

**Heavy metals and other hazardous chemicals discharged
from an industrial wastewater treatment company
into the Greater Pearl River Delta, China, 2009**

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1 Executive Summary

Greenpeace recently released a report highlighting the discharge of hazardous chemicals from industrial facilities into surface waters of the Greater Pearl River Delta. This follow up study investigated the discharge of hazardous chemicals from a facility in the same area that receives and treats wastewaters from many separate facilities, most of which are either involved in electroplating activities or the manufacturing of electronic products.

Shenzhen Resources Environmental Technology Co., Ltd (herein referred as Shenzhen Resources) is situated within Guangdong Province in Southern China. A variety of wastes are treated at this facility, primarily to address the acids and metal compounds contained in the various wastes. Treated wastewaters are discharged from Shenzhen Resources to the adjacent Dongbao River.

Three samples of wastewaters and two sediments were collected in June 2009, including wastewater samples from all identifiable and accessible discharge points emanating from the site, as well as sediment samples from channels through which wastewaters are released. 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.

Shenzhen Resources receives wastes with the intention that they will be adequately treated, however this study has demonstrated the discharge of wastewaters containing hazardous chemicals to the receiving freshwater environment of the Pearl River basin, including acidic wastes, heavy metals and organic chemicals. Wastewater discharged during the night contained numerous metals at high concentrations including manganese, beryllium, copper and lead at levels which exceeded the most stringent limits of the Guangdong effluent standard by between 4 times and 25 times, as well as being highly acidic with a pH far outside the allowable range allowed under this standard. Numerous organic chemical pollutants were also identified in this wastewater, including chlorinated and brominated compounds. A wastewater from a separate discharge point contained copper at a level almost two times the most stringent limit set under the Guangdong effluent standard, while wastewater overflowing from a storage tank into the river was acidic with a pH outside the allowable range of this standard. Furthermore, sediment from a discharge channel contained high levels of metals including copper, nickel and zinc, at levels that exceeded the acceptable environmental quality standards for these metals in soils in China, indicating accumulation due to ongoing releases of contaminated wastewaters.

Many of the metals identified can have toxic effects, particularly at high concentrations. Of particular concern were the very high levels of lead, a highly toxic and bioaccumulative metal, and dissolved copper, 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 toxicity of metals present in the wastewater. Additional information on the metals identified in this study are presented in Appendix 1 of the main report.

The results of this study indicate that the treatment processes used by Shenzhen Resources, or the way in which they are being employed, are failing to address hazardous chemicals within wastes that are being transferred to Shenzhen Resources for treatment.

Many of the substances identified in the wastewaters can not be addressed effectively through the use of 'end-of-pipe' measures, including conventional wastewater treatment plants. The type of end-of-pipe solutions employed by Shenzhen Resources will, at best, simply move metals from one waste stream to another, such as from wastewaters into solid wastes. The treatment processes employed are primarily designed to address metals in the wastewaters, and not to treat the types of organic chemicals identified. Furthermore, the release of highly contaminated wastewater during the night raises concerns regarding the regular monitoring of discharges from this facility.

Many of the chemicals identified in wastewaters release by Shenzhen Resources are able to accumulate in the environment, either within sediments or in some cases in biota as a result of bioaccumulation. Ongoing releases are likely to lead to ever increasing levels in the receiving environment, which may not significantly decrease for long periods of time even after controls on their release have been introduced.

The most effective measures to prevent releases of hazardous substances are those based upon the use of alternative substances or processes that enable hazardous substances to be progressively replaced with less hazardous, and preferably non-hazardous, alternatives. This approach can bring about rapid reductions and the ultimate cessation in the discharges, emissions and losses of hazardous chemicals (the principle of substitution), eliminating the pervasive threats to the environment and human health which the ongoing use and release of hazardous chemicals entails.

