

# Organic chemical and heavy metal contaminants from communal wastewater treatment plants with links to textile manufacturing, and in river water impacted by wastewater from a textile dye manufacturing facility, in China

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## Executive Summary

The manufacture of textile products takes place within a large and complex global industry that employs a diverse range of techniques and processes to produce finished products. Many processes are chemically-intensive, and some of the process and finishing chemicals used are known to have intrinsic hazardous properties. For many other chemicals used, little or no information is publicly available on their toxicology or other potential impacts should they be released to the environment.

This study follows on from previous investigations of the discharge of hazardous chemicals from parts of the textile manufacturing industry, as well as their presence in various clothing products. These investigations have highlighted the ongoing use of a wide range of hazardous and potentially hazardous chemicals by this sector, and their resulting releases into the environment, particularly the aquatic environment.

To extend the earlier work, this investigation was carried out to further document releases of hazardous chemicals into surface waters in China, including those related to the manufacture of textile products, either within discharged industrial wastewaters or due to an accidental release. This investigation focussed on three individual cases, including two cases where industrial wastewaters are intentionally discharged via large outfalls from communal wastewater treatment plants (WWTPs). These two WWTPs treat effluents from multiple facilities, many of which, and in one case the majority, are involved in the manufacture of textiles. For the third location, the presence of hazardous chemicals in river water was investigated following an accidental release of wastewater to the river from an individual facility that manufactures dyes for use by the textile sector.

The three locations, all of which were situated close to the estuary of the Qiantang River, were:

- Binhai Industrial Zone (Shaoxing County, Shaoxing City, Zhejiang Province); discharge of treated wastewater from the Shaoxing communal WWTP within the zone into the river estuary (2 samples),
- Linjiang Industrial Zone (Xiaoshan County, Hangzhou City, Zhejiang Province); discharge of treated wastewater from the Xiaoshan Linjiang communal WWTP within the zone into a lagoon adjacent to the river estuary (1 sample),
- A river adjacent to the Zhejiang Deou Chemical Manufacture Co. facility, in the Binhai Industrial Zone, that received the accidental wastewater spill (1 sample).

Samples were collected from these three locations in May 2012. The sample of river water from the affected river adjacent to the Zhejiang Deou facility was collected within 36 hours of the accidental spill.

For each location either a single sample, or in the case of the Binhai Industrial Zone WWTP two samples collected at approximately the same time, were collected for subsequent analysis. The samples were not intended to provide a comprehensive understanding of the chemical makeup of discharged wastewater or surface water for each location, something that can vary over time. Rather, they were intended to provide a snapshot of the type of hazardous chemicals present within either complex industrial wastewaters or within surface water affected by an uncontrolled release of industrial wastewater. For the three samples of discharged wastewaters, due to the nature of the two outfalls it cannot be excluded that some or all of the samples also contained some surface water. All samples were analysed at the Greenpeace Research Laboratories (University of Exeter, UK) using qualitative analysis to detect the presence, though not the concentrations, of semi-volatile and volatile organic compounds, as well as to determine the concentrations of a range of metals and metalloids. In addition, for certain subsamples, the concentrations of a range of perfluorinated chemicals (PFCs) that cannot be identified using the qualitative analysis, were quantified at an accredited independent laboratory.

All samples analysed in this study contained a diverse range of chemicals, many of which have known hazardous properties.

For a large proportion of the chemicals identified in the samples of wastewater originating from the two communal WWTPs there are links to the manufacture of textiles, through the chemicals identified (1) having known uses during manufacturing processes, (2) being intermediates used to manufacture other chemicals that are employed in textile manufacturing, or (3) being degradation products derived from process chemicals. Many of these chemicals can arise from the manufacture or use of dyes or dye formulations, and for these types of chemicals there were similarities between the samples from the two sites. However, the two industrial zones do not exclusively house facilities that manufacture textile products. Some of the chemicals identified, including certain dye-related compounds, also have uses in other industrial sectors, and these cannot be excluded as possible contributory sources. Other hazardous chemicals identified have no known connection to the manufacture of textiles, as may be expected given the mixed nature of effluents handled by the WWTPs.

Similarly, many of chemicals identified in the water sample from the river impacted by the wastewater spill are associated with textile manufacturing, primarily being dye-related chemicals, though other sources cannot be excluded for some.

Key findings for samples analysed in this study can be summarised as follows:

- Some chemicals were identified in samples from the outfalls of both communal WWTPs. These included:
  - A range of chlorinated anilines, compounds related to the manufacture and use of dyes, many of which are toxic to a wide range of organisms, including aquatic life. Some chlorinated anilines identified at the Linjiang site are known or suspected carcinogens, and as such listed under regulations in China (among other countries) related to the use of azo dyes in textiles.
  - A perfluorinated chemical (PFC), perfluorooctanoic acid (PFOA), with concentrations at both sites within the range previously reported for effluents from industrial wastewater treatment plants. This highly persistent and bioaccumulative toxic chemical can arise from use of PFCs in textile manufacture, as well as from many other industrial applications. Three other perfluorinated carboxylic acids (PFCAs) were also detected at the Linjiang site, though in these cases at concentrations below those typically reported for industrial and municipal effluents.
  - Trace levels of a number of hazardous chlorinated chemicals of uncertain source, including 1,2-dichloroethane (EDC) at both sites, and a tetrachlorophenol at the Binhai site – both of which are carcinogenic to animals and possibly carcinogenic to humans. Other examples were also identified at the Linjiang site, including chloroethane.
- Some additional hazardous chemicals were identified in samples from one or other of these two sites. For the outfall from the Shaoxing WWTP within the Binhai Industrial Zone these included:
  - Benzothiazolamines (including some chlorinated derivatives), prominent compounds amongst the complex mixture of chemicals identified in the sample. These chemicals are commonly associated with the manufacture and use of dyes, though for which there is limited information on their toxicity.
  - TMDD, a surfactant associated with the use of dye formulations (amongst other industrial applications) that is persistent in the aquatic environment and moderately toxic to aquatic life.
  - Dibutylphthalate (DBP), a chemical with numerous industrial uses, including the manufacture of textiles. DBP is a widespread environmental contaminant that is toxic to reproduction.
- For the outfall from the Xiaoshan Linjiang WWTP within the Linjiang Industrial Zone, these included:
  - A range of chlorinated benzenes (three dichlorobenzenes, and trace levels of tri- and penta-chlorobenzene), widely recognised hazardous chemicals with many industrial uses, including some related to the manufacture of textiles. Many are persistent chemicals and well known environmental contaminants.
  - Chloronitrobenzenes (CNBs) and nitrobenzene, both widely-used toxic industrial chemicals with many applications, including dye manufacture. Nitrobenzene, together with some chemicals that are derived from CNBs for use in dye manufacture, are carcinogenic in animals and possibly to humans.
  - Hexachlorobutadiene (HCBD), a toxic and hazardous chemical not directly related to textile manufacture, which mainly arises as a by-product during the manufacture of certain chlorinated hydrocarbons.
- Water from a river impacted by an accidental spill of wastewater from the Zhejiang Deou textile manufacturing facility contained a number of chemicals similar to those identified in the wastewater discharges described above. These included:
  - A range of substituted anilines, compounds related to the manufacture and use of dyes. N-alkyl anilines predominated (including a toxic chemical that is harmful to aquatic life with long lasting effects), as well as some toxic brominated anilines, with a toxic chlorinated aniline as a minor component. Unlike some anilines identified at the Linjiang site, the anilines identified in the river water are not known to be carcinogenic.
  - A range of brominated benzenes with hazardous properties, including toxicity to aquatic life.
  - A similar range of chlorinated benzenes to that found at the Linjiang site (di-, tri- and tetra-chlorobenzenes), albeit at trace levels.

In addition to the similarities in chemicals or chemical groups identified in samples from these three sites, there are parallels also with results from our previous studies of textile manufacturing wastewaters in China.

For a number of chemicals identified in the samples from these three locations, little or no information is publicly available on their toxicology, such that the consequences of their release to the environment remain unknown. In

addition, a significant proportion and, in some cases, most of the chemicals isolated from each of these samples could not be reliably identified, not uncommon for complex industrial effluents, and their properties and potential impacts cannot be assessed.

Overall, this investigation has provided an indication of the diverse range of chemicals currently being used and released from facilities within the Binhai Industrial Zone and the Linjiang Industrial Zone, including a range of chemical markers indicative of textile manufacturing or finishing operations.

While this small number of samples are clearly not representative of wastewaters released from Industrial Zones throughout China, or even of the textile manufacturing sector, they do provide an illustrative snapshot of what is likely to be a much wider problem of the discharge or loss of industrial effluents still containing a wide array of harmful contaminants.

Given the lack of information on the various individual industrial sources contributing effluent to the WWTPs within the Industrial Zones, it is not possible to carry out more detailed source reconciliation. As a result, although it would be possible through the techniques available to us to monitor the release to the environment of hazardous chemicals passing through common effluent treatment plants, without knowing the sources, it will remain difficult to use this information to bring about changes in chemical use and management within individual facilities. While this information is vital to highlight the nature of what is likely a widespread problem, a focus on documenting and progressively reducing the upstream use of hazardous chemicals at facility and process level will ultimately be necessary to facilitate a shift towards less hazardous or preferably non-hazardous alternatives, including within the textile industry. Making information on the current use and release of hazardous chemicals by individual facilities publicly available will be an important contribution towards that goal. Until such time that toxic and persistent chemicals are substituted at source, common WWTPs will remain an inefficient tool for protection of the aquatic environment from chemical pollution.

## 1. Introduction

The manufacture of textile products makes use of a diverse range of techniques and processes, many of which rely on the use of numerous process and finishing chemicals. Some of the chemicals currently employed within different parts of this sector are known to have intrinsic hazardous properties, while for many others little or no information is publicly available on their toxicology or other potential impacts should they be released to the environment.

Greenpeace has recently conducted a number of investigations into hazardous chemicals in wastewaters discharged from parts of the textile manufacturing industry (Brigden *et al.* 2009, Greenpeace 2011a), as well as their presence in various clothing products (Greenpeace 2011b, Brigden *et al.* 2012a, Brigden *et al.* 2012b). These studies have highlighted the on-going use of a wide range of hazardous and potentially hazardous chemicals by parts of the textile manufacturing sector, and the resulting releases of such substances into the environment, particularly the aquatic environment.

This study extends the scope of the previous work by further investigating releases of hazardous chemicals in industrial wastewaters being discharged into surface waters in China, including those related to the manufacture of textile products.

