in whole organisms. In rodents, exposure to OP caused adverse effects on male and female reproductive systems, including lower sperm production and increased sperm abnormalities (Blake *et al*. 2004). Chitra *et al*. (2002) and Adeoya-Osiguwa *et al*. (2003) describe effects on mammalian sperm function, while DNA damage in human lymphocytes has also been documented (Harreus *et al*. 2002), although the significance of these findings has been challenged by some. Impacts on immune system cells *in vitro* have also been described (Iwata *et al*. 2004).

More than 10 years ago, the Ministerial Meeting under the OSPAR Convention agreed on the target of cessation of discharges, emissions and losses of hazardous substances to the marine environment by 2020 and included NP/NPEs on the first list of chemicals for priority action towards this target (OSPAR 1998). Since then, NP has been included as a 'priority hazardous substance' under the EU Water Framework Directive, such that action to prevent releases to water within 20 years will be required throughout Europe (EU 2001). A decision on the prioritisation of OP/OPEs under the Directive remains under consideration. Already, however, the widely-recognised environmental hazards presented by AP/APEs have led to some long-standing restrictions on use. Of particular note in the European context is the Recommendation agreed by the Paris Commission (now part of the OSPAR Commission) in 1992, which required the phase-out of NPEs from domestic cleaning agents by 1995, and industrial cleaning agents by the year 2000 (PARCOM 1992). However, the precise extent to which this measure was effective is unclear.

The EU risk assessment for nonylphenol identified significant risks to the aquatic environment, to the soil and to higher organisms through secondary poisoning arising through numerous uses of NPEs (EU 2002). According to Directive 2003/53/EC, as of January 2005 products containing greater than 0.1% NP or NPEs may no longer be placed on the market within Europe, with some minor exceptions principally for 'closed-loop' industrial systems (EU 2003). At the same time, very little information exists regarding the ongoing uses of OP and its derivatives in consumer products and, as a consequence, our direct exposure to them.

One long chain fatty acid, hexadecanoic acid (also known as palmitic acid) was identified. Fatty acids are aliphatic monocarboxylic acids derived from their esterified forms that are present in animal or vegetable fats, oils, or wax. Natural fatty acids commonly have a chain-length of between 4 and 28 carbons (usually unbranched and even-numbered), which may be saturated or unsaturated. Fatty acids, in addition to their nutrition and medical usage, also have some industrial applications (Wittcoff *et al*. 2004). For example, fatty acids are used in construction of non-linear optical materials and photoelectric devices (Oishi *et al*. 2003) and as stabilisers of silver nanoparticles (Rao & Trivedi 2005). There are no known specific uses in the manufacture of printed circuit boards. Fatty acids and their derivatives are not of particular environmental concern due to their low toxicity and being readily biodegradable.

In addition to the organic chemicals discussed, this wastewater (CN09003) also contained a moderately high concentration of dissolved copper (246 µg/l) and a slightly elevated concentration of dissolved nickel (39 µg/l) compared to local background surface water levels (Cheung *et al*. 2003), while other metals were generally either below limits of detection for the methods used or within concentration ranges expected for uncontaminated surface waters (Cheung *et al*. 2003, Field 2001, Salomons & Forstner 1984). The level of copper is below the maximum allowable concentrations under the Guangdong effluent standard (Guangdong Province 2001). For more information on these metals and relevant standards see Box D.

In contrast, far fewer groups of organic chemicals were identified in the sample of wastewater (CN09005) collected from a concealed pipe that passes underneath the site's perimeter wall adjacent to the TECHWISE facility. In addition to TBBPA mentioned above, the sample contained two other brominated compounds that could not be fully identified, and two dichlorobenzenes, though only at trace levels.

However, this second wastewater did contain high concentrations of numerous metals, and was also highly acidic (pH=1), a property that is likely to have a significant impact on aquatic life in the vicinity of the discharge. This sample was milky in appearance due to the presence of high levels of suspended solids, and some metals were partly present in suspended forms (see Table 2b). However, for those metals present at high concentrations in this sample, dissolved forms contributed to over 50% of the total load of each metal, other than for lead.

Metals found at high concentrations in the sample included beryllium, cadmium, chromium, lead, manganese, tin and zinc. The levels of all these metals in the wastewater far exceeded levels typically found in uncontaminated surface waters (Cheung *et al*. 2003, Field 2001, Salomons & Forstner 1984) and, for many metals, the concentrations were the highest found in all wastewater samples analysed for this study. Furthermore, the levels of beryllium and manganese exceeded the highest allowable levels under the Guangdong effluent standard by 25 times and 3 times respectively, while the concentration of zinc exceeded all but the highest allowable level for this metal, and that of chromium was just below the allowable level (Guangdong Province 2001). No limit exists under this standard for tin, one of the metals present at a very high level in the wastewater. See Box D for individual limits set under the effluent standard. Although the concentrations of some metals in the wastewater were below legal discharge limits, these levels nonetheless indicate significant inputs to the receiving river which could, individually or in combination, be of toxicological relevance.

All of the metals present at high concentrations are known to be used in the manufacture of electronic devices, including the use of beryllium alloys and manganese compounds in the manufacture of printed circuit boards (Nuzzi & Duffy 1984, OECD 2003, Walters *et al*. 2006). Most of these metals can have toxic effects, particularly at high concentrations. Although some metals were present at relatively low concentrations, some such as lead and cadmium are highly toxic even at very low doses, to humans as well as many animals and plants, and are usually found in the environment at only very low levels. More information on the metals discussed for this sample is given in Box D.

Many metals discharged in wastewaters tend to bind to sediment particles and accumulate in bottom sediments of receiving waterways. Ongoing discharges of wastewaters containing high concentrations of metals, even if those levels are below regulatory discharge limits, can lead nonetheless to increasing levels of metals in sediments in receiving water bodies, which can in turn result in long-term impacts in sensitive aquatic species and, potentially, predators further up the food web.

Box D. Metals

Beryllium (Be) is a metal with unique properties, being lighter than aluminium and stronger than steel, as well as being a very good conductor of heat and electricity. It is used in electrical equipment, primarily as an alloy with copper in electrical contacts (OECD 2003, Taylor *et al*. 2003). The principal hazard associated with beryllium is the exposure of workers to beryllium dust and fumes generated during manufacturing process, or during the treatment of waste products at their end of life, including those beryllium-copper alloys used in electronics (Balkissoon & Newman 1999, Schuler *et al*. 2005). Exposure, even at very low levels and for short periods of time, can cause beryllium sensitisation that can lead to chronic beryllium disease (CBD), a debilitating lung disease (Field 2001, Schuler *et al*. 2005, Infante & Newman 2004). Furthermore, for workplace dust/fume exposures, beryllium and beryllium compounds are recognised as known human carcinogens(IARC 1993). Concentrations of beryllium in uncontaminated sediments are commonly below 5 mg/kg (Taylor *et al*. 2001)

Cadmium (Cd) is a rare metal, found naturally in the environment at very low concentrations, typically below 2 mg/kg in soils and sediments (Alloway 1990, ATSDR 2008a). When released to aquatic environments cadmium is more mobile than most other metals (ATSDR 2008a). Cadmium and its compounds are used in a number of applications within electrical and electronic products, including uses in contacts, switches and solder joints as well as in rechargeable batteries (OECD 2003). Cadmium has no known biochemical or nutritional function and is highly toxic to plants, animals and humans (ATSDR 2008a, WHO 1992). It is a cumulative toxicant and long-term exposure can result in damage to the kidneys and bone toxicity (Godt *et al*. 2006, WHO 1992). Relatively recently, studies have also demonstrated kidney damage in humans at lower levels of exposure than previously anticipated (Hellstrom *et al*. 2001). Other health effects from cadmium exposure include disruption to calcium mechanisms causing bone effects, as well as the development of hypertension (high blood pressure) and heart disease (ATSDR 2008a, Godt *et al*. 2006, WHO 1992).

Copper (Cu) is a widely-used metal, including uses in the manufacture of electronics products, primarily due to its high electrical conductivity as a pure metal or as part of mixtures (alloys) with other metals. Copper compounds are also used as components of dyes and printing inks (ATSDR 2004, OECD 2003, TAPPI 2008). The manufacture of printed circuit boards has been recognised as a major source of copper in Hong Kong waters (EPD 1991). Levels of copper in the environment are typically quite low, commonly less than 50 mg/kg in uncontaminated freshwater sediments (ATSDR 2004). Background concentration of copper in uncontaminated surface waters can vary significantly, but levels are typically below 10 µg/l (ATSDR 2004, Comber *et al*. 2008). Copper is an important element for humans and animals in low doses, though exposure to high levels can lead to bioaccumulation and toxic effects (ATSDR 2004). However, many aquatic organisms are extremely sensitive to copper, particularly in soluble forms which are generally far more bioavailable and toxic to a wide range of aquatic plants and animals (ATSDR 2004, Adams & Chapman 2006), with some effects occurring at extremely low concentrations (Sandahl *et al*. 2007).

Lead is found naturally in the environment, though usually at very low concentrations unless affected by inputs from human activities, with uncontaminated soils and freshwater sediments typically containing less than 30 mg/kg of lead (Alloway 1990, ATSDR 2007). Lead has no known biochemical or nutritional function and is highly toxic to humans as well as many animals and plants (ATSDR 2007, WHO 1989). Levels can build up in the body through repeated exposure and have irreversible effects on the nervous system, which is of particular concern for the developing nervous system in young humans. Other effects include damage to the blood system and impacts on the kidneys and on reproduction (ATSDR 2004, Sanders *et al*. 2009). Recent studies indicate that there may be no safe level of exposure, particularly in the developing central nervous system (Canfield *et al*. 2003).

Manganese (Mn) and its compounds have numerous industrial applications, including the manufacture of steel, batteries and ceramics (ATSDR 2008b). There are reported uses in printed circuit board manufacturing, though these processes may not be commonly employed (Nuzzi & Duffy 1984). Manganese is present in the environment at higher concentrations than most other trace metals, with background levels in soils ranging from 40 to 900 mg/kg, and average levels in sediments of around 1000 mg/kg, though levels vary significantly with location (Cooper 1984, ATSDR 2008b). Concentrations in surface waters are typically below 200 µg/l, and often far lower (Barceloux 1999). Manganese is an essential trace metal for humans and animals. However, exposure to high levels can produce toxic effects, primarily multiple symptoms of neurotoxicity that includes damage to the brain. In humans these effects are known as manganism and are usually the result of high-level occupational exposures (ATSDR 2008b, Burton, & Guilarte 2009, Michalke *et al*. 2007).

Nickel has many industrial uses, including in the manufacture of printed circuit boards (ATSDR 2005, USEPA 1998). Levels of nickel in the environment are typically low, with uncontaminated soils and sediments generally containing below 60 mg/kg (Alloway 1990, ATSDR 2005c). Very small amounts of nickel are essential for normal growth and reproduction in most animals and plants, and this is most likely also true for humans (ATSDR 2005c, Alloway 1990). However, toxic and carcinogenic effects can result from exposure to higher concentrations for a wide range of life forms, including gastrointestinal and cardiac effects (ATSDR 2005c, Cempel & Nikel 2006). In humans, around 2-5% of the population are nickel sensitive, and toxic effects can occur in sensitised individuals at far lower concentrations than usual (ATSDR 2005c). For some aquatic organisms, impacts can occur at very low nickel concentrations (Deleebeeck *et al*. 2008). Furthermore, some nickel compounds have been classified as carcinogenic to humans, and there is also evidence of carcinogenicity in animals (DHHS 2005, IARC 1990).

Tin is extensively used in printed circuit board manufacture, in layering and etching processes as well as in electrical solder (Walters *et al*. 2006). Exposure to inorganic tin does not usually cause toxic effects in humans or animals, unless ingested in extremely large amounts (ATSDR 2005a). However, the high concentrations of tin in wastewaters and sediments, together with other more toxic metals, demonstrate poor waste treatment and disposal practices. Concentration of tin in uncontaminated sediments at typically below 10 mg/kg (ATSDR 2005a).

Zinc (Zn) has numerous industrial uses, primarily as metallic alloys. Zinc compounds also have many uses including in some printing processes and as mordents in dying (ATSDR 2005b). Levels of zinc are generally quite low in the environment, with levels typically below 100 mg/kg in uncontaminated soils and sediments (ATSDR 2005b).