2 Introduction

The Pearl River, the third longest river in China, flows into the South China Sea via the Pearl River Delta (PRD), an area situated adjacent to the regions of Hong Kong and Macau. The PRD is a highly industrialised area, 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 recent study by Greenpeace (Brigden *et al.* 2009, Greenpeace 2009) highlighted inputs of hazardous chemicals, including heavy metals and organic pollutants, from five industrial facilities located within the Greater PRD, through the ongoing direct discharge of contaminated wastewaters. This follow up study investigated the discharge of hazardous chemicals in wastewaters from a facility that receives and treats wastewaters from many separate facilities within the surrounding area.

The Shenzhen Resources Environmental Technology Co., Ltd facility (herein referred as Shenzhen Resources) is located in the 3rd Industry Zone, Bitou Village, Songgang Town, Baoan District, Shenzhen, China. The facility is situated adjacent to the Dongbao River, part of the Maozhou River Catchment of the Pearl River system (SZEPA 2008). Shenzhen Resources receives and treats wastewaters from numerous facilities, most of which are either involved in electroplating activities, or the manufacturing of electronic products, including printed circuit boards. Many of these facilities are located within the same industrial park as Shenzhen Resources (Shenzhen Resources 2009).

The treatment processes employed by Shenzhen Resources are primarily designed to treat wastes containing acids and metals, particularly lead and iron. The facility houses three treatment workshops; an iron oxide workshop, a lead workshop, and a sodium sulfate and wastewater treatment workshop. The iron oxide workshop primarily focuses on the removal of iron, tin and nitric acid from wastes, including those derived from soldering processes. The lead workshop recovers lead from wastes containing this metal. The third workshop is intended to neutralise acidic or basic wastewaters, and remove metals (primarily copper) from wastewaters, as well as treating wastewaters using an aeration process (Shenzhen Resources 2009).

3 Sampling programme

The Shenzhen Resources Environmental Technology site was visited on a number of occasions in the first half of 2009, and samples of wastewaters and sediments were collected in June 2009. Wastewater samples were collected from all discharge points that could be identified and accessed on the perimeters of the site. Samples of sediment were also collected from discharge channels through which wastewaters flow, in order to investigate the accumulation of pollutants in the sediments as a result of the ongoing discharge of wastewaters. Details of individual samples are given in Section 5.

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 chemical residues. Wastewater samples were collected in 1 litre screw-cap bottle 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 2.

4 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. Some wastewater samples contained suspended solids and therefore, for all water 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 Appendix 2.

5 Results and discussion

The following section includes a description of the samples of wastewater and associated sediments that were collected, and a discussion of the results from the analyses of these samples. 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 discharges can, however, result in levels that far exceed natural background concentrations. The following section focuses on those metals found at levels in the various samples that indicate levels above background due to inputs from industrial or other anthropogenic sources.

Sample #	Type	Description
CN09022	wastewater	minor outfall on the bank of the Dongbao River, adjacent to the south-west perimeter of the facility, visible only at low tide
CN09024	wastewater	wastewater storage tank located at the rear of the facility, which overflows into a channel leading to the adjacent Dongbao River (see CN09025)
CN09025	sediment / soil	from overflow channel between the wastewater storage tank located at the rear of the facility, and the adjacent Dongbao river (see CN09024)
CN09027	wastewater	pipe immediately behind the WWTP of the facility. Occasional wastewater discharge, only observed during the night
CN09023	sediment	From the channel into which wastewater is occasionally discharged, behind the WWTP (see CN09027). Wastewater not discharging at time of collection

Table 1. Description of samples collected from the vicinity of the Shenzhen Resource Environmental Technology Co., Ltd, 3rd Industry Zone, Bitou Village, Songgang Town, Baoan District, Shenzhen, China, 2009