This study investigated three individual cases. For two of the cases, the investigations centred on locations where industrial wastewaters are intentionally discharged via large outfalls from communal wastewater treatment plant (WWTP). These two WWTPs treat effluents from multiple facilities many, and in one case the majority, of which are involved in the manufacture of textiles. For the third location, the presence of hazardous chemicals in river water was investigated following an accidental release of wastewater to the river from an individual facility that manufactures dyes for use by the textile sector.

## 2. Sampling programme

Samples of discharged wastewater were collected in the vicinity of two large outfalls, each of which discharges treated wastewater from a communal WWTP within an industrial zone adjacent to it, namely the Binhai Industrial Zone (Shaoxing County, Shaoxing City, Zhejiang Province), and the Linjiang Industrial Zone (Xiaoshan County, Hangzhou City, Zhejiang Province).

The study also included an investigation of environmental contamination by hazardous chemicals in a river which had received an accidental release of wastewaters from the Zhejiang Deou Chemical Manufacture Co. facility, located in the Binhai Industrial Zone.

In May 2012, samples of discharged wastewaters and surface waters were collected from these three locations. Details of the samples collected are provided below, and summarised in Table 1.

### **Shaoxing Communal WWTP within the Binhai Industrial Zone**

Two water samples (CN12008 & CN12009) were collected from the Qiantang River estuary in the vicinity of an underwater outfall from a large discharge pipe, which originates from the Shaoxing Water Treatment Development Co., Ltd. (Shaoxing WWTP), the communal WWTP within the Binhai Industrial Zone. This WWTP receives and treats effluents from all facilities within the zone. These are involved in a range of different industrial activities, though the majority are engaged in various aspects related to the manufacture of textiles (BHSX 2012). The WWTP may also treat wastewater generated from several surrounding villages.

At the time that the samples were collected, the discharge of large volumes of wastewater via the submerged pipe resulted in a surface “boil” immediately above the submerged outfall, and the two samples were collected from this feature on the same date (28 May 2012) and at approximately the same time. The potential for some mixing of surface water with discharged wastewater within the surface boil, and therefore within the waters sampled, cannot be excluded.

### **Xiaoshan Linjiang Communal WWTP within the Linjiang Industrial Zone**

One water sample (CN12010) was collected on the same day from a lagoon, containing discharged wastewater, which is located on the bank of the Qiantang River estuary, approximately 4 kilometres upstream from the outfall of the Binhai Industrial Zone WWTP discharge pipe mentioned above. At this location, wastewater is discharged to the lagoon via a pipe, with an outfall below the surface of the lagoon. The pipe carries treated wastewater from the Xiaoshan Linjiang communal WWTP within the Linjiang Industrial Zone. This WWTP treats wastewaters from almost all facilities within the Linjiang Industrial Zone, from all facilities within the smaller Jiangdong Industrial Zone, as well as wastewater from five nearby towns and villages (Hangzhou 2006). Textile manufacturing is one of the key sectors within the Linjiang Industrial Zone, alongside other industrial activities (Xiaoshan 2012). The smaller Jiangdong Industrial Zone, also located in Xiaoshan District, houses a range of industries including textiles (XETZ 2012).

## River adjacent to the Zhejiang Deou Chemical Manufacture Co.

One further sample had been collected on 10 May 2012 in response to an accidental release of wastewater from the Zhejiang Deou Chemical Manufacture Co. facility, located in the Binhai Industrial Zone, which produces substances for use in dyeing by the textile industry. Under normal operations, wastewater from this facility is treated by the communal WWTP within the industrial estate. However, on the afternoon of 8 May 2012, it was reported that an incident occurred which resulted in a large volume of wastewater being released to a river on the north-east side of the facility, in Xiner Village of the Binhai Industrial Zone, causing the river water to become red in colour (QQ 2012). It is not known whether this wastewater had undergone any form of treatment prior to release.

Less than 36 hours after this incident, a sample of water (CN12011) was collected from the receiving river in the vicinity of the facility. The river water was no longer red at the time when the sample was collected, and it must be kept in mind that the sample may have contained substances arising from multiple inputs to the river, not just those arising from the facility involved in the accidental release.

Each sample consisted of two or three subsamples collected in different types of bottles depending on the subsequent analyses to be carried out on each subsample. In all cases, one subsample was collected in a 0.5 litre screw-cap glass bottle, for use in the quantitative analysis of metals and metalloids as well as the qualitative analysis of solvent extractable (semi-volatile) organic compounds. In addition, a duplicate sample was collected in a separate 50 ml amber glass bottle with a ground-glass stopper (filled to leave no headspace) to be analysed for volatile organic chemicals (VOCs). All glass bottles had been pre-cleaned, including being rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metal and organic residues.

	Sample code	Collection point	Sample type	Time & Date	Description
Shaoxing & Xiaoshan Linjiang communal WWTPs	CN12008	Surface boil above submerged outfall	Wastewater/ estuary water	12.30 28 May 2012	<b>Shaoxing WWTP, Binhai Industrial Zone;</b> Surface boil located above the outfall of the submerged WWTP discharge pipe to the Qiantang River, Shaoxing County
	CN12009				
	CN12011	Wastewater lagoon	Wastewater/ estuary water	13.30 28 May 2012	<b>Xiaoshan Linjiang WWTP, Linjiang Industrial Zone;</b> Lagoon of wastewater located on the bank of the Qiantang River, Xiaoshan County, above the submerged WWTP discharge pipe
River adjacent to the Zhejiang Deou Chemical Manufacture Co.	CN12011	River adjacent to facility	River water	00.30 10 May 2012	Collected from a river that received a wastewater spill on 8 May, on the northeast side of the facility, in Xiner Village of the Binhai Industrial Zone

Table 1: Details of samples collected for this study, from locations in China, 2012

In addition, for all samples except the one associated with Zhejiang Deou Chemical Manufacture Co. facility (CN12011), a third duplicate sample was collected in a 500 ml polypropylene bottle previously rinsed with analytical grade methanol, for use in the quantification of a range of perfluorinated chemicals (PFCs) in the water.