Zinc is an essential nutrient for humans and animals, but exposure to high concentrations of zinc can result in significant bioaccumulation with possible toxic effects, including for aquatic organisms (Adams & Chapman 2006, ATSDR 2005). Symptoms of high doses in humans include pancreatic damage, anaemia and gastrointestinal distress, with similar effects also reported for animals (ATSDR 2005, IPCS 2001).

Maximum permissible metal concentrations in discharged wastewaters

The Guangdong effluent standard regulation sets maximum permissible levels of pollutants, including many metals and pH, in discharged wastewaters. For certain metals the regulations define three different levels depending on how the receiving water body is used (Guangdong Province 2001). These levels are summarised in Table D1, along with the highest concentrations found for all wastewaters analysed in this study.

Table D1. Maximum permissible metal concentrations in discharged wastewaters under the Guangdong effluent standard, and the highest level found in this study. All metal concentrations are in µg/l

	pH	Beryllium	Cadmium	Chromium	Copper	Lead	Manganese	Nickel	Zinc
Guangdong effluent standards	6-9	5	100	1500	500 1000 2000	1000	2000 2000 5000	1000	2000 3000 5000
Maximum level found	1 (Min)	123	21	1230	25600	382	17100	520	3240

Contaminated sediments threshold levels and local background levels for metals

Standards defining thresholds for acceptable levels of metals in sediments have not been defined in mainland China. As a result, previous studies that investigated sedimentary metal concentrations in China have made use of various standards from other countries for comparison, including threshold levels for seriously contaminated sediments in the Netherlands (Cheung 2003, NMHSPE 2000) and levels defined by the National Oceanic and Atmospheric Administration (NOAA) of America, above which adverse biological effects have been usually observed in aquatic organisms (Wang *et al*. 2009, Long & Morgan 1990). Though somewhat different in composition, acceptable environmental quality standards have been set for soils in China (MEP 1996). Some published data indicate general local background levels of metals in sediments, both for deep sediments in the Pearl River Delta Estuary (Wang *et al*. 2008) and sediments from a relatively uncontaminated inland area in Guangdong province (Cheung *et al*. 2003). These threshold and background levels are summarised in Table D2. In all cases, no data are available for beryllium, manganese and tin.

Table D2. Contaminated sediments threshold levels and local background levels for certain metals, in mg/kg. (a) NMHSPE 2000, (b) Long & Morgan 1990, (c) MEP 1996, (d) Wang *et al*. 2008, (e) Cheung *et al*. 2003

	Beryllium	Cadmium	Chromium	Copper	Lead	Manganese	Nickel	Tin	Zinc
Dutch threshold (a)	-	12	380	190	530	-	210	-	720
NOAA level (b)	-	9.6	145	390	110	-	50	-	270
Soil level, China (c)	-	1	300	400	500	-	200	-	500
Background, estuary (d)	-	-	65	38	28	-	34	-	100
Background, inland (e)	-	2.5	30	25	80	-	70	-	80

image Local fishing boats moored by the Kingboard (Panyu Nansha) Petrochemical Limited outflow discharge pipe

The sediment sample collected by the concealed pipe (CN09006) contained high levels of many of the metals that were also present at high levels in the wastewater discharged at this location (CN09005), including beryllium, cadmium, chromium, copper, lead, tin and zinc. The levels of these metals in the sediment indicate their accumulation over time as a result of ongoing discharge of contaminated wastewaters. It is likely that the sediment levels of these metals would have been far higher at this location had the wastewaters not been so acidic, which greatly increases the mobility of discharged metals. As this discharged wastewater mixes with water from the receiving water body, the acidity will decrease, which is likely to result in the partitioning of these metals into sediments further from the outfall.

None of the organic chemicals identified in the associated wastewater (CN09005) were identified in this sediment (CN09006). Two benzoic acid derivatives were identified, though with no known uses in the manufacturing of printed circuit boards, as well as two brominated compounds that could not be fully identified. The source of these chemicals in this sediment is not clear.

Sediment collected from ground below the main discharge pipe (CN09004) was contaminated with metals to an even greater extent, containing extremely high levels of copper and tin, as well as high levels of cadmium and nickel. In contrast, the wastewater collected from this pipe (CN09003) contained only moderate to low levels of these metals. The very high levels of certain metals in this sediment indicate that wastes containing high levels of these metals have been previously, or are periodically, discharged via this pipe, though this was not the case at the time of sampling. This may reflect discharge of wastewaters that vary significantly in quality over time, but could also result from historic releases that no longer take place. As this sediment was collected from ground below the pipe, and not from the open channel itself, it is not likely that the high metal levels in the sediment are due to the discharge of wastewater via the other, concealed pipe into the upstream section of this channel.

For this sediment, the level of copper (30500 mg/kg) was more than 800 times higher than levels commonly found in uncontaminated sediments (ATSDR 2004, Wang *et al*. 2008, Cheung *et al*. 2003). Although there is no Chinese contaminated sediment standard for comparison, the level of copper was over 70 times higher than the acceptable environmental quality standard for soils in China (MEP 1996), and also far exceeded contaminated sediment threshold levels from other countries, by up to 160 times (NMHSPE 2000). The manufacture of printed circuit boards has been recognised as a major source of copper in Hong Kong waters (EPD 1991). In addition, the level of nickel was over 5 times higher than typical background sediment levels (Salomons & Forstner 1984, Cheung *et al*. 2003) and also exceeded acceptable environmental quality standards for soils in China (MEP 1996) and contaminated sediment threshold levels from other countries. The sediment threshold levels and Chinese soil standard do not define limits for tin, a metal usually found in uncontaminated sediments at below 10 mg/kg (ATSDR 2005a). The level of tin in CN09004 was, however, over 2600 times this background level. See Box D for details on these metals and the threshold levels discussed.

This sediment (CN09004) also contained a brominated compound that could not be fully identified, and a trace of pentachlorobenzene. The source of pentachlorobenzene is not clear as it was not present in any other sample collected from this site, including wastewaters. This toxic and persistent chemical is known to be formed unintentionally during the combustion of solid wastes, or as a by-product of the partial degradation of other chlorinated organic compounds, such asthe agricultural fungicide, quintozene. Due to its highly persistent nature, this chemical has been found to be widespread in the environment (Bailey *et al*. 2009).

Two other sediments not associated with identified wastewater discharges were also analysed, one from a lagoon bordering the Pa River (CN09002) and one from the Pa River itself, the latter collected from approximately 1 km upstream from this site, to control for chemical residues arising from upstream sources.

The sediment from the lagoon (CN09002) contained a very high level of copper (30300 mg/kg), as may have been expected from its distinctive colouration, as well as beryllium, zinc and, to a lesser extent, lead at levels somewhat higher than usually found in uncontaminated sediments (Cheung *et al*. 2003, Salomons & Forstner 1984, Taylor *et al*. 2003). The copper level is virtually identical to that in the sediment collected by the main pipe (CN09004), which is over 800 times higher than background levels in sediments, up to 160 times higher than contaminated sediment threshold levels from other countries (NMHSPE 2000), and over 70 times higher than the acceptable level for soil in China (MEP 1996). The level of beryllium was approximately 10 times that found in sediment collected from the Pa River upstream of this site (CN09001). In contrast, this upstream sample contained cadmium, zinc and lead at similar concentrations to those found in the lagoon sediment (CN09002), indicating that other upstream sources may be largely responsible for the elevated levels of these metals in the main river, and possibly also the lagoon.

Although no direct wastewater discharges into the lagoon were observed, these data indicate that there have been significant inputs of metals to this area, particularly for copper and beryllium, though it is not clear if such inputs are ongoing.

No significant organic chemicals were identified in the sediment from the lagoon (CN09002) or the upstream sediment (CN09001), other than traces of polybrominated diphenyl ethers (PBDEs) in the lagoon sediment. These chemicals were not found in other samples associated with this site and may be present in the lagoon due to historic inputs to the lagoon. However, PBDEs are persistent chemicals and have been found to be widespread in the environmental, including within the Pearl River system, even at sources far from their point of release (Guan 2009a, Watanabe & Sakai 2003). Such long-range transport may have contributed to their presence at trace levels in this lagoon.

4.2) Kingboard (Panyu Nansha) Industrial Area

This facility is part of Kingboard Chemical Holdings Ltd., one of the world's largest manufacturers of laminates and printed circuit boards, with upstream capabilities in manufacture of chemicals, copper foil, glass fabric, glass yarn, bleached kraft paper, liquid crystal displays and magnetic products (Kingboard 2009).

The Kingboard (Panyu Nasha) Industrial Area is located in the Nansha Economic and Technological Development Area, Panyu (Guangdong Province). This site includes three separate facilities, the Kingboard (Panyu Nansha) Petrochemical facility, New Poly Chemical (Guangzhou), and Guangzhou Chung Shun Century Fibre Glass. Activities within the site include the manufacture of epoxy resins, low and high brominated resins, as well as tetrabromobisphenol-A (TBBPA), which is used in the manufacture of brominated laminate materials. Other products include melamine and sulphuric acid amine. These products are all manufactured in the range of thousands of tonnes annually at this facility (Kingboard NS 2009).

The New Poly Chemical facility, a subsidiary of Kingboard Laminates Holdings (Deloitte 2006), manufactures brominated epoxy resins, some of which are used within the Kingboard facility (New Poly Chemical 2009). The Guangzhou Chung Shun Century Fibre Glass plant manufactures non-alkali glass yarn for electronic use (Kingboard Zhongz 2009). Other petrochemical facilities are located adjacent to the Kingboard Industrial Area. These include BP Guangdong Oil Product, Guangzhou Huakai Gas and the Zhujiang Natural Gas Power Plant. Adjacent to the Kingboard site is a separate WWTP (Guangzhou Nansha Water Sewage Plant). According to available information, this treatment plant does not treat the industrial wastewaters from the Kingboard facility (Guangzhou Nansha 2009)

The discharge of wastewaters from the Kingboard Industrial Area into the Pearl River was observed at four separate locations. The specific sources for each of the individual discharges could not be confirmed, other than that they originated from within the Kingboard site.

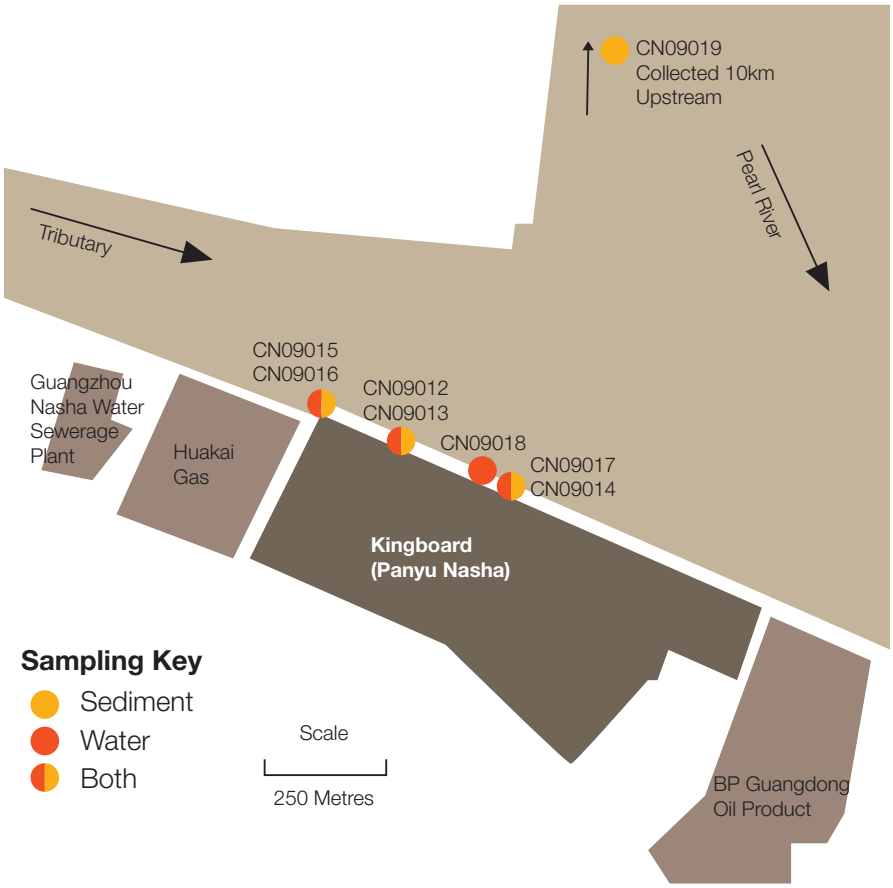
For three of the outfalls, a sample of discharged wastewater was collected along with sediment close to the point of discharge. For the smaller of the four discharges (Outfall 4), only wastewater was collected, as no sediment was available at this location. In addition, a sample of sediment was collected from the Pearl River approximately 10 km upstream of the Kingboard (Panyu Nasha) Industrial Area in order to distinguish chemicals due to releases from upstream sources. Details of these samples are presented in Table 3a, and their collection locations are shown on a map in Figure 3.