Three wastewater samples and two sediments/soils were collected from the vicinity of this facility. One wastewater (CN09022) was collected from a small discharge channel on the bank

of the Dongbao River adjacent to the south-west perimeter of the facility. This outfall is visible only when the tidal river is at low tide. A second wastewater sample (CN09024) was collected from an open wastewater storage tank which is located at the rear of the facility. It has been reported that this tank was historically used to store wastewater and that it is no longer used (Shenzhen Resources worker 2009). However, the level of water in the tank has been observed to increase over time, and on a number of occasions wastewater from this tank was observed to overflow into a channel that flows to the adjacent Dongbao River. A sample of sediment/soil (CN09025) was collected from this channel. A discharge pipe is located immediately behind the wastewater treatment plant (WWTP). On many occasions there was no active discharge from this pipe, despite the appearance that wastewater had recently flowed within the channel below the pipe. A sample of sediment (CN09023) was collected from the channel. On a subsequently visit during the night, the discharge of wastewater via this pipe was observed and a sample was collected (CN09027). A summary of the samples collected are presented in Table 1, along with a map showing the locations from where samples were collected (Figure 1).



Figure 1. Map of the Shenzhen Resource facility showing the locations from which samples of wastewater and sediment were collected.

5.1 Results

Wastewater discharged via the minor outfall channel (CN09022) contained high concentrations of copper (980 $\mu\text{g/l}$), nickel (387 $\mu\text{g/l}$), and to a lesser extent zinc (260 $\mu\text{g/l}$), all considerably higher than local background surface water levels for these metals (Cheung *et al.* 2003). Copper and zinc in this wastewater were present mainly in suspended forms, rather than dissolved forms. The level of copper in this wastewater was almost double the most stringent limit set under the

Guangdong effluent standard (Guangdong Province 2001), details of which are given in Appendix 1.

A similar composition of metals was found in wastewater collected from the storage tank (CN09024), with copper, nickel and zinc being the predominant metals. Their concentrations were, however, somewhat different to those in CN09022, with the levels of copper and nickel each being about a third of the respective levels in CN09022, while the level of zinc was almost double the level found in CN09022. Copper, nickel and zinc in the storage tank wastewater (CN09024) were predominantly present in dissolved forms, which is likely to be due to this wastewater being more acidic (having a lower pH) than CN09022. The pH value (pH=4) of CN09024 falls outside the allowable range of pH 6-9 defined by the Guangdong effluent standard (Guangdong Province 2001). The acidic nature of this wastewater is likely to have an impact on aquatic life in the river in the vicinity of the input from this storage tank overflow. Furthermore, the acidity of the wastewater greatly increases the solubility and mobility of metals present, thereby increasing their potential bioavailability and toxicity (Gerhardt 1993).

These two wastewaters (CN09022 & CN09024) contained only a limited range of organic chemicals, primarily aliphatic hydrocarbons, however a phthalate ester (DiBP) was identified on the wastewater from the storage tank (CN09024).

Sediment/soil (CN09025) collected from the channel into which wastewater from the storage tank overflows contained high levels of copper, nickel, tin and zinc. High levels of these metals were also found in the overflow wastewater (other than for tin), which indicates the accumulation of metals in the sediment from wastewater released when the storage tank overflows. The sediment level of copper (698 mg/kg) was more than 20 times higher than levels commonly found in uncontaminated sediments, while the levels of nickel and zinc were approximately 3 and 7 times higher than typical background levels (ATSDR 2004, ATSDR 2005b&c, Cheung *et al.* 2003, Salomons & Forstner 1984, Wang *et al.* 2008). Although there is no Chinese contaminated sediment standard for comparison, the levels of copper, nickel and zinc exceeded the acceptable environmental quality standards for these metals in soils in China (MEP 1996), and also exceeded contaminated sediment threshold levels from other countries (NMHSPE 2000). 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 CN09025 was almost 20 times this background level. For more information on these metals and their relevant standards, see Appendix 1. No significant organic chemicals were identified in the sediment from the channel.

Although high levels of metals were identified in the two samples of wastewaters released during the day, the sample of wastewater discharged during the night from a pipe located immediately behind the wastewater treatment plant (WWTP) was far more contaminated. This wastewater (CN09027) contained numerous organic chemical pollutants, high levels of many metals, and was highly acidic.