All samples in glass bottles were immediately chilled and kept cool and dark, while those collected for PFC analysis were frozen and kept frozen and dark, during transit to the Greenpeace Research Laboratories at the University of Exeter in the UK. Upon arrival, samples in glass bottles were stored cool and dark at the Greenpeace Research Laboratories prior to analysis at that laboratory, while those collected for PFC analysis were cooled to -20°C for 24 hours, before being transported in a frozen state to an accredited independent laboratory where they were subsequently analysed.

### **3. Methodology**

For those samples analysed at the Greenpeace Research Laboratories, each sample was analysed quantitatively for a range of metals and metalloids. Each sample was also analysed qualitatively for the presence of semi-volatile (solvent-extractable) organic compounds, and separately for the presence of volatile organic compounds (VOCs), including quantitative analysis for a range of common VOC environmental contaminants.

Metal and metalloid 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. Total concentrations in the whole (unfiltered) sample and the concentrations of dissolved forms in a filtered sample were determined separately for each sample. Hexavalent chromium concentrations (in filtered samples only) were determined colourimetrically using a diphenylcarbazide method.

Semi-volatile organic compounds were isolated from each sample using solid phase extraction (SPE) with ethyl acetate, pentane and toluene. Extracted compounds were subsequently identified as far as possible using gas chromatography - mass spectrometry (GC-MS). Volatile organic chemicals (VOCs) were identified and quantified in all samples as received (with no pre-treatment) using GC/MS with headspace sample introduction technique. Quantification of any VOC detected was carried out using external standards calibration. More detailed descriptions of the sample preparation and analytical procedures are presented in the Appendix 1.

Those samples in which PFCs were quantified were analysed at an accredited independent laboratory using liquid chromatography-mass spectrometry (LC-MS/MS), employing appropriate quality control procedures, including the use of certain <sup>13</sup>C labelled PFCs as internal and recovery standards.

### **4. Results and Discussion**

The results for the samples are outlined in the following sections, divided into the locations from which the samples were collected. For all samples, semi-volatile (solvent-extractable) organic compounds identified in each of the individual samples using chemical screening are summarised in Table 2, with a full list of organic chemicals identified in each sample provided in Appendix 2. The concentrations of selected volatile organic compounds (VOCs) identified in each sample and the concentrations of PFCs are given in Table 3 and Table 4 respectively, with full data for all quantified PFCs provided in Appendix 3. The concentrations of metals and metalloids in filtered (dissolved concentrations) and in whole waters (dissolved and suspended concentrations) are reported in Table 5.

#### **4.1 Shaoxing Communal WWTP within the Binhai Industrial Zone**

##### ***4.1.1 Organic chemical contaminants***

The two samples collected from this location (CN12008 & CN 12009) had very similar compositions in terms of the organic chemicals identified. The prominent compounds in the chromatograms for both samples were a range of substituted 2-benzothiazolamines (also known as 2-aminobenzothiazoles), including some chlorinated derivatives. Many of the mono- and di-substituted 2-aminobenzothiazoles, including halogenated, nitrated and methylated derivatives, appear in commercial dyes with a range of hues from orange-red to deep violet and blue (Peters & Gbadamosi 1992 a&b, Yen & Wang 2004, Deligeorgiev *et al.* 1995). There is limited information on the toxicity of 2-aminobenzothiazole derivatives and, for some of them (including for the two dichloro-2-benzothiazolamines identified), no hazard information has been specified. 6-Chloro-2-benzothiazolamine has been classified under the Globally Harmonised System (GHS)<sup>1</sup> as irritating to eyes and skin (H315, H319) and harmful if swallowed (H302). 6-Nitro-2-benzothiazolamine has been classified under GHS as irritating to eyes and skin (H315, H319) and harmful if swallowed, inhaled and in contact with the skin (H302, H332, H312), while 4-methyl-2-benzothiazolamine has been classified as harmful if swallowed (H302).

<sup>1</sup> The Globally Harmonised System of Classification and Labelling of Chemicals (GHS), a system set up under the UN, provides a way of assessing the hazardous properties of chemicals through the use of hazard statements (UN 2011). The hazard statements used for individual substances within Section 3.4 are a composite of information drawn from a number of sources including material safety data sheets (MSDSs) supplied by Sigma-Aldrich (<http://www.sigmaaldrich.com>); Landolt-Börnstein (<http://lb.chemie.uni-hamburg.de>); Merck Millipore (<http://www.millipore.com>); Alfa (<http://www.alfa.com>); ACROS (<http://www.acros.be>)