Table 3a. Description of samples collected from the vicinity of the Kingboard (Panyu Nansha) Industrial Area in the Nansha Economic and Technological Development Area, Panyu, Guangdong Province, China, 2009

Sample	Type	Description
CN09012	wastewater	Outfall 1: discharged via a large concrete pipe (as CN09013)
CN09013	sediment	Outfall 1: from point of wastewater discharge via large concrete pipe (as CN09012)
CN09015	wastewater	Outfall 2: discharged via a large concrete pipe adjacent to a security post (as CN09016)
CN09016	sediment	Outfall 2: shallow channel between the discharge pipe and the main river (as CN09015)
CN0901	wastewater	Outfall 3: discharged via a smaller concrete pipe (as CN09014)
CN0901	sediment	Outfall 3: from point of wastewater discharge via smaller pipe (as CN09017)
CN0901	wastewater	Outfall 4: milky white liquid discharged via a small concrete pipe through perimeter wall of the facility. No sediment present at this location
CN09019	sediment	Control: From the Pearl River approximately 10 km upstream of the Kingboard facility

image Kingboard (Panyu Nansha) Petrochemical Company Limited outflow waste discharge pipe

Figure 3. Sketch map of the Kingboard (Panyu Nansha) Industrial Area showing the locations from which samples were collected



4.2.1) Results

A limited range of organic chemicals was identified in the wastewater samples collected from the two larger discharge pipes (CN09012 from outfall 1, and CN09015 from outfall 2). This included TBBPA, a brominated flame retardant, in both wastewaters, and three phthalate esters (di(ethylhexyl) phthalate (DEHP), also known as dioctyl phthalate, di-n-butyl phthalate (DnBP) and di-iso-butyl phthalate (DiBP)) in CN09012 from Outfall 1

The brominated flame retardant TBBPA is produced and used in the manufacture of printed circuit boards within this facility. This chemical was also identified in wastewaters discharged from the Kingboard (Fogang) Industrial Area, and discussed in Section 4.1, and further in Box A.

Table 3b. Organic chemicals identified, and concentrations of volatile organic chemicals (VOC), metals and metalloids, in samples of wastewater and sediment associated with the Kingboard (Panyu Nansha) Industrial Area in Panyu, Guangdong Province, China, 2009. For wastewater samples, concentrations are given for whole (unfiltered) samples, dissolved concentrations accounted for greater than 75% of the whole sample concentration unless otherwise indicated; 50-75%[a], 25-50%[b], <25%[c]

Sample	CN09012	CN09015	CN09017	CN09018	CN09019	CN09013	CN09016	CN09014
Brief description	Wastewater				Sediment			
Type	Outfall 1 large pipe	Outfall 2 large pipe	Outfall 3 large pipe	Outfall 4 large pipe	Pearl River Upstream	Outfall 1 large pipe	Outfall 2 large pipe	Outfall 3 large pipe
PH	8	7	7	6	-	-	-	-
METAL	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Antimony	<50	<50	<50	<50	<20	<20	<20	<20
Arsenic	<50	<50	<50	<50	24	<20	22	23
Beryllium	<5	<5	<5	<5	2.0	1.5	0.8	0.7
Cadmium	<5	<5	<5	<5	1.0	1.0	<1.0	<1.0
Chromium	<20	<20	<20	<20	69	54	55	20
Chromium (VI)	<50	<50	<50	<50	-	-	-	-
Cobalt	<20	<20	<20	<20	17	11	7	5
Copper	43	<20	<20	<20	72	56	59	13
Lead	<50	<50	<50	<50	58	42	43	18
Manganese	150	319[a]	563	257	6	7	6	2
Mercury	<2	<2	<2	<2	<0.2	0.7	0.7	0.2
Nickel	<20	<20	<20	97	43	49	57	13
Selenium	<200	<200	<200	<200	<30	<30	<30	<30
Thallium	<20	<20	<20	<20	<10	<10	<10	<10
Tin	<100	<100	<100	<100	<10	<10	<10	<10
Vanadium	<20	<20	<20	<20	55	67	58	16
Zinc	292[b]	41	197[c]	1370[c]	197	179	183	144

Table 3b. continued

Sample	CN09012	CN09015	CN09017	CN09018	CN09019	CN09013	CN09016	CN09014
Brief description	Wastewater				Sediment			
Organic compound isolated	10	34	99	125	9	9	22	33
No. Reliably identified (% of total)	6 (60%)	16 (47%)	59 (59%)	52 (42%)	7 (78%)	7 (78%)	18 (82%)	19 (58%)
Brominated compounds								
Tetrabromobisphenol A	1	1	1					
Deca-BDE (a PBDE)					1	1	1	1
Tri-bromophenol			1					
Other bromine compounds	1	3	19	3		3	1	8
Alkyl phosphate compounds								
Tris(2-ethylhexyl) phosphate			1					
Photoinitiators and related compounds								
Anthraquinone derivative			1					1
Benzoquinone derivative			2					
Naphthalenedione derivative			1					
Decadiene-dione derivative			1					
Phthalate esters								
DiBP/DnBP	2							
DEHP	1							1
Fatty acids and derivatives								
Acids			1	12				
Esters			1	8				
Amides				2				
Nitriles				1				
Aldehyde				1				
Thiol			1	1				
Alkene alcohol				1				
Other oxygen compounds								
Bisphenol-A			1					
Bisphenol-A derivatives			2					1
Dioctyl /diphenyl ether				1		1		1
Hydrocarbons								
PAHs			2					
Alkyl benzenes			6	1				2
Aliphatic hydrocarbons	1	12	18	21	6	2	16	4

Box E. Phthalates (phthalate esters)

Phthalates (or, more accurately, phthalate diesters) are non-halogenated chemicals with a diversity of uses, dominated by use as plasticisers (or softeners) in plastics, especially PVC (e.g. in cables and other flexible components). Other applications included uses as components of inks, adhesives, sealants, surface coatings and personal care products. Some phthalates are discrete chemicals, such as the well-known di(2-ethylhexyl) phthalate (DEHP), while others are complex mixtures of isomers, such as diisononyl phthalate (DINP).

All uses of phthalates, especially the major use as PVC plasticisers, result in large-scale losses to the environment (both indoors and outdoors) during the lifetime of products, and again following disposal. Within the EU alone, this amounts to thousands of tonnes a year (CSTEE 2001a). As a result, phthalates are among the most ubiquitous man-made chemicals found in the environment. They are widely found in the indoor environment, including in air and dust (Otake *et al*.2001, Butte & Heinzow 2002, Fromme *et al*. 2004) at concentrations that commonly reflect the prevalence of plastics and certain textiles within the rooms sampled (Abb *et al*. 2009). Phthalates are commonly found in human tissues, including in blood and, as metabolites, in urine (Colon *et al*. 2000, Blount *et al*. 2000, Silva *et al*. 2004), including reports of significantly higher levels of intake in children (Koch *et al*. 2006). In humans and other animals they are relatively rapidly metabolised to their monoester forms, but these are frequently more toxic than the parent compound (Dalgaard *et al*. 2001).

Substantial concerns exist with regard to the toxicity of phthalates to wildlife and humans. For example, DEHP, one of the most widely used to date, is known to be toxic to reproductive development in mammals, capable (in its monoester form MEHP) of interfering with development of the testes in early life, thought to be mediated through impacts on testosterone synthesis (Howdeshell *et al*. 2008, Lin *et al*. 2008). Even at low doses, exposure to mixtures of phthalates can result in cumulative effects on testicular development in rats (Martino-Andrade *et al*. 2008). In addition, adverse impacts on female reproductive success in adult rats and on development of the young have been reported following exposure to this chemical (Lovekamp-Swan & Davis 2003, Grande *et al*. 2006, 2007, Gray *et al*. 2006).

Butylbenzyl phthalate (BBP) and dibutyl phthalate (DBP) have also been reported to exert reproductive toxicity (Ema & Miyawaki 2002, Mylchreest *et al*. 2002, Aso *et al*. 2005). Both DEHP and DBP are classified as 'toxic to reproduction' within Europe. Other research has revealed a correlation between phthalate exposure during pregnancy and decreased ano-genital index (distance from the anus to the genitals) in male children (Swan *et al*. 2005).

Decreased AGI correlated with concentrations of four phthalate metabolites, namely monoethyl phthalate (MEP), mono-n-butyl phthalate (MBP), monobenzyl phthalate (MBzP), and monoisobutyl phthalate (MiBP). It was also found that DBP can not only be taken up by crops and enter the food chain, but also affects proteome formation as well as the physiology and the morphology of some crops during growth (Liao 2006). Other commonly used phthalates, including the isomeric forms DINP and DIDP (diisodecyl phthalate), are of concern because of observed effects on the liver and kidney, albeit at higher doses.

At present, there are relatively 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 that do exist, however, probably the best known is the EU-wide ban on the use of six phthalates in children's toys and childcare articles, first agreed as an emergency measure in 1999 and finally made permanent in 2005 (EC 2005). While this addresses one important exposure route, exposures through other consumer products have so far largely escaped regulation. Within Europe, at least, this could be about to change with the selection by the European Chemicals Agency (ECHA) of three phthalates (DBP, BBP and DEHP) as 'substances of very high concern' under the REACH Regulation (ECHA 2008), and the further proposal that these chemicals should be among the first shortlist of seven substances for which detailed justification and authorisation will be required for any proposed continued uses (ECHA 2009).

Regarding their release from industrial facilities, the discharge of wastewaters containing two phthalates, DEHP and DnBP, is regulated in Guangdong Province, with maximum permissible levels of between 0.2 mg/l and 2.0 mg/l depending on how the receiving water body is used (Guangdong Province 2001). Similarly, DEHP is listed within the EU as a priority substance under the Water Framework directive, a regulation designed to improve the quality of water within the EU (EU 2008). DEHP and DnBP have also been identified as substances for priority action under the OSPAR convention, under which signatory countries have agreed a target of cessation of discharges, emissions and losses of all hazardous substances to the marine environment of the North-East Atlantic by 2020, the 'one generation' cessation target (OSPAR 1998).

Phthalates (also known as phthalate esters) have many uses, primarily as plasticisers (or softeners) in plastics, with other uses including uses as components of inks and surface coatings. Substantial concerns exist with regard to the toxicity of phthalates to wildlife and humans. DEHP, one of the most widely used phthalates, is known to be toxic to reproductive development in mammals (Howdeshell *et al*. 2008, Lin *et al*. 2008) and dibutyl phthalate (DnBP) has also been reported to exert reproductive toxicity (Mylchreest *et al*. 2002).

For two of the phthalate esters that were identified, DEHP and DnBP, their discharge is regulated under the Guangdong effluent standard (Guangdong Province 2001), which sets limits of between 0.2 mg/l and 2.0 mg/l, though the third phthalate (DiBP) is not covered. The concentrations of phthalates in the wastewater sample (CN09012) were not quantified. Due to concerns about the environmental and human health effects associated with phthalate, regulations have also been put in place in certain regions outside of China that control their use and release. DEHP and DnBP are generally regarded as the more hazardous of this group of compounds and listed under such regulations (ECHA 2008, EU 2008). More information on phthalates and their regulation is given in Box E.

The concentrations of metals in the wastewater samples collected from the two larger discharge pipes (CN09012 & CN09015) were generally either below limits of detection for the methods used or within concentration ranges expected for uncontaminated surface waters. The exceptions to this were the concentrations of zinc (246 µg/l) and copper (43 µg/l) in the wastewater from Outfall 1 (CN09012), which are moderately higher than average background levels in surface waters (Cheung *et al*. 2003, ATSDR 2005b), though both far below the maximum allowable concentrations under the Guangdong effluent standard (See Box D).