Sample	CN09022	CN09024	CN09027	CN09023	CN09025
Type	wastewater			sediment/soil	
Brief description	minor outfall	wastewater storage tank	discharge pipe by WWTP	channel under pipe by WWTP	overflow channel of storage tank
pH	6	4	1	-	-
METAL	(µg/l)	(µg/l)	(µg/l)	(mg/kg)	(mg/kg)
Antimony	<50	<50	<50	<20	<20
Arsenic	<50	<50	<50	<20	<20
Beryllium	<5	<5	40	1.1	0.8
Cadmium	<5	<5	<5	<1.0	1.2
Chromium	<20	<20	304	95	301
Chromium (VI)	<50	<50	<50	-	-
Cobalt	<20	<20	49	11	10
Copper	980 ^(b)	372	36800	580	698
Lead	86	<50	24700	1010	116
Manganese	450	391	19200	4	2
Mercury	<2	<2	<2	0.3	0.2
Nickel	367	117	1270	99	232
Selenium	<200	<200	<200	<30	<30
Thallium	<20	<20	<20	<10	<10
Tin	<100	<100	1530	388	191
Vanadium	<20	<20	50	54	36
Zinc	260 ^(a)	464	3980	167	765
volatile organic chemicals, VOC	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)
chloroform	<0.5	<0.5	3.6	-	-
ethane, 1,2-dichloro-	<1	<1	7.6	-	-
methane, dibromochloro-	<1	<1	18.2	-	-
bromoform	<2	<2	22.2	-	-
Organic compound isolated	24	22	67	31	66
Number reliably identified (% of total)	9 (38%)	4 (18%)	31 (46%)	9 (29%)	19 (29%)
Chlorinated & brominated compounds					
chlorinated benzaldehyde			2		
brominated benzaldehyde			3		
chlorinated phenols			2		
brominated phenols			2		
chlorinated ether			1		
hexachloro benzene			(1)		
Related non-halogenated compounds					
substituted benzaldehyde			1		
substituted phenol			1		
Other oxygenated compounds					
phthalate esters		1	3		
acetophenone/ benzophenone			2		
long chain fatty acid			5		
Other sulphur compounds					
dibenzothiophene derivative				2	
di- & tri-sulphide			3		
alkyl thiols	1		1		
sulphur			1		
Hydrocarbons					
PAHs			1	4	
aliphatic hydrocarbons	8	3	2	3	19

Table 2. Organic chemicals identified, and concentrations of metals and metalloids, in samples of wastewater and sediment associated with the Shenzhen Resource, 3rd Industry Zone, Bitou Village, Songgang Town, Baoan District, Shenzhen, China, 2009. (..) signifies compounds identified at trace level using a selective SIM method. For wastewater samples, metal concentrations are given for whole (unfiltered) samples, dissolved concentration accounted for greater than 75% of the whole sample concentration unless otherwise indicated; 25-50%^(a), <25%^(b)

This wastewater contained extremely high concentrations of manganese, copper and lead, at levels which exceeded the most stringent limits of the Guangdong effluent standard by 4 times, 18 times and 25 times respectively. Though at a somewhat lower absolute concentration, the level of beryllium exceeded the limit of the Guangdong effluent standard by 8 times. In addition, the concentrations of nickel and zinc exceeded individual limits under this standard. No such limit exists for tin, another metal present at a high level in the wastewater. The levels of all these metals far exceeded levels typically found in uncontaminated surface waters (Cheung *et al.* 2003, Field 2001, Salomons & Forstner 1984). Individual limits set under the effluent standard are given in Appendix 1, along with information on these metals.

The wastewater was also highly acidic (pH = 1), 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 likely to have a significant impact on aquatic life in the vicinity of the discharge, as well as greatly increase the mobility and toxicity of metals present in the wastewater.

Sediment from the channel into which wastewaters is discharged from this pipe (CN09023) contained high concentrations of copper, lead and tin, all at over 20 times typical background levels (Cheung *et al.* 2003, ATSDR 2004, 2005a, 2007). As mentioned above, there is no contaminated sediment standard in China for comparison, however, the levels of copper and lead exceeded the acceptable environmental quality standards for soils in China (MEP 1996), and contaminated sediment threshold levels from other countries (NMHSPE 2000). Although the sediment levels of copper, lead and tin indicate their accumulation in the sediment as a result of the discharge of contaminated wastewaters, it is likely that these and other metals in wastewater discharged via the channel (CN09027) would have been present at far higher concentrations in the sediment had the wastewaters not been so acidic, which greatly increases the water solubility and mobility of discharged metals.