	Shaoxing WWTP, Binhai Industrial Zone	Xiaoshan Linjiang WWTP, Linjiang Industrial Zone	Zhejiang Deou facility
	Surface boil at outfall, Qiantang River	Wastewater lagoon, edge of Qiantang River	River adjacent to facility
Sample type	WW/EW	WW/EW	WW/EW
Sample code	CN12008	CN12009	CN12010
Number of compounds isolated	60	41	67
Number identified to >90%	19	16	48
Percentage identified to >90%	32%	39%	72%
<b>Halogenated anilines:</b>			
Monochloro- & methyl derivative			2*
Dichloro-	✓	✓	5
Dichloro-, nitro-			✓
Trichloro-	✓*		✓*
Dibromo- & methyl derivative			2
Tribromo-			✓
Chloro-5-(trifluoromethyl)-	✓*	✓*	
N-alkyl anilines			5*
Methoxy anilines			✓
Aniline-propiononitriles			2
<b>2-Amino-benzothiazoles:</b>			
Mono- and di-chloro	3	3	
Nitro-	✓	✓	
Methyl-	✓*	✓	
<b>Halogenated benzenes:</b>			
Monochloro, methoxy-			✓
Monochloro, nitro-			2
Dichloro-	2(SIM)	2(SIM)	2 + SIM
Trichloro-			2(SIM)
Tetrachloro-			SIM
Pentachloro-			SIM
Dibromo- & 2-methyl derivative			2*
Bromo, chloro, 2-methyl-			✓*
<b>Nitrobenzene</b>			
Tetrachlorophenols	SIM		
1-(4-Chlorophenyl)- ethanone			✓*
Hexachlorobutadiene			SIM
TMDD	✓*	✓	
Quinoline, ethyl derivative	✓	✓	
Phthalate	DBP*		
2,6-di-tert-butylbenzoquinone (DBQ)	✓*	✓*	
Benzonitrile, methyl-			✓
Methylenediphosphonate, tetraethyl	✓	✓	
Ethers			3
Long chain fatty acids & esters	2	3	
Naphthalene & alkyl derivates			7
<b>Polycyclic aromatic hydrocarbons (PAHs)</b>			
1,1'-Biphenyl & methyl derivatives			3
Alkanes	1		5

Table 2: summary of organic contaminants present in the samples of wastewater (WW)/ estuary water (EW) or river water (RW) associated with the three locations, in which semi-volatile (solvent extractable) organic compounds were identified (to >90% reliability), including an indication of presence for the compounds most commonly identified in these samples, (or number of individual compounds where more than one compound was identified for a group). "SIM" indicates detection at trace levels only using Selected Ion Monitoring mode of analysis. \* indicates being a minor component of the total ion chromatogram

	Shaoxing WWTP, Binhai Industrial Zone	Xiaoshan Linjiang WWTP, Linjiang Industrial Zone	Zhejiang Deou facility
	Surface boil at outfall, Qiantang River	Wastewater lagoon, edge of Qiantang River	River adjacent to facility
Sample type	WW/EW	WW/EW	WW/EW
Sample code	CN12008 (mg/l)	CN12009 (mg/l)	CN12010 (mg/l)
<b>Benzene, 1,2-dichloro-</b>	n/d	n/d	2
<b>Benzene, 1,4-dichloro-</b>	n/d	n/d	<1
<b>Benzene, chloro-</b>	n/d	n/d	n/d
<b>Butadiene, hexachloro-</b>	n/d	n/d	2
<b>Chloroform</b>	n/d	n/d	2
<b>Ethane, 1,2-dichloro-</b>	<1	n/d	22
<b>Ethane, chloro-</b>	n/d	n/d	81
<b>Methane, dichloro-</b>	n/d	n/d	6

Table 3: Concentrations of selected volatile organic compounds (VOCs) in wastewater (WW) / estuary water (EW) or river water (RW) samples (mg/l). Limit of quantification was 1 mg/l for all detected VOCs. n/d - not detected. Where presented as '<', the VOC was identified, but at a concentration below the level that could be accurately quantified.

	Shaoxing WWTP, Binhai Industrial Zone	Xiaoshan Linjiang WWTP, Linjiang Industrial Zone
	Surface boil at outfall, Qiantang River	Wastewater lagoon, edge of Qiantang River
Sample type	WW/EW	WW/EW
Sample code	CN12008 (ng/l)	CN12009 (ng/l)
<b>Perfluorooctanoic acid (PFOA)</b>	88.7	112
<b>Perfluoropentane acid (PFPeA)</b>	< 3	< 3
<b>Perfluorohexanoic acid (PFHxA)</b>	< 10	< 10
<b>Perfluoroundecanoic acid (PFUnA)</b>	< 3	< 3
		93.2
		13.0
		10.7
		10.2

Table 4: Concentrations of PFCs in wastewater (WW) / estuary water (EW) samples (ng/l) collected from the vicinity of a wastewater discharge from communal wastewater treatment plants (WWTPs) within the Binhai Industrial Zone and the Linjiang Industrial Zone.