Samples of sediment were collected by each of these two larger outfalls (CN09013 from Outfall 1, and CN09016 from Outfall 2). TBBPA was not identified in either sediment sample, although some other brominated compounds were isolated. Deca-BDE, a PBDE widely used as a flame retardant in plastics, textiles and other materials, was identified in both samples, along with some other brominated compounds that could not be fully identified. Deca-BDE was not identified in the wastewater samples from these outfalls and its presence in these sediments, as well as in all other sediments associated with this facility including one collected from the Pearl River upstream of the site, is likely to be due to the widespread presence of this relatively persistent chemical in the environment, including within the Pearl River basin (Guan *et al*. 2009a, Watanabe & Sakai 2003).

The only other chemicals identified in these two sediments were some simple hydrocarbons, and diphenyl ether in CN09013. The source of the diphenyl ether in this sample is not clear. Similarly, only simple hydrocarbons were identified in sediment collected from the Pearl River approximately 10 km upstream of the Kingboard Industrial Area (CN09019).

Furthermore, no metals were present in the sediments collected by these larger outfalls at concentrations significantly higher than the ranges of concentrations typically found in uncontaminated sediments, with levels being very similar to those found in the Pearl River upstream sediment (CN09019).

The analysis of samples associated with the two smaller outfalls that were identified for this facility showed a markedly different situation compared to samples associated with the two larger outfalls described above. Wastewater samples collected from a discharge via a smaller concrete pipe (CN09017) and via a small concrete pipe passing through the perimeter wall of the facility (CN09018) both contained a wide range of organic chemicals, though groups of chemicals were generally present in either one or the other (but not both) sample. It is noteworthy that the majority of the organic chemicals isolated from these wastewaters could not be fully identified, and therefore their properties and potential impacts remain unknown.

A complex range of compounds representing many different chemical groups were identified in CN09017, including:

- brominated flame retardants TBBPA and 2,4,6-tribromophenol, along with 19 other brominated compounds that could not be fully identified;
- an alkyl phosphate flame retardants, tris(2-ethylhexyl) phosphate;
- five photoinitiators, or closely related chemicals:
  - 2,6-di-tert-butyl-p-benzoquinone and two closely related compounds;
  - a naphthoquinone derivative; and
  - an anthraquinone derivate and a closely related chemical, 2-ethylanthracene
- bisphenol-A, and two derivatives; and
- a long chain fatty acid, and two derivatives.

Of the two brominated flame retardants, TBBPA was also identified in the two larger outfalls (CN09012 and CN09015) as discussed above. The other brominated chemical, 2,4,6-tribromophenol (2,4,6-TBP) is also used as a flame retardant (IUCLID 2003), but can additionally be formed by the degradation of TBBPA (Eriksson & Jakobsson 1998). There are reports that 2,4,6-TBP may cause development neurotoxicity, embryotoxicity and foetotoxicity. More information on this chemical is given in Box A.

Another flame retardant, which was also identified in the wastewater sample CN09017, tris(2-ethylhexyl)phosphate or TEHP, belongs to a family of organophosphorus esters (OPs). TEHP has been extensively used as a flame retardant, and as a solvent (WHO 2000a). TEHP has low acute toxicity for mammals and, while there is some evidence of carcinogenicity in animals at high levels of exposure, it is unlikely that TEHP poses a significant carcinogenic risk to humans (WHO 2000a). Further details are given in Box A.

A number of chemicals that are used as photoinitiators, as well as closely related chemicals, were again present in this wastewater. The photoinitiator-related chemicals were, however, of different types to those identified in the wastewaters from the Kingboard (Fogang) Industrial Area, where phenylethanone (acetophenone) and thioxanthenone compounds were identified. In contrast, the wastewater from the Kingboard (Panyu Nansha) site (CN09017) predominantly contained quinone-related compounds. Very limited information is available on the toxicity and fate of these chemicals. More detail is given in Box B.

Bisphenol A (BpA) is a very high production volume chemical. Globally its use is dominated by the manufacture of polycarbonate plastic and various epoxy resins, including those used in the manufacture of laminates for printed circuit boards (Lau *et al*. 2003). Bisphenol A has long been recognised as a potential endocrine disruptor, and animal experiment have shown impacts on reproductive systems (Sakaue *et al*. 2001, Soto *et al*. 2008) and brain development (Leranth *et al*. 2008) in mammals. Associations between BpA levels in urine and the prevalence of certain common medical conditions in humans have also been reported (Lang *et al*. 2008). Bisphenol A is also of great concern in the aquatic environment, particularly with regard to disruption of hormone systems in aquatic organisms. Contamination of sediments within the Pearl River Estuary with BpA has been previously reported (Peng *et al*. 2007).

The two Bisphenol-A derivates, a diglycidylether of bisphenol A (DGEBA) also known as bisphenol A diglycidylether (BADGE), and diallyl bisphenol A (DABPA) are used in, or associated with, the manufacture of printed circuit boards (Bimax 2009, Maw-Ling & Ze-Fa 2006, Yan *et al*. 2002). There are few data on the toxicity of these compounds, though what is available indicates that acute toxic effects in humans are unlikely (Poole *et al*. 2004). More information on BpA and the two derivatives is given in Box F.

A very large number of long chain fatty acids and fatty acid derivatives were identified in the wastewater discharged via one of the two smaller outfalls, collected from a small concrete pipe through perimeter wall of the facility (CN09018). The long chain fatty acid, hexadecanoic acid (also known as palmitic acid), was also identified in wastewater from the Kingboard (Fogang) facility. As discussed in Section 4.1, there are no known specific uses of fatty acids and their derivatives in the manufacture of printed circuit boards. Fatty acids and their derivatives are not of particular toxicological concern due to their low toxicity and being readily biodegradable.

For both wastewater samples collected from the two smaller discharges (CN09017 & CN09018), the only metal present at a high concentration was zinc, particularly in the wastewater from a small concrete pipe exiting through the perimeter wall of the facility (CN09018). The concentration in this sample (1370 µg/l) does not exceed discharge limits set under the Guangdong effluent standard (Guangdong Province 2001) but does further demonstrate poor management of contaminated wastewaters. For both wastewater samples, the zinc was predominantly absorbed onto suspended particles rather than in dissolved forms.

A sample of sediment collected by the smaller concrete pipe (CN09014) contained two chemicals present in the wastewater discharged via this pipe (CN09017), one of the bisphenol-A derivatives (DABPA) and an anthraquinone derivative. The presence of these chemicals in the sediment indicates their accumulation over time due to their ongoing discharge in wastewaters from this facility. The levels of all metals in this sediment were not significantly elevated above local background levels (CN09019).

Two other compounds present in the sediment, while not identified in the wastewater collected at this outfall, were identified in other samples collected from this site. These chemicals were a phthalate ester (DEHP), present in wastewater collected from one of the two larger discharge pipes (CN09012 from outfall 1), and diphenyl ether, a chemical also present in sediment collected by one of the two larger outfalls (CN09013 from outfall 1). Their presence in the sediment collected by the smaller concrete pipe (CN09014) may indicate their previous or periodic presence in wastes discharged via this outfall.

No associated sediment data are available for the other small discharge (CN09018) as no sediment as available for collection at this location.

Box F. Bisphenol-A

Bisphenol A (BpA) is a very high production volume chemical (one of the highest global production volumes of any man-made chemical), manufactured globally for a variety of uses, dominated by the manufacture of polycarbonate plastic and various epoxy resins and including widespread use in food-contact applications. Despite its polymeric form, repeated use and wear of polycarbonate plastics, especially at high temperatures, can result in significant hydrolysis of the plastic, releasing free bisphenol A (Brede *et al*. 2003, Kubwabo *et al*. 2009). As a result of the widespread use of polycarbonate and other bisphenol A-derivatives, human exposure to bisphenol A is ubiquitous; a recent study by the US Center for Disease Control (CDC) reported detectable 'conjugated' residues of BpA in 93% of human urine samples (Calafat *et al*. 2008). Furthermore, its occurrence in more biologically-active 'unconjugated' form in human blood also appears to be common, at levels which are thought to already exceed the presumed 'safe daily exposure' dose (Vandenberg *et al*. 2007), challenging long-held assumptions that BpA is rapidly metabolised and, therefore, detoxified in the human body.

Bisphenol A was recognised as a potent synthetic oestrogen (and therefore potential endocrine disruptor) as long ago as the 1930s, well before the polymerisation to epoxies and polycarbonate became commercially significant. Observed impacts of low dose BpA exposure in animals include decreased daily sperm production in rats (Sakaue *et al*. 2001), changes in maternal behaviour in mice (Palanza *et al*. 2002) and anomalous brain development in both rodents and primates (MacLusky *et al*. 2005, Leranth *et al*. 2007, 2008), themselves linked to aspects of sexual differentiation. Soto *et al*. (2008) summarise evidence for low dose BpA effects on the development of reproductive organs in rodents. Low dose exposure has also recently been found to interfere with insulin secretion in mice (Ropero *et al*. 2008), raising the concern that BpA exposure could be a contributory factor in the rise in type 2 diabetes in some parts of the world. Associations have also been reported between BpA levels in urine and the prevalence of certain other common medical conditions in humans in the US (Lang *et al*. 2008). Recent reviews of the mammalian toxicology of BpA are provided by Wellshons *et al*. (2006) and Crain *et al*. (2007).

Bisphenol A is also of great concern in the aquatic environment, to which it is estimated around 90% of emissions to the environment primarily occur (whether from industrial operations, discharges via sewers or leachates from landfills and waste dumps). BpA is widely distributed in freshwater systems (Fromme *et al*. 2002, Rodriguez-Mazaz *et al*. 2004), at concentrations that, though generally low away from industrial point sources, are nonetheless toxicologically relevant to a range of aquatic organisms, including through mechanisms of endocrine disruption (Kang *et al*. 2007). Although degradation of the parent compound can occur quite rapidly under aerobic conditions, some of its partial breakdown products are more environmentally persistent and can themselves show some oestrogenic activity (Suzuki *et al*. 2004). Furthermore, under conditions of low oxygen tension, including in sediments, degradation of BpA is considerably slower, allowing the compound to accumulate to higher levels (Planelló *et al*. 2008). Endocrine disrupting effects of BpA, often at environmentally relevant concentrations, have been reported in reptiles (Stoker *et al*. 2003), amphibians (Levy *et al*. 2004) and fish (Sohoni *et al*. 2001, Jurgella *et al*. 2006), as well as in molluscs (Oehlmann *et al*. 2006) and a range of other invertebrates (see Segner *et al*. 2003 for review). In the sediment-dwelling larvae of chironomid flies, for example (a keystone species in many aquatic systems), BpA interferes with the hormone ecdysone which controls moulting and structural development (Planelló *et al*. 2008), indicating that impacts on steroid hormone systems may be common across much of the animal kingdom.

Despite the increasing level of evidence regarding exposure and effects of bisphenol A, regulation of its manufacture and use remains a controversial issue globally as a result of long-standing disagreements in both scientific and policy terms regarding the significance of low dose effects. Nonetheless, the widespread contamination of freshwater systems, combined with the potential for effects at low doses, have recently contributed to proposals by the Government of Canada to list BpA as a toxic substance under the Environmental Protection Act (1999) (Government of Canada 2009). Moreover, in response to the particular concerns relating to human exposure to BpA through use of polycarbonate products (especially in children under 18 months), the Government of Canada recently announced its intention to tighten regulations on the use of BpA in consumer goods, including a ban on the advertising, sale and import of polycarbonate baby bottles (Health Canada 2009). Canada is the first country to introduce such controls.

One of the Bisphenol-A derivates identified, a diglycidylether of bisphenol A (DGEBA), also known as bisphenol A diglycidylether (BADGE), is used the manufacture of composite laminates, including those for use in printed circuit boards (Yan *et al*. 2002). From the currently available data for this compound, no significant acute toxicological effects on humans have been observed (Poole *et al*. 2004). The second derivative, diallyl bisphenol A (DABPA) is also known to be used by this sector, including in the manufacture of laminate resins (Bimax 2009, Wang & Lee 2006). No information is available on the toxicity or other hazards relating to this compound.

image Residents living on fishing boats near the Kingboard (Panyu Nansha) Petrochemical Company Limited

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4.3) Wing Fung P.C. Board Co., Ltd.