In addition to the high levels of many metals, numerous organic chemicals were identified in the wastewater discharged at night (CN09027). Amongst these were a range of chlorinated and brominated compounds, including chloro- and bromo-benzaldehydes, chloro- and bromo-phenols, a chlorinated ether, and hexachlorobenzene. Related non-halogenated benzaldehyde and phenol derivatives were also identified, along with other oxygenated compounds; three phthalate esters, including di(ethylhexyl) phthalate (DEHP) and di-n-butyl phthalate (DnBP), and two aromatic ketones, namely acetophenone and benzophenone. A number of hydrocarbons and organo-sulphur compounds were also identified. A full list of all organic chemicals identified in this wastewater (CN09027) is given in Appendix 3.

This wastewater also contained trace levels of four halogenated volatile organic compounds (VOCs). Three of these compounds belong to the group known as trihalomethanes (THMs), compounds which are generally not used in industrial processes, but are by-products of chlorine based water disinfection, and this is their most likely source in this sample. The other VOC (1,2-dichloroethane) was present at a very low level (7.6 µg/l), far below the maximum level recommended for drinking water, for example the WHO guidance value of 50 µg/L (WHO 2006).

The majority of organic chemicals present in the wastewater were not identified in the associated sediment (CN09023), in which two organosulphur compounds (dibenzothiophene derivatives), along with four polycyclic aromatic hydrocarbons (PAHs) (fluoranthene and three phenanthrene derivatives), and three aliphatic hydrocarbons were identified.

6 Conclusions

This study has demonstrated that wastewaters discharged from the Shenzhen Resources facility contain numerous hazardous chemicals, including very high levels of toxic heavy metals, high levels of acidity, and numerous organic chemicals. Concentrations of some metals, as well as the level of acid (pH), in some wastewaters exceeded allowable discharge limits set by the Guangdong effluent regulations, by up to 25 times in one instance. The majority of the organic chemicals identified in wastewaters are not regulated under the Guangdong effluent standard (Guangdong Province 2001).

These results indicate that the treatment processes within this facility, or the way in which they are being employed, are totally inadequate in dealing with the hazardous chemicals within wastes that are being transferred to Shenzhen Resources for treatment. The extremely high levels of metals and acidity in one sample of wastewater which was discharged during the night, including metals which this facility is specifically designed to remove from wastes that it receives, suggests either that wastewaters are sometimes discharged untreated, or that wastewaters are treated in such a poor manner as to be largely ineffective. The discharge of such materials during the night raises additional concerns regarding the monitoring of discharges from this facility by regulatory bodies.

Some of the chemicals identified in discharged wastewaters, particularly certain metals, are able to accumulate in the environment following their release, either within sediments or in some cases in biota as a result of bioaccumulation. Ongoing discharges of these chemicals are likely to lead to ever increasing levels in the receiving environment. In many cases, levels will not significantly decrease for long periods of time, even after any controls on their release have been introduced. Contamination of sediment in the Pearl River Delta with heavy metals and persistent organic pollutants has been demonstrated in numerous previous studies (for example Wang *et al.* 2008, Chau 2006).

Many of the substances identified in the wastewaters can not be addressed effectively through the use of 'end-of-pipe' measures, including conventional wastewater treatment plants. Metals cannot be destroyed, only converted from one form into another. At best, the type of end-of-pipe solutions employed by Shenzhen Resources will simply move metals from one waste stream to another, such as from wastewaters into solid wastes. Furthermore, the treatment processes employed are primarily designed to isolate metals from wastewaters and not to treat the types of organic chemicals identified in discharged wastewaters.