A range of chlorinated anilines was also identified in these two samples, examples of which were also identified in samples collected from both other locations investigated in the current study (See Sections 4.2 and 4.3) and in wastewater samples analysed in a previous investigation of textile manufacturing facilities in China (Greenpeace 2011a). Chlorinated anilines identified in CN12008 & CN12009 included 3,5-dichloroaniline (in both samples), 2,4,6-trichloroaniline (a minor constituent in CN12008), and 2-chloro-5-(trifluoromethyl)aniline (a minor constituent in both samples). Substituted anilines, including chlorinated anilines, are used as dye intermediates, including for certain azo dyes. The chlorinated anilines identified in these samples are not amongst the carcinogenic amines listed by regulations which prohibit, in various countries (including China and EU member states), the use in textiles of azo dyes that can degrade to form unacceptable concentrations of certain carcinogenic amines (EU 2002, SAPRC 2012). However, these chemicals are nonetheless toxic to a wide range of organisms including aquatic organisms, other animals, and humans, though information on latter is quite limited. 3,5-Dichloroaniline and 2,4,6-trichloroaniline are both classified under GHS as very toxic to aquatic life with long lasting effects (H410), toxic if swallowed, inhaled and through contact with the skin (H301, H331, H311), and may cause damage to organs through prolonged or repeated exposure (H373). 2-Chloro-5-(trifluoromethyl)-aniline is classified under GHS as harmful if swallowed, inhaled and through contact with the skin (H302, H333, H312). More detailed information on the properties of halogenated anilines is presented in Box A.

Some aniline derivatives are also carcinogenic, including chloroaniline, chloromethylaniline (also known as chlorotoluidine) and 2-methoxy-aniline (also known as *o*-anisidine) which were identified in this study (Section 4.2). These three anilines are amongst the carcinogenic amines listed in regulations in various countries, including China and EU member states, which prohibit the use in textiles of azo dyes that can degrade to form unacceptable concentrations of certain carcinogenic amines (EU 2002, SAPRC 2012). In addition, chlorotoluidine has been classified as probably carcinogenic to humans (group 2A) and chloroaniline have been classified as possibly carcinogenic to humans (group 2B) by the International Agency for Research on Cancer (IARC 2012).

Other substances identified in both samples included a decynediol derivative known as TMDD, an alkyl quinoline, a diphosphonate ester and some long chain fatty acids/esters. Other less prominent peaks identified in one or both of the samples were 2,6-di-tert-butylbenzoquinone (DBQ) and a phthalate ester (dibutylphthalate, DBP), as well as some chlorinated compounds that were present at only trace levels (two dichlorobenzenes in both samples, as well as tetrachlorophenol and 1,2-dichloroethane (EDC) in CN12008 only). Furthermore, the quantification of PFCs identified one compound (perfluorooctanoic acid, PFOA) in both samples from this location. The substances identified in samples from this location are discussed below.

The decynediol derivative (2,4,7,9-tetramethyl-5-decyne-4,7-diol, also known as TMDD), which was also identified in a previous investigation of textile manufacturing wastewaters in China (Greenpeace 2011a), is produced and used in large quantities, primarily as an industrial defoaming non-ionic surfactant under the trade name Surlynol 104, including in dye and printing ink formulations. Other uses include the production of polyethylene glycol ether surfactants, and in adhesive formulations (Air Products and Chemicals 2002, HSDB 2002, Musselman & Chander 2002, USDA 2009, US EPA 2002, US EPA 2011).

Though not commonly reported as an environmental contaminant, TMDD has been identified in river water in Germany, including for some locations where its presence was attributed to inputs via sewage effluents (Dsikowitzky *et al.* 2004a&b, Schwarzbauer and Heim 2005, Guédez *et al.* 2010), in the river Meuse in the Netherlands (Hankemeier *et al.* 1999), and in the Colorado River in the US (Snyder *et al.* 2001). Once released in wastewaters, TMDD is not readily degraded and is therefore persistent in the aquatic environment (US EPA 2008a). TMDD has been found to be moderately toxic to aquatic organisms in laboratory experiments on fish (fathead minnows and carp), aquatic invertebrates (*Daphnia magna*), and green algae (*Selenastrum capricornutum*) (US EPA 2002). Furthermore, this substance has been classified under GHS as harmful to aquatic life with long lasting effects (H412).

No information could be identified on the toxicity of the alkyl-quinoline identified (2-ethyl-quinoline), nor on the potential use of this substance in the manufacture of textiles. The situation is similar for many other alkyl-quinolines, though there is some evidence that certain alkyl-quinolines are used as precursors to certain dyes (Gu *et al.* 2010, Shindy *et al.* 2002), and can be present in wastewater from facilities manufacturing dyestuffs and intermediaries (Yuan *et al.* 2006, Oliveira *et al.* 2007). Quinoline derivates were also identified in wastewater samples analysed in a previous investigation of textile facilities in China (Greenpeace 2011a). Certain other related alkyl-quinolines have been reported to have moderate aquatic toxicity in bioassay tests (Birkholz *et al.* 1990).

## Box A. Aniline derivatives

Halogenated anilines (also called halogenated benzenamines), along with other substituted anilines, are used in many applications including in manufacture of dyes, rubbers and plastics, pesticides, herbicides and pharmaceuticals (Stellman *et al.* 1998, WHO 2003a, Sokolowska *et al.* 2001). Specifically, 2-methoxy-aniline (also known as *o*-anisidine) is used as a raw/starting material in manufacture of cross-linking polyamine dyes (Li *et al.* 2008a) and is an intermediate for a number of direct yellow, red and blue azo dyes and pigments and some acid dyes (Lawrence & Marshal 1985, Srour 1996). There is also some evidence that some hair dyes are based on *o*-anisidine or, at least, have been in the past (Van Duuren 1980). Propanenitrile aniline derivatives are used to prepare azo dyes suitable for cellulose fibres, and are especially suited to dyeing or printing fibres or fabrics of nitrogen-containing fibres (Fuchs & Meininger 1977). One of these compounds (N-ethyl-N-cyanoethyl-aniline) is also used in the preparation of photosensitive diazo resin for lithographic printing (European Patent 1993).