The Wing Fung P.C. Board Co., Ltd. Facility (herein referred to as Wing Fung) is located in the Jiao Yuan Industrial Zone, Shajing Town, Shenzhen, in an industrial area together with many other types of industrial facilities. This facility is reported to produce multi-layered printed circuit boards (Jobcn 2009). What appears to be a WWTP can be observed within the Wing Fung site as well as a number of storage tanks for corrosive and toxic liquids. It is suspected that some of the wastes produced by this facility are transported offsite for treatment, though this could not be confirmed.

The Wing Fung facility discharges wastewater into an open channel via an outfall indicated to be the 'Wing Fung Inspection Site'. This open channel, which also receives wastewater from other facilities both upstream and downstream of the Wing Fung facility, flows into a tributary of the Pearl River system, ultimately reaching the ocean close to the mouth of the Pearl River itself (Bao'An Government 2008).

A sample of wastewater (CN09028) was collected at the point of discharge, along with a sample of sediment (CN09029) from the open channel at the discharge point. To distinguish other chemicals present in the channel sediment that may have been discharged by facilities upstream of Wing Fung, a second sample of sediment (CN09026) was collected from the open channel 10m upstream of the discharge point. Details of these samples are presented in Table 4a.

4.3.1) Results

The discharged wastewater (CN09028) contained copper at an extremely high level (25600 µg/l), as well as a high level of nickel (520 µg/l). The level of copper, the highest for all wastewater samples in this study, far exceeds the maximum allowable concentrations set under the Guangdong effluent standard, which sets limits of between 500 and 2000 µg/l depending on how the receiving water body is used (Guangdong Province 2001). It has not been possible to determine the use category of the water body in this situation. The level in the wastewater was over 12 times the highest limit and over 50 times the lower limit. The level of nickel, though below the Guangdong effluent standard for this metal, was over 50 times local background levels for surface water (Cheung *et al*. 2003), and indicates significant releases of this metal with the wastewater. Both metals were present in the wastewater in dissolved forms, which generally indicates relatively high mobility and bioavailability.

The wastewater also contained a number of organic chemicals, including:

- TBBPA, a brominated flame retardant, and 10 other brominated compounds;
- two phthalate esters: DnBP and BiBP;
- six photoinitiators, or closely related chemicals, including:
  - Quantacure ITX;
  - Benzophenone;
  - diphenylethandione or 'benzil', a phenylethanone derivative;
  - a diphenylethanone derivative known as DMPA or 'Photocure 51'; and
  - a coumarin derivative.
- benzoic acid, and two derivatives - a benzoic acid ester and a benzoic acid thiol; and
- N-formylmorpholine.

Table 4a. Description of samples collected from the vicinity of the Wing Fung P.C. Board facility in the Jiao Yuan Industrial Zone, Shenzhen, China, 2009

Sample	Type	Description
CN09028	wastewater	Collected at point of discharge from the Wing Fung facility into a communal channel
CN09029	sediment	Wastewater channel, at the point of wastewater discharge from the Wing Fung facility
CN09026	sediment	Wastewater channel, 10m upstream of the discharge from the Wing Fung facility

Sample	CN09028	CN09029	CN09026
Type	Wastewater	Sediment	
Brief description	discharge	by discharge	upstream
pH	8	-	-
METAL	**(µg/l)**	**(mg/kg)**	**(mg/kg)**
Antimony	<50	<20	<20
Arsenic	<50	<20	<20
Beryllium	<5	<0.5	<0.5
Cadmium	<5	<1.0	<1.0
Chromium	<20	111	147
Chromium (VI)	<50	-	-
Cobalt	<20	7	6
Copper	25600	2480	380
Lead	<50	28	22
Manganese	140	2	1
Mercury	<2	<0.2	<0.2
Nickel	520	72	46
Selenium	<200	<30	<30
Thallium	<20	<10	<10
Tin	<100	203	86
Vanadium	<20	25	15
Zinc	31[a]	587	456
Organic compound isolated	60	31	44
No. Reliably identified (% of total)	28 (47%)	26 (84%)	44 (100%)
Brominated compounds			
Tetrabromobisphenol A	1		
Deca-BDE (a PBDE)		1	1
Other PBDEs		7	15
Other bromine compounds	10		
Photoinitiators and related compounds			
Diphenylethandione	1		
Diphenylethanone derivative	1		
Phenylethanone derivative	1		
Quantacure ITX	1		
Benzophenone	1		
Coumarin derivative	1		
Phthalate esters			
DiBP/DnBP	2		
Other oxygen compounds			
Benzoic acid and esters	2		
Benzoic acid thiol	1		
Alkyl alcohols	1		
Nitrogen compounds			
N-Formyl morpholine	1		
Hydrocarbons			
PAHs	1		3
Alkyl benzenes	1	1	1
Alkenyl benzene		1	1
Aliphatic hydrocarbons	2	15	21
Natural sesquiterpenoid		1	2

Table 4b. Organic chemicals identified, and concentrations of metals and metalloids, in samples of wastewater and sediment associated with the Wing Fung P.C. Board Co., Ltd. facility in Shenzhen, China, 2009. For wastewater samples, concentrations are given for whole (unfiltered) samples, dissolved concentration accounted for greater than 75% of the whole sample concentration unless otherwise indicated; 50-75%[a]

Many of the organic chemicals were also identified in wastewaters discharged from other facilities and are discussed above. These include TBBPA and the two phthalate esters (DnBP and DiBP), which were also identified in samples from the Kingboard Panyu Nasha Industrial Area (CN09012, see Section 4.2), as well as four of the photoinitiator related compounds (Quantacure ITX, DMPA or 'Photocure 51', a phenylethanone morpholine derivative, and the coumarin derivative) all identified in samples from the Kingboard Fogang Industrial Area (CN09003, see Section 4.1).

Of the other two photoinitiator compounds present in the Wing Fung wastewater, benzophenone is known to have uses as a photoinitiator (Eustis *et al*. 2006), though it also has many other industrial uses including as an additive for plastics and adhesives (US DHHS 2000), while benzil (diphenylethanedione) can be used in the production of DMPA (Kitamura *et al*. 1992). Benzophenone has been found to have toxic effects to liver and kidney on experiments animals (US DHHS 2000) and has displayed potential hormone disrupting properties in several tests (Matsumoto *et al*. 2005, Kawamura *et al*. 2003). Further information on photoinitiators and related compounds is given in Box B.

Benzoic acid esters are not of particular environmental concern as they can occur as natural components of plants (Dudareva *et al*. 2000), though their presence in the wastewaters at other similar facilities suggests their industrial application in this case. The benzoic acid ester, as well as many of the photoinitiator related compounds present in the wastewater, have been found in the discharges from other facilities involved in the manufacture of printed circuit boards, both in China and elsewhere (Brigden *et al*. 2007).

The wastewater also contained N-formylmorpholine, a chemical with uses as a solvent (Alqattan *et al*. 1995) that is reported to have very low toxicity (BASF 2007). The source of this chemical to the wastewater for this facility is not clear, but it may originate from the degradation of a phenylethanone morpholine-based photoinitiator also identified in the same wastewater.

Sediment collected from the receiving channel near to the discharge (CN09029) contained certain metals at high levels, particularly copper, and to a lesser extent nickel, tin and zinc. The levels of copper and nickel indicate the accumulation of these metals in the channel due to the ongoing discharge of wastewaters from the Wing Fung facility. Although tin was not detected in the wastewater at the time of sample collection, it is likely that the elevated level of tin in the sediment is also due to releases from Wing Fung as this metal is commonly used in the manufacture of printed circuit boards, and has been found in discharges from this type of facility elsewhere (Section 3.1 above and Brigden *et al*. 2007).

The level of copper in the channel sediment (CN09029, 2480 mg/kg) was over 60 times typical background levels (Cheung *et al*. 2003, ATSDR 2004) and, although there is no relevant contaminated sediment standard in China for comparison, the level was 6 times higher than the acceptable environmental quality standards for soils in China (MEP 1996), and exceeded contaminated sediment threshold levels from other countries by up to 13 times (NMHSPE 2000). Sediment collected from the same channel upstream of the outfall (CN09026) also contained copper (380 mg/kg) at a concentration higher than usually found in sediments, though far lower than that in the sediment by the Wing Fung outfall, indicating that there may be additional sources of copper to the channel upstream of the identified Wing Fung outfall. Chromium and zinc were found at similar levels in both the sediment collected near to the discharge (CN09029) and in the upstream sample (CN09026), indicating that their presence in the channel is largely due to other upstream sources rather than discharges from Wing Fung. See Box D for more details on these metals and their threshold levels.

The sediment by the outfall (CN09029) did not contain any of the organic chemicals identified in the discharged wastewater, other than some hydrocarbons. This sediment did, however, contain some compounds that were not found in the Wing Fung wastewater, including some PBDEs and an alkenyl benzene, but these substances were also identified in the upstream sediment (CN09026) indicating their presence in the canal is once again unrelated to discharges from the Wing Fung facility.

4.4) QingYuan Top Dragon Textile Co., Ltd.

The QingYuan Top Dragon Textile facility (herein referred to as Top Dragon) is located in the Taihe Industry Zone, Qingxin, Qingyuan (Guangdong Province). This facility is situated adjacent to Leyuan Village, on the banks of a stream flowing from the Taihe Ancient Cave area. The stream ultimately flows into the North River (Beijiang River), one of the main branches of the Pearl River system.

This facility produces various textiles, primarily hemp and cotton-based denim products. Processes carried out within the facility include sizing, dyeing, weaving and finishing, and includes the use of indigo-based and sulphur black-based dyes (Qingyuan Top Dragon 2009). There is a WWTP within the facility for treating industrial wastewaters arising from the dyeing processes, with a capacity of 500 tonnes of wastewater per day. The quality of treated wastewater discharged from this facility is only checked for a limited range of general parameters, including chemical and biological oxygen demands, suspended solids, pH and colour (Environmental Technology Centre GDETC 2009). There are previous media reports that discharged wastewaters have exceeded applicable effluent standards, though details are not available (GD Xinhua 2008)

There are no known significant industrial wastewater inputs to the stream upstream of the Top Dragon facility, though four very small workshops are located adjacent to Top Dragon, including a chemical workshop and an electroplating workshop.

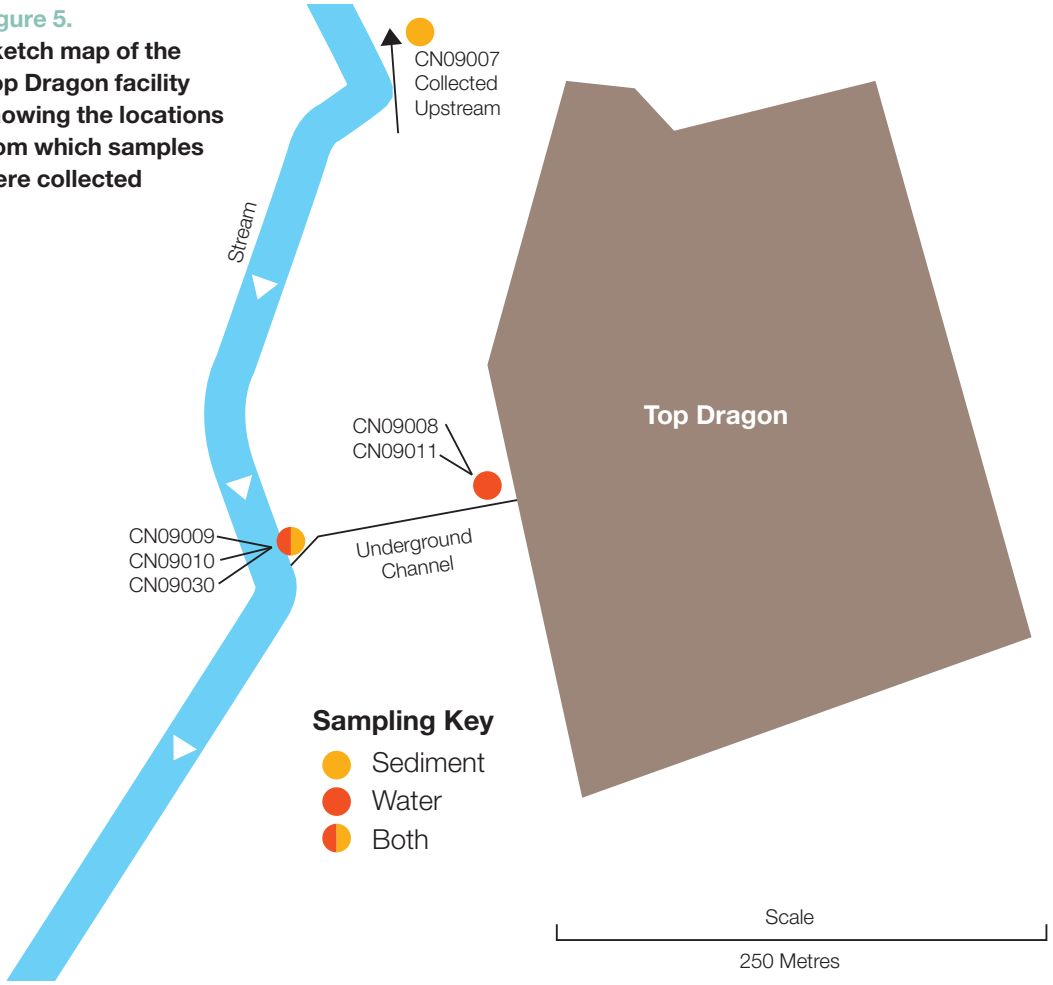
Wastewater is discharged from Top Dragon via an underground channel which flows into the nearby stream approximately 100m from the facility. Samples of wastewater (CN09008 and CN09011) were collected from the start of the underground channel via a hatch located just outside the Top Dragon wastewater treatment facility. Samples of wastewater (CN09009 and CN09030) were also collected at the point where the underground channel flows into the stream, along with sediment from the stream at this point (CN09010). To determine whether there are any significant chemical inputs to the stream upstream of Top Dragon, a sample of stream sediment (CN09007) was also collected, approximately 0.5 km upstream of the outfall. Details of these samples are presented in Table 5a, and their collection locations are shown on a map in Figure 5.