The most effective measures to address releases of hazardous substances are those based upon the use of alternative substances or processes to progressively replace hazardous substances 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 redesigning products and processes in order to progressively reduce industry's reliance on hazardous chemicals, 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: 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 dusts 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 as a result of (IARC 1993). Concentrations of beryllium in uncontaminated sediments are commonly below 5 mg/kg (Taylor *et al.* 2001).

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 dyeing (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 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 A1, along with the highest concentrations found for all wastewaters analysed in this study.

	pH	Beryllium	Copper	Lead	Manganese	Nickel	Zinc
Guangdong effluent standards	6-9	5	500 1000 2000	1000	2000 2000 5000	1000	2000 3000 5000
Maximum level found	1 (Min)	40	36800	2470 0	19200	1270	3980

Table A1. Maximum permissible metal concentrations in discharged wastewaters under the Guangdong effluent standard, and the highest levels found in this study. All metal concentrations are in µg/l

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 A2. In all cases, no data are available for beryllium, manganese and tin.

	Beryllium	Copper	Lead	Manganese	Nickel	Tin	Zinc
Dutch threshold (a)	-	190	53 0	-	210	-	720
NOAA level (b)	-	390	11 0	-	50	-	270
Soil level, China (c)	-	400	50 0	-	200	-	500
Background, estuary (d)	-	38	28	-	34	-	100
Background, inland (e)	-	25	80	-	70	-	80

Table A2. Contaminated sediment 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

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Appendix 2. 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	Chloroform	Propene, 1,3-dichloro-, trans-
Ethane, chloro-	Ethane, 1,1,1-trichloro-	Ethene, tetrachloro-
Ethene, 1,1-dichloro-	Methane, tetrachloro-	Methane, dibromochloro-
Methane, dichloro-	Ethane, 1,2-dichloro-	Bromoform
Ethene, 1,2-dichloro-, trans-	Ethene, trichloro-	Ethane, 1,1,2,2-tetrachloro-
Ethane, 1,1-dichloro-	Methane, dibromo-	Ethane, hexachloro-
Ethene, 1,2-dichloro-, cis-	Methane, bromodichloro-	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 μ m 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 μ m 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 for 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.

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 130°C. 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 130°C 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 μ g/l and 100 μ g/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 manner 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 µg/l and 80 µg/l), prepared internally from different reagent stock.

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

Appendix 3. Organic chemicals identified in CN09027

CAS number	Name
000117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP)
000084-74-2	1,2-Benzenedicarboxylic acid, dibutyl ester
000131-11-3	1,2-Benzenedicarboxylic acid, dimethyl ester
000292-46-6	1,2,3,5,6-Pentathiepane
000291-22-5	1,2,4,5-Tetrathiane
000289-16-7	1,2,4-Trithiolane
002885-00-9	1-Octadecanethiol
000112-88-9	1-Octadecene
000090-59-5	3,5-Dibromosalicylaldehyde
000098-86-2	Acetophenone
005779-95-3	Benzaldehyde, 3,5-dimethyl-
003132-99-8	Benzaldehyde, 3-bromo-
001122-91-4	Benzaldehyde, 4-bromo-
000104-88-1	Benzaldehyde, 4-chloro-
000587-04-2	Benzaldehyde, 3-chloro-
000118-74-1	Benzene, hexachloro- (SIM)
000334-48-5	Decanoic acid
000143-07-7	Dodecanoic acid
000112-26-5	Ethane, 1,2-bis(2-chloroethoxy)-
000119-61-9	Methanone, diphenyl-
000091-20-3	Naphthalene
000112-05-0	Nonanoic acid
000088-06-2	Phenol, 2,4,6-trichloro-
000000-00-0	Phenol, 2,4-di-t-butyl-6-nitro-
000000-00-0	Phenol, 2,4,6-tribromo-
000615-58-7	Phenol, 2,4-dibromo-
000609-89-2	Phenol, 2,4-dichloro-6-nitro-
010544-50-0	Sulfur, mol. (S8)
000544-63-8	Tetradecanoic acid
000112-37-8	Undecanoic acid
001120-21-4	Undecane