Anilines can be released into the environment directly within industrial effluent from the textile (Pinheiro *et al.* 2004) or leather industry, or indirectly as breakdown products of herbicides and pesticides such as diuron, linuron and propanil (Stasinakis *et al.* 2009, Badawi *et al.* 2009, Mestankova *et al.* 2011, Carvalho *et al.* 2010). In addition, halogenated anilines, such as 2,4,6-tribromoaniline, may be present as impurities in colour additives as a result of incomplete reaction of starting materials or low grade of starting material (Weisz *et al.* 2004). Anilines are an important class of environmental water pollutants due to their wide usage and high solubility in water.

Aniline and its chlorinated derivatives, including mono-, di- and trichlorinated isomers, are toxic to wide range of aquatic organisms (Dom *et al.* 2010). Among dichloroanilines (DCA), 3,4-DCA is the most investigated for aquatic toxicity. In one early study (Adema & Vink 1981), the aquatic toxicity of 3,4-DCA was determined for about 15 marine and fresh water animals and several unicellular algae. Sub-lethal effects were detectable after exposure to very low concentrations of DCAs in those test organisms. Reproduction of *Ophryotrocha diadema* and of *Daphnia magna* were the most sensitive criteria. Significant effects were obtained with both test species at a concentration of 0.010 mg/l. Similar results were obtained in later studies of 3,4-DCA aquatic toxicity (Crossland 1990, Guilhermino *et al.* 1994). 3,4-DCA has been also found to be toxic to fish (Monteiro *et al.* 2006, Schäfers & Nagel 1993). Because 3,4-DCA induces *cyp1a1* expression through *ahr2* activation in zebrafish embryos, this chemical is used as a reference toxic compound for examining Ahr/Cyp1a1 pathway reaction (Ito *et al.* 2010). Two other isomers, 3,5-DCA and 2,6-DCA, have been also used as model toxic compounds in experiments with algae *Chlorella vulgaris* for the estimate of novel toxic compounds (Xia *et al.* 2009).

2,6-dichloro-4-nitroaniline (also known as dicloran or dichloran) is toxic for freshwater fish and invertebrates and has been classified by the US EPA as highly toxic for freshwater fish and moderately toxic under acute exposure for freshwater invertebrates (US EPA 2006). This aniline derivative is also mutagenic (Shirasu *et al.* 1976), and was previously detected in wastewaters from an azo dye processing textile plant in Sao Paulo, Brazil, where it was shown to contribute to the mutagenicity of water from the Cristais River that receives effluents from this facility (de Oliveira *et al.* 2009). In general, effluents from some textile industrial sites are known to contribute to mutagenic activity of receiving waters (Kwon *et al.* 2008), an effect mostly attributed to a presence of azo dye-related chemicals (Umbuzerio *et al.* 2005).

The toxicity of halogenated anilines to mammals is also well known. For example, DCA, as well as other aromatic amines, may induce an increase of blood methemoglobin content (Guilhermino *et al.* 1998), anaemia and kidney and liver injury (Lo *et al.* 1990; Valentovic *et al.* 1995 & 1997). It was also shown in the liver and kidney *in vitro* cytotoxicity study with structural isomers of DCA that the kidney was more sensitive than the liver to DCA isomers, and that the most toxic isomer was 3,5-DCA (Valentovic *et al.* 1995). However, a later toxicity study (Hong *et al.* 2000) has shown that among the 3,5-dihaloanilines, 3,5-dibromoaniline proved to be the most potent nephrotoxicant, and 3,5-difluoroaniline the least potent. The reproductive toxicity of 3,4-DCA was confirmed in a study on the activities of testicular enzymes of male rats treated with this chemical (Zhang & Lin 2009). Monohalogenated anilines have been found to induce neurotoxicity in rats after a single oral dose, with 4-bromoaniline showing the greatest neurotoxic potential compared to the corresponding fluoro-, chloro- and iodo-substituted anilines (Okazaki *et al.* 2003).

There is limited information on the human toxicity of DCAs. The *in vitro* investigation of toxic effects of herbicide propanil and its main metabolite 3,4-DCA, on hematopoiesis using human mononucleated cord blood cells has shown that both compounds interfered with erythroid colony formation, albeit at different stages of the differentiation pathway and with different effects according to the dose or the time of exposure (Malerba *et al.* 2002). Two DCAs (3,4-DCA and 3,5-DCA) have been detected in human urine in the general population in Bavaria, Germany as metabolites of pesticides that were taken up with diet (Angerer *et al.* 2007).

There is limited information on the toxicity of propanenitrile aniline derivatives, though they have been classified under GHS as capable of causing irritation to the eyes and skin (H315, H319).

The diphosphonate ester identified (tetraethyl methylenediphosphonate) has uses as an intermediate in the preparation of pharmaceuticals and other substances (Cheng *et al.* 2000, Huang *et al.* 2003), though no information on the potential use or release of this substance related to textile manufacturing could be found. The source of this chemical at this location remains uncertain. Very little information could be found on the toxicity of this compound, which is classified under the GHS as irritating to eyes and skin (H315, H319).