Locals have reported that the quality of discharged wastewaters is worse, and the volume greater, during the late evening. To investigate the variability in chemical composition over time, the discharged wastewater was sampled from the two locations both in the morning and afternoon or night time. During both sampling periods, a strong sulphurous smell was present in the vicinity of this facility.

Table 5a. Description of samples collected from the vicinity of the Top Dragon facility in the Taihe Industry Zone, Qingxin, Qingyuan in Guangdong Province, China, 2009

Sample	Type	Description	Date / Time
CN09008	wastewater	From a wastewater outfall into an underground channel, collected via a hatch located just outside the Top Dragon wastewater treatment facility. Channel flows approximately 100 m underground before entering a stream, see CN09009 and CN09030	01-06-09 11pm
CN09011	wastewater		02-06-09 11am
CN09009	wastewater	From the outfall of the underground channel, where it flows into a stream approx. 100 m from the Top Dragon facility (as CN09010)	02-06-09 10am
CN09030	wastewater		05-06-09 4pm
CN09010	sediment	From the outfall of the underground channel, where it flows into a stream approx. 100 m from the Top Dragon facility (as CN09009 and CN09030)	
CN09007	sediment	Receiving stream, approximately 0.5 km upstream of the underground channel outfall	

Figure 5.
Sketch map of the Top Dragon facility showing the locations from which samples were collected



4.4.1) Results

Similar results were obtained from the analyses of the two wastewater samples collected during the morning time (2 June 2009), from the start of the underground channel via a hatch at the boundary of the facility (CN09011), and from the outfall of the underground channel into the stream (CN09009). The two samples had almost identical metal concentrations, both with a reasonably high level of manganese (978 µg/l and 1110 µg/l respectively). Other metal concentrations were generally either below limits of detection for the methods used or within concentration ranges expected for uncontaminated surface waters.

The sample collected from the start of the channel during the previous night (MI09008) contained manganese at a far higher level (5390 µg/l). A sample collected from the outfall of the channel into the stream at 4pm a few days later (CN09030) was somewhat different in composition. The level of manganese was far lower than in all other wastewater samples, while the levels of zinc and vanadium were somewhat higher, though only slightly above the typical ranges of concentrations for these metals in uncontaminated surface waters.

Table 5b. Organic chemicals identified, and concentrations of metals and metalloids, in samples of wastewater and sediment associated with the Top Dragon Textile facility in the Taihe Industry Zone, Guangdong Province, China, 2009. (..) signifies compounds identified at trace levels using a selective SIM method. For wastewater samples, concentrations are given for whole (unfiltered) samples, dissolved concentration accounted for greater than 75% of the whole sample concentration unless otherwise indicated; 50-75%[a], 25-50%[b]

Sample	CN09003	CN09005	CN09004	CN09006	CN09002	CN09001
Type	Wastewater				Sediment	
Brief description	channel start, via hatch		channel outfall		channel	stream,
	11am	11pm	10 am	4 pm	outfall	upstream
pH	8	7	7	6	-	-
METAL	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(mg/kg)	(mg/kg)
Antimony	<50	<50	<50	<50	<20	<20
Arsenic	<50	<50	<50	<50	<20	<20
Beryllium	<5	<5	<5	<5	<0.5	<0.5
Cadmium	<5	<5	<5	<5	1.3	<1.0
Chromium	<20	<20	<20	<20	94	8
Chromium (VI)	<50	<50	<50	<50	-	-
Cobalt	<20	<20	<20	<20	17	4
Copper	<20	<20	<20	<20	41	4
Lead	<50	<50	<50	<50	19	<5
Manganese	978	5930	1110	163	10	1
Mercury	<2	<2	<2	<2	<0.2	<0.2
Nickel	27	40	29	<20	58	8
Selenium	<200	<200	<200	<200	<30	<30
Thallium	<20	<20	<20	<20	<10	<10
Tin	<100	<100	<100	<100	<10	<10
Vanadium	<20	<20	<20	62[a]	22	9
Zinc	12	34[b]	14	90	138	38
Organic compound isolated	59	34	33	12	19	16
No. Reliably identified (% of total)	20 (34%)	15 (44%)	10 (30%)	5 (42%)	7 (37%)	4 (25%)
Chlorinated compounds						
Di-chlorinated benzenes		(1)				
Alkyl phosphate compounds						
Tris(2-ethylhexyl)phosphate		1	1			
Photoinitiators and related compounds						
Benzoquinone derivative	1					
Tetrahydro naphthalenedione derivative	1					
Alkylphenols and derivatives						
Nonyl phenols	3					
Fatty acids and derivatives						
Acids	2	3	1			
hydroxy ester derivatives	2					
Other oxygen compounds						
Furanone derivative		1				
Cyclodecanone derivative		1				
Alkyl alcohols	1		1			
Other nitrogen or sulphur compounds						
Indole	1			1		
Amine; N-methyl aniline	1	1	1	1		
Amide; formanilide		1	1			
Alkyl thiols	1					
Sulphur			1	1	1	
Hydrocarbons						
Alkyl benzenes	1		1			
Aliphatic hydrocarbons	6	6	3	2	6	4

The highest concentration of manganese in the wastewater samples (5390 µg/l, CN09008 collected during the night) exceeds the Guangdong effluent standard (Guangdong Province 2001). As noted above, this regulation sets different levels depending on the use category for the receiving water body, with limits for manganese ranging from 2000 to 5000 µg/l. It has not been possible to determine the use category in this situation. Separate legislation that sets effluent standards for this specific sector does not define a limit for manganese (MEP 1992). Concentrations of manganese in surface waters are typically below 200 µg/l, and often far lower (Barceloux 1999). The source of manganese from this facility is not clear as this metal is not recognised to be commonly used in the textile industry (IPPC 2003). Manganese is an essential trace metal, although exposure to high levels can result in toxic effects for human and animal, including neurotoxic effects in humans following high doses (ATSDR 2008b, Michalke *et al*. 2007). More information is given in Box D.

Many groups of organic chemicals were also identified in the various wastewater samples. All four wastewaters contained N-methyl aniline. Other than this compound, there were substantial differences between the two samples collected during the morning. Among the compounds identified in the sample from the start of the channel (CN09011) were:

- three nonyl phenols;
- two photoinitiator and related compounds; and
- two long chain fatty acids and their hydroxyesters.

In contrast, other than N-methyl aniline, these chemicals were not identified in the sample from the outfall of the channel (CN09009), in which different chemicals were identified, including:

- N-phenyl-formamide (formanilide);
- alkyl phosphate flame retardant, tris(2-ethylhexyl) phosphate; and
- a different long chain fatty acid.

Some of the above mentioned compounds were also identified in the wastewater collected at the start of the channel during the previous night (CN09008), including the alkyl phosphate flame retardant, some long chain fatty acids, N-phenyl-formamide and N-methyl aniline. This sample also contained a dichlorobenzene, though only at a trace level. None of the compounds discussed above for other wastewater samples were identified in the wastewater collected from the outfall of the channel into the stream at 4pm a few days later (CN09030), other than N-methyl aniline which, as noted above, was present in all wastewater samples.

Substituted aniline compounds such as N-methyl aniline are used in some dyeing processes (IPPC 2003). N-methyl aniline is readily degraded under aerobic conditions and is therefore not expected to be a persistent chemical in the environment (Watson 1993). N-methyl aniline can cause impacts on aquatic life, though generally only at high levels of exposure (Groth *et al*. 1993). For humans, exposure may lead to impacts on haemoglobin, though again only following high levels of exposure (ACGIH 1991). The closely related chemical N-phenyl-formamide (formanilide) is likely to have been present due to the degradation of N-methyl aniline within the channel (Lyons *et al*. 1984).

Nonyl phenols (NPs) are closely related chemicals to octyl phenol (OP), which was identified in wastewaters from the Kingboard (Fogang) Industrial Area. Alkyl phenols (APs), which include NPs and OPs, are persistent, bioaccumulative and toxic to aquatic life, including through hormone disrupting effects (OSPAR 2001, Jobling *et al*. 1996). Nonyl phenols have been reported to be widespread in sediments from the Pearl River Estuary (Chen *et al*. 2006, Peng *et al*. 2007).

Due to concerns about the hazardous nature of NPs, regulations have also been put in place in certain regions outside of China that control their use and release. Within the EU, NP has been included as a 'priority hazardous substance' under the Water Framework Directive, such that action to prevent releases to water within 20 years will be required throughout Europe (EU 2001). Furthermore, signatory countries of the OSPAR Convention agreed a target of cessation of discharges, emissions and losses of hazardous substances to the marine environment of the North-East Atlantic by 2020 and included NP/NPEs on the first list of chemicals for priority action towards this target (OSPAR 1998). More information on nonyl phenols is given in Box C.

Alongside the alkyl phosphate flame retardants, tris(2-ethylhexyl) phosphate, tThe two photoinitiator-related compounds (2,6-Di-tert-butyl-p-benzoquinone and a naphthoquinone derivative) were also identified in wastewater from the Kingboard (Panyu Nasha) Industrial Area, and are discussed in Section 4.2 and Boxes A and B.

Along with two long chain fatty acids, hexadecanoic (palmitic) and Octadecanoic (stearic) acids, their hydroxyesters known as 2 monopalmitin and 2-monostearin were also identified. As noted above, long chain fatty acids and their derivates were also identified in wastewaters from the Kingboard (Fogang) and Kingboard (Panyu Nansha) facilities. As discussed in Section 4.1, there are no known specific uses of these compounds in the manufacture of printed circuit boards. Fatty acids and their derivatives are not of particular environmental concern due to their low toxicity and being readily biodegradable.

These data from the four wastewater samples collected at different times confirms that there is a high degree of variability in the quality of discharged wastewaters over time. The highest manganese concentration was found in wastewater discharged during the night. Similarly, there were significant differences in the types of organic chemicals present in wastewater discharged during the night to those discharged during the day, with nonyl phenols and photoinitiator related chemicals only present in night time discharges. However, other organic chemicals were present only in wastewaters collected during the daytime, including an alkyl phosphate flame retardant. The underlying reasons for these temporal differences in the quality of effluents discharged warrants further investigation.

Many of the discharged chemicals can accumulate in sediment within a receiving water body. Sediment collected from the receiving stream at a location upstream of the underground channel outfall (CN09007) contained very low concentrations of the metals quantified in this study, and no organic chemicals other than some hydrocarbons. The levels of many metals in the stream sediment collected by the outfall of the underground channel (CN09010) were somewhat higher, though all were within background concentration ranges for sediments (Wang *et al*. 2008, Cheung *et al*. 2003). The somewhat higher sediment levels by the outfall could indicate some accumulation of discharged metals at this location, including nickel and zinc, though these were not present at high concentrations in the wastewaters at the times of samplingIt is possible that the slightly higher levels in the sediment at this point compared to the upstream sample may simply result from differing sediment composition at the two locations. For manganese, the metal present in the highest concentration in the wastewater samples, the sediment concentration (10 mg/kg) does not indicate accumulation of this metal by the outfall due to discharges via the channel. Similarly, none of the organic chemicals present in the wastewaters that are discussed above were identified in sediment by the channel outfall.

4.5) Dongguan Cheongming Printing Co. Ltd.

The Dongguan Cheongming Printing facility (herein referred to as Cheongming Printing) is located in Daisha District, Daling Shan, Dongguan (Guangdong Province). This facility produces a range of printed products including paper cartons, packaging boxes and books, using various processes including printing, varnishing and coating (Cheongming 2001). It is situated on the banks of a small river, adjacent to Daisha Village, which is located within the catchment of the East River (Dongjiang) of the Pearl River system. This small river ultimately flows to the Tongsha Reservoir which is located in the Dongjing River catchment in Dongguang, part of the Pearl River system.

Locals have reported that this facility regularly discharges highly coloured (red) and strong smelling wastewaters. Soil surrounding the outfall pipe has clearly been stained red/orange in colour. Wastewater is discharged from the Cheongming Printing facility into the river at the rear of the facility. A sample of wastewater (CN09021) was collected from a pipe discharging from Cheongming Printing. A sample of sediment (CN09021) was also collected from the open channel that carries wastewater from the pipe into the river. Details of these samples are presented in Table 6a. This small river also received wastewater from an adjacent mirror manufacturing facility.

Table 6a. Description of samples collected from the vicinity of the Cheongming Printing facility in Daisha District, Daling Shan, Dongguan, Guangdong Province, China, 2009

Sample	Type	Description
CN09021	wastewater	Discharged from Cheongming Printing via a pipe at the rear of the facility
CN09020	sediment	Wastewater channel immediately below the discharge pipe. This channel has been formed due to the flow of wastewater

Table 6b. Organic chemicals identified, and concentrations of metals and metalloids, in samples of wastewater and sediment associated with the Dongguan Cheongming Printing facility in Dongguan, Guangdong Province, China, 2009. For wastewater sample, concentrations are given for whole (unfiltered) samples, dissolved concentration accounted for greater than 75% of the whole sample concentration

4.5.1) Results

The sample of discharged wastewater (CN09021) was highly acidic (pH = 2), far outside the allowable range of pH 6-9 defined by the Guangdong effluent standard (Guangdong Province 2001). The highly acidic nature of the wastewater is expected to have a significant impact on aquatic life in the vicinity of the discharge.

The wastewater also contained a number of metals at high concentrations, including chromium, copper and zinc each at over 1000 µg/l, nickel at just below 500 µg/l, and to a lesser extent lead (122 µg/l). In all cases the metals were present exclusively in dissolved forms, as expected in such highly acidic wastewater. The concentration of copper (1680 µg/l) exceeded some of the maximum allowable concentrations set under the Guangdong effluent standard, which sets limits of 500, 1000 or 2000 µg/l depending on how the receiving water body is used (Guangdong Province 2001).
It has not been possible to determine the use category of the water body in this situation. The concentrations of chromium, nickel and zinc in the wastewater were between 45% and 72% of the maximum allowable concentrations under the Guangdong effluent standard. Though below these regulatory limits, the concentrations of these metals far exceed local background levels in uncontaminated surface waters (Cheung *et al*. 2003) and indicate that the discharge is acting as a significant point source of toxic metals to the aquatic environment.

Sample	CN09003	CN09005
Type	Wastewater	Sediment
Brief description	pipe	below pipe
pH	2	-
METAL	(µg/l)	(mg/kg)
Antimony	<50	<20
Arsenic	<50	<20
Beryllium	<5	<0.5
Cadmium	<5	<1.0
Chromium	1080	213
Chromium (VI)	<50	-
Cobalt	<20	4
Copper	1680	163
Lead	122	38
Manganese	673	1
Mercury	<2	0.2
Nickel	448	29
Selenium	<200	<30
Thallium	<20	<10
Tin	<100	21
Vanadium	<20	45
Zinc	1230	179
Chlorinated volatile organic chemicals		
Methane, dichloro-	940	-
Ethene, trichloro-	8.8	-
Other organic compounds isolated	37	19
No. Reliably identified (% of total)	17 (46%)	19 (100%)
Photoinitiators and related compounds		
Quantacure ITX	1	
Benzophenone	1	
Tetrahydro naphthalenedione deriv.	1	
Phthalate esters		
DiBP/DnBP	2	
Fatty acids and derivatives		
Acids	1	
Esters	2	
Other oxygen compounds		
Alkyl-enone	1	
Hydrocarbons		
PAHs	1	3
Alkyl benzenes	2	
Aliphatic hydrocarbons	5	16

The metals present at high concentrations in the discharged wastewater can be toxic to aquatic life, particularly under acidic conditions, which increases their water solubility, mobility and toxicity (Gerhardt 1993). Of particular concern is the very high level of copper, as many aquatic organisms are highly sensitive to this metal, particularly in dissolved forms, and impacts can occur at very low concentrations (ATSDR 2004, Bryan & Langston 1992, Sandahl *et al*. 2007). Additional information on these metals and the Guangdong effluent standard is given in Box D.

A number of organic chemicals were also identified in the wastewater. These included two chlorinated volatile organic chemicals (VOCs), namely dichloromethane (940 µg/l) and a trace level of trichloroethene (8.8 µg/l). The trace level of trichloroethene was significantly below the Guangdong effluent standards for this chemical. However, no such limit exists for dichloromethane, the predominant VOC in the wastewater, though maximum allowable concentrations of between 30µg/l and 1000µg/l are set for similar chlorinated VOCs for which limits do exist (Guangdong Province 2001). Dichloromethane, otherwise known as methylene chloride, is a widely used chlorinated solvent which is harmful if inhaled or swallowed and which can cause irritation and burning of the skin. Further information is provided in Box G.

Box G. **Dichloromethane**

Dichloromethane, also known as methylene chloride, is a commonly used industrial solvent, especially in degreasing and paint-removing applications. It is a highly volatile compound, such that inhalation can be a primary route of exposure in the vicinity of industrial facilities or spills involving the chemical. Contact with skin can result in localised irritation and some penetration into the body. Once in the body, it undergoes degradation in the liver, generating carbon monoxide among other by-products. It is also capable of passing through internal membranes, including the placenta (WHO 2000b).

Within Europe, dichloromethane is classified as harmful if swallowed, inhaled or absorbed through the skin, as a possible mutagen and possible human carcinogen (category 3) (EC 2008b). Short term exposure can cause headaches, dizziness, nausea or, at high concentrations, loss of consciousness (ATSDR 2000). The effects of repeated or long-term exposure in the workplace or through the use of products containing dichloromethane can include damage to the liver and, in severe cases, permanent damage to the nervous system (Kobayashi *et al*. 2008).

In recognition of the possible hazards to health from prolonged contact with dichloromethane, and the significant numbers of both fatal and non-fatal injuries associated with its use over the past 20 years, the use of dichloromethane in paint strippers for use by consumers and professionals is soon to be banned within the European Union (EP 2009). Dichloromethane is already listed as a 'priority substance' under the EU Water Framework Directive (EU 2001, 2008) and its uses are therefore likely to come under increasing scrutiny and control.

A number of other organic chemicals were identified in the wastewater, though the levels were not quantified. Of greatest significance among these were three compounds commonly used as photoinitiators, or closely related compounds (Quantacure ITX, benzophenone and a tetrahydro-naphthalenedione derivative), two phthalate esters (DiBP and DnBP) as well as some long chain fatty acid and related esters. It is likely that the photoinitiators and related compounds result from the use of photoinitiators in printing processes within this facility. Phthalate esters are also known to be used in some printing processes, a potential source to this wastewater (EC 2003).

The two phthalate esters (DnBP and DiBP) were also identified in wastewater from the Kingboard Panyu Nasha Industrial Area, as well as one of the photoinitiator related chemicals, a tetrahydro-naphthalenedione derivative (CN09017, Section 4.2). One other photoinitiator-related chemical, Quantacure ITX, was identified in wastewater from the Kingboard Fogang Industrial Area (CN09003, Section 4.1). The third photoactive compound, benzophenone, was identified in wastewater from the Wing Fung P.C. facility (CN09028, Section 4.3). These two groups of compounds are further discussed in Box E (phthalate esters) and Box B (photoinitiator related chemicals).

Examples of long chain fatty acid and related ester were identified in wastewaters from the three facilities involved in the manufacture of printed circuit boards. There are no known specific uses in the printing industry. Fatty acids and their derivatives are not of particular environmental concern due to their low toxicity and being readily biodegradable.

None of these three groups of organic chemicals were identified in sediment collected from a channel that carries discharged wastewater to the adjacent river (CN09020). However, this sediment did contain levels of chromium, copper and to a lesser extent zinc moderately elevated above usual levels in uncontaminated sediments (ATSDR 2004, Cheung *et al*. 2003, Salomons & Forstner 1984). These levels indicate some accumulation of metals due to ongoing discharge of contaminated wastewaters via this channel. However, as noted above, the high acidity of the wastewater greatly increases the solubility and mobility of the discharged metals, thereby reducing their tendency to accumulate in sediments close to the discharge point. This effect also increases the bioavailability of the metals, and is likely to result in greater impacts to aquatic life in the stream receiving the discharged wastewaters.

image The Fei Lai Xia natural mountain water company located in the upper stream of the North River which pumps the spring water from the mountains. The arrea still preserves it's beauty however some industry from the Pearl River Delta is planning to relocate to the upper stream and mountain area which will pose a huge threat to this area of natural beauty.

image Waste water discharge the Dongguan Cheong Ming printing limited

5: Conclusions

Taken together, the results from this study demonstrate that wastewater discharges from the five facilities sampled act as significant point sources of heavy metals as well as hazardous or potentially hazardous organic substances to the receiving freshwater environment of the Pearl River basin. The results provide a valuable snapshot of the quality and complexity of discharges to water from certain industrial facilities in this area.

For all three facilities involved in the manufacture of printed circuit boards, some similar patterns in the nature and extent of chemical discharges emerged. Some similarities were also found between these three facilities and the two other facilities involved in seemingly unrelated activities (textile manufacturing and printing), most notably the common presence of photoinitiator compounds.

Overall, the results highlight the presence of various metals at high concentrations in just a small sample of the industrial wastewaters routinely discharged to the Pearl River system and its tributaries. The levels of individual metals exceeded the maximum allowable concentrations under the Guangdong effluent standard (Guangdong Province 2001) for three sites, namely Kingboard (Fogang) Industrial Area, the Wing Fung P.C. Board Co. and QingYuan Top Dragon Textile Co. In one instance, the level of copper exceeded the lower limit by 50 times and the higher limit by 12 times (CN09028, Wing Fung P.C. Board Co.), which is of particular concern for a metal to which many aquatic organisms are extremely sensitive. Furthermore, discharges from two sites, Kingboard (Fogang) Industrial Area and Dongguan Cheongming Printing Co., were highly acidic, far outside the permissible pH range under the Guangdong effluent standard. Highly acidic discharges can be expected to have a significant impact on aquatic life in the vicinity of the discharge, and also greatly increase the water solubility, mobility and therefore toxicity of metals present in the wastewater. In many other examples, concentrations of metals were found which, although below limits set by the Guangdong effluent regulations, still indicate significant point source inputs for substances that will generally accumulate and persist in the receiving environment.

Numerous organic chemicals were also identified in the various wastewaters, many with known hazardous properties. Key examples (and the sites at which they were identified) include:

- brominated flame retardants including TBBPA (Kingboard Fogang & Kingboard Panyu Nasha);
- alkyl phenols (Kingboard Fogang & QingYuan Top Dragon Textile Co.);
- phthalate esters (Kingboard Panyu Nansha, Wing Fung & Dongguan Cheongming Printing);
- dichloromethane (Dongguan Cheongming Printing); and
- bisphenol-A (Kingboard Panyu Nansha)

Other than for two phthalate esters (DEHP and DnBP), the discharge of wastewaters containing these substances are not regulated under the Guangdong effluent standard (Guangdong Province 2001). In the majority of cases (all but bisphenol-A), these chemicals are specifically listed as priority substances in one or more regulation or convention that address their use and release in certain regions outside of China, as a result of concerns about environmental and/or human health impacts associated with them. The alkyl phenols (octyl and nonyl phenols), one phthalate ester (DEHP) and dichloromethane are listed as priority substances under the European Water Framework directive, a regulation designed to improve the quality of water within the EU (EU 2008). All but dichloromethane have been identified as substances for priority action under the OSPAR convention, under which signatory countries have agreed a target of cessation of discharges, emissions and losses of all hazardous substances to the marine environment of the North-East Atlantic by 2020, the 'one generation' cessation target (OSPAR 1998). Furthermore, two phthalates (DEHP and DnBP) have been listed as Substances of Very High Concern (SVHC) under the European REACH Directive, which regulates chemicals management within the EU (ECHA 2008).

Other substances, such as bisphenol-A (BpA), while not currently monitored or controlled under these or similar regulations and conventions, are widely recognised as hazardous pollutants, particularly for the aquatic environment.

Clearly, for some substances identified in discharged wastewaters, there are well-recognised environmental or human health concerns, however, this study has also demonstrated the widespread presence in discharged wastewaters of many other substances, such as the photoinitiator-related chemicals, about which little is known in terms of their toxicology or potential impacts following release to the environment. Furthermore, for many samples, including at least one wastewater from each of the five sites, the majority of organic chemicals being discharged to, or already present in, the environment simply could not be reliably identified, such that their properties and potential impacts, alone or as components of complex mixture of contaminants, remain unknown.

This study has also highlighted instances where wastewaters discharged from facilities via the larger and most visible outfalls, or which are discharged during the daytime, may differ greatly from other discharges arising from the same sites but which are less visible because of their location or the time of their release. This situation raises additional difficulties and concerns regarding the monitoring of discharges from industrial facilities.

Many of the metals and organic chemicals present in various discharged wastewaters are able to accumulate in the environment following their release, either within sediments or in some cases in biota as a result of bioaccumulation. For these substances, ongoing releases are likely to lead to ever increasing levels in the receiving environment, which in many cases will not significantly decrease for long periods of time, even after any controls on their release have been introduced. Numerous studies have already demonstrated contamination of the Pearl River Delta sediment with heavy metals and persistent organic pollutants (for example Chau 2006, Wang *et al*. 2008). This situation highlights the limitations of regulations that seek to address impacts of industrial waste discharges by setting either acceptable levels of discharge or acceptable levels in the receiving environment, especially as such limits are, other than for a very limited number of individual chemicals, largely based on general measurements of chemical load such as biological and chemical oxygen demand (BOD and COD). Such permitted discharge approaches are unable to address the serious and potentially irreversible consequences arising from ongoing releases to the environment of persistent organic and inorganic pollutants as components of industrial wastes.

Moreover, for many of these most hazardous substances, their presence in waste streams can not be addressed effectively through the use of 'end-of-pipe' measures, including conventional wastewater treatment plants. Many persistent organic pollutants, for example, will either pass through the treatment process unchanged, be converted through partial degradation into other hazardous substances or accumulate in treatment plant 'sludges' which then become hazardous wastes in themselves. The most effective measures to address hazardous substances are those which seek alternatives to the use of such hazardous substances in manufacturing processes, progressively replacing them with less hazardous, and preferably non-hazardous, alternatives in order to bring about rapid reductions and ultimate cessation in their discharges, emissions and losses (the principle of substitution).

This can be achieved by focusing 'upstream' in industrial terms, systematically rethinking and redesigning products and processes in order to progressively reduce industry's reliance on hazardous chemicals, to build a more sustainable global industry and to eliminate both the waste of resources and the pervasive threats to the environment and human health which the ongoing use and release of hazardous chemicals entails.

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Appendix 1. Analytical methodology

Analysis for Volatile Organic Compounds (VOCs)

Method

VOCs were analysed using an Agilent 6890 gas chromatograph with an Rtx-624 column (30m, 0.25mm ID, 1.4µm film thickness) connected to an Agilent 7694 Headspace Sampler and linked to an Agilent 5973N MSD operated in EI mode. The GC oven temperature program included an initial temperature of 35°C (held for 4min), rising to 55°C at 5°C/min, and then to 210°C at 15°C/min. The carrier gas was helium, supplied at 1ml/min. From each sample, three 10ml portions were sub-sampled into 20ml headspace vials. One sub-sample was analysed with the GC-MS in total ion monitoring (SCAN) mode to identify as many of the volatile organic compounds present as possible. Identification of compounds was carried out by matching spectra against the Wiley7N Library, employing expert judgment in order to avoid misidentifications. The two remaining sub-samples were then used for duplicate quantitative analysis for those halogenated (chlorinated, brominated and mixed) VOCs which had been detected in the samples through screening. Quantification was performed in Selective Ion Monitoring (SIM) mode using a 5 point external calibration method. Halogenated VOCs quantified in the water samples were:

Vinyl chloride
Ethane, chloro-
Ethene, 1,1-dichloro-
Methane, dichloro-
Ethene, 1,2-dichloro-, trans-
Ethane, 1,1-dichloro-
Ethene, 1,2-dichloro-, cis-
Chloroform
Ethane, 1,1,1-trichloro-
Methane, tetrachloro-
Ethane, 1,2-dichloro-
Ethene, trichloro-
Methane, dibromo-
Methane, bromodichloro-
Propene, 1,3-dichloro-, trans-
Ethene, tetrachloro-
Methane, dibromochloro-
Bromoform
Ethane, 1,1,2,2-tetrachloro-
Ethane, hexachloro-
Butadiene, hexachloro-

Quality control

Standard deviation (SD), relative standard deviation (RSD) and limits of detection (LOD) were calculated using data from the analysis of seven replicates of a standard mixture of commonly occurring VOCs, containing 1ppb of each analyte. Limits of quantification (LOQ) were determined as the lowest concentration in the linear regression used for quantification. A number of blanks of laboratory air capped at the time that sub-sampling had taken place were also analysed, alongside samples of the ultra pure reagent water which was used for the preparation of standard calibration solutions. The initial calibration curve for each compound of interest was verified immediately prior to sample analysis by analysing a calibration standard at a concentration near the midpoint concentration for the calibration range of the GC-MS.

Analysis for extractable organic compounds

Preparation

20 µg of deuterated naphthalene was added as an Internal Standard (IS) to each portion of sample that was subject to extraction. For sediment samples, approximately 30 g of each sample (wet weight) was extracted for two hours using a mixture of 15ml pentane and 5ml acetone, at a temperature of 69°C with sonication to increase solvent contact with the sediment. After cooling and decanting off the solvent fraction, the samples were acidified to a pH of approximately 2 using nitric acid (10% v/v) and the heated, sonicated extraction process repeated with fresh solvent, following which the two portions of solvent extract were combined. Water samples (approximately 500ml) were also extracted twice, both before and after acidification to pH 2, using 20ml portions of pentane and a bottle roller to ensure efficient contact between the solvent and the sample.

Clean-up procedures were the same for the crude extracts from both aqueous and sediment samples. For each sample, the two extracts obtained were combined, concentrated to 3ml under a stream of analytical grade nitrogen, shaken with 3ml isopropyl alcohol and 3ml TBA-reagent (mixture of 3% tetrabutylammonium hydrogen sulphate and 20% sodium sulphite in deionised water) and left to stand until the aqueous and organic phases had separated. The pentane phase was collected and eluted through a Florisil column, using a 95:5 pentane:toluene mixed eluent, and the cleaned extract concentrated to a final volume of 2ml as before. 20 µg of bromonaphthalene was added to each extract as a second IS prior to GC-MS analysis.

Analysis

For the total organic compounds screening, samples were analysed using an Agilent 5890 Series II GC with Restek Rtx-XLB column (30m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5972 MSD operated in EI mode and interfaced with an Agilent Enhanced Chem Station data system. The GC oven temperature program employed was as follows: an initial temperature of 35°C, held for 2 minutes, raised to 260°C at 10°C/min, then to 320°C at 6°C/min (held for 8min). The carrier gas was helium, supplied at 1ml/min. Identification of compounds was carried out by matching spectra against both the Wiley 7N and Pesticides Libraries, using expert judgment as necessary in order to avoid misidentifications. Additionally, both the spectra and retention times of compounds isolated from the samples were matched against those obtained during GC-MS analysis of standard mixtures containing a range of chlorinated benzenes, phenols and pesticides, polychlorinated biphenyls (PCBs), phthalates, polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons.

For the TBBPA analyses, PBDEs and total bromine-containing organic compounds screening, samples were analysed using 6890 Series gas chromatograph with a Restek Rtx-XLB column (15m, 0.25mm ID, 0.1 µm film thickness) linked to an Agilent 5973 Inert MSD operated in CI mode (with methane as reagent gas) and interfaced with an Agilent Enhanced Chem Station data system. The GC oven temperature programs employed was as follows: a) for TBBPA analysis: an initial temperature of 110°C, hold for 2 min., raised to 300°C at 30°C/min (held for 2min); b) for PBDEs and total bromine-containing organic compounds screening; an initial temperature of 120°C, hold for 1 min., raised to 295°C at 30°C/min (held for 7min), The carrier gas was helium, supplied at 1ml/min and 2ml/min fro TBBPA and bromine-containing organic compounds respectively. Identification of compounds was carried out by matching of compound-specific ions and corresponding retention times of compounds isolated from samples against those obtained during GC-MS analysis of standard mixtures containing a range of PBDEs from mono- to deca-brominated (BDE-MXE mixture obtained from Wellington Laboratories) and a single standard of TBBPA also obtained from Wellington Laboratories. Ions monitored for TBBPA analysis were 543.7; 541.7; 545.7 and 80.9. Ions monitored for PBDEs were 80.9; 78.9, 486,6 and 488.6. Ions monitored for total bromine-containing organic compounds analysis were 80.9 and 78.9.

Quality control

A number of extraction and solvent blanks were also analysed to ensure the detection of any possible contamination resulting from sample handling in the laboratory.

image Local anglers fish in the river next to Kingboard Industrial park. The company manufactures hazardous chemicals and discharges waste water onto the river

Analysis for metals and metalloids

Preparation

A representative portion of each sediment sample was air dried to constant weight, homogenised, sieved through a 2mm mesh and then ground to a powder using a pestle and mortar. Approximately 0.5g of each sample was digested with 7.5ml concentrated hydrochloric acid, 2.5 ml concentrated nitric acid and 10 ml deionised water, firstly overnight at room temperature, then for 4 hours under reflux at 130oC. Digests were filtered and made up to 50ml with deionised water. For water samples, a representative portion of each whole sample was acidified by the addition of concentrated nitric acid to give a final concentration of 10% v/v. In addition, a portion of each whole sample was filtered and then acidified in the same way. 25ml of each acidified sample was refluxed at 130oC for 4 hours. Cooled digests were filtered and made up to 25ml with deionised water.

Analysis

Prepared sample digests were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Varian MPX Simultaneous Spectrometer. Multi-element standards at concentrations of 0.5mg/l, 1 mg/l and 10 mg/l, and matrix matched to the samples, were used for instrument calibration. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed. Analysis of the mercury content in the samples was carried out separately. Mercury (Hg) was determined using cold vapour generation ICP-AES. Ionic mercury, Hg (II), was reduced to elemental mercury, Hg (0), through reaction of the sample 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.

Quality control

For sediment samples, three samples were prepared in duplicate and analysed to verify method reproducibility, along with an identically prepared blank. To check the method efficiency, certified reference material (CRM) samples were prepared in an identical manner; GBW07311, stream sediment certified by the China National Analysis Centre for Iron and Steel, Beijing, China, and LGC6187, leachable metals in river sediment certified by the Laboratory of the Government Chemist, UK.

For water samples, four whole samples and four filtered samples were prepared in duplicate and analysed to verify method reproducibility, along with a blank sample (10% v/v nitric acid in deionised water) and a mixed metal quality control solution of 8 mg/l, other than mercury at 80 µg/l. All control samples were prepared in an identical manor to the samples.

Calibration of the ICP-AES was validated by the use of quality control standards at 8 mg/l and 0.8 mg/l prepared from different reagent stocks to the instrument calibration standards. For cold vapour generation mercury analysis, the calibration was validated using two quality control standards (10 ug/l and 80 ug/l), prepared internally from different reagent stock.

Further details of the methods employed can be provided on request.

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