Long-chain fatty acid esters such as those of palmitic and stearic acid, which were identified at this location, are present in animal or vegetable fats, oils, or wax. These substances are used in a variety of textile manufacturing processes, including as defoaming and dispersing agents in dye formulations, and as sizing agents (IPPC 2003). These compounds are not of particular environmental concern due to their low toxicity and being readily biodegradable.

Other less prominent peaks identified in one or both of the samples collected from this location included 2,6-di-tert-butylbenzoquinone and dibutylphthalate.

2,6-di-tert-butylbenzoquinone (DBQ), identified in both samples, was also reported in previous investigations of textile manufacturing facilities in China (Brigden *et al.* 2009, Greenpeace 2011a). Benzoquinone derivatives, including DBQ, can be used as photo initiators in various industrial processes (van der Graaf *et al.* 1991). DBQ has also been found among semi-volatile chemicals emitted during heating of certain plastics (Watanabe *et al.* 2007). There is some evidence for the toxicity of DBQ to mammalian cells from in vitro tests, in that 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 is classified under the GHS as irritating to eyes and skin (H315, H319).

Dibutylphthalate (DBP), identified in CN12008, has uses in textile manufacture, though it also has numerous other uses, primarily as a plasticiser (or softener) in plastics. Other applications include uses as components of inks, adhesives, sealants, surface coatings and personal care product. DBP is widely distributed in the environment, primarily due to losses from products in which it had been incorporated (Fromme *et al.* 2002). As a consequence, the presence of DBP within the river estuary water cannot be excluded, and this may contribute to the presence of DBP in the samples analysed. Substantial concerns exist with regard to the toxicity of phthalates to wildlife and humans. DBP, along with certain other phthalates, can cause toxic effects on reproduction in animals and humans (Mylchreest *et al.* 2002, Swan *et al.* 2005). As a result DBP, along with other phthalates, has been classified as “toxic to reproduction” within Europe, and has been included on the list of candidates as “substances of very high concern” under the EU REACH Regulation (ECHA 2010). DBP is classified under the GHS as having the potential to damage fertility or the unborn child (H360) and very toxic to aquatic life (H400).

The chlorinated compounds that were found at only trace levels (dichlorobenzenes, tetrachlorophenol and 1,2-dichloroethane, which is also known as EDC) were identified using a sensitive Selective Ion Monitoring (SIM) method. The presence of these chemicals in the samples at trace levels may be due to dilution within the mixed wastewater, which originates from many sources. However, the presence of these chemicals within the river estuary water cannot be excluded which could explain their presence in the analysed samples of mixed wastewater and surface water from this location.

The two dichlorobenzenes identified in both samples at trace levels are well known environmental contaminants, largely due to widespread use as a deodoriser and disinfectant in sanitary products (in the case of 1,4-dichlorobenzene), which may be a contributory source also at this location. However, dichlorobenzenes, particularly 1,2-dichlorobenzene after its conversion to 1,2-dichloroaniline, are also used as intermediates for the production dyes (ATSDR 2006). Dichlorobenzenes were also identified in samples from all other locations investigated in this study (Sections 4.2 & 4.3). One of the dichlorobenzenes identified (1,4-chlorinated isomer) has been classified as a category 2 carcinogen, relating to inhalation exposure to this compound (ECHA 2012), and is also toxic to the liver and kidneys following repeated exposures (EURAR 2004). As a result, a proposal has recently been made for restrictions on the marketing and use of 1,4-dichlorobenzene in toilet disinfectants and air fresheners in the EU (ECHA 2012). The tetrachlorophenol was present in CN12008 as a very minor trace component. It has been reported that tetrachlorophenols could be contaminants in some dispersal dyes (Zhejiang Longsheng 2011). However, an alternative source may be due to the presence of tetrachlorophenols as contaminants in commercial formulations of pentachlorophenol (Kalliokoski & Kauppinen 1990), which has uses as a fungicide primarily for wood but also for textiles (ATSDR 1999, OSPAR 2004). Polychlorophenols, including tetrachlorophenol, have been listed as possibly carcinogenic for humans (Group 2B, IARC 1999a). In addition, classifications for tetrachlorophenol under the GHS include being toxic if swallowed (H301) and very toxic to aquatic life (H400).

The chlorinated VOC, 1,2-dichloroethane (EDC), was present in CN12008 at a trace level (below 1 mg/l, see Table 4). This hazardous chemical is primarily used in the manufacture of PVC, with smaller amounts of EDC used in the manufacture of other chemicals including the synthesis of aziridines, and ethylene diamines (ATSDR 2001). The International Agency Research on Cancer (IARC 1999b) has placed 1,2-dichloroethane in Group 2B (possibly carcinogenic to humans), and the US EPA has classified 1,2-dichloroethane as a Group B2 carcinogen (probable human carcinogen) (US EPA 2000).

In addition to the organic chemicals identified using qualitative chemical screening, as described above, one PFC was identified and its concentration quantified in both samples from this location. Perfluorooctanoic acid (PFOA) was detected in CN12008 and CN12009 at 88.7 ng/l (0.0887 mg/l) and 112 ng/l (0.112 mg/l), respectively. All other quantified PFCs were below method detection limits (see Appendix 3 for details).

The concentrations of PFOA in these two samples are similar to those found in samples of wastewater discharged from a textile manufacturing facility in 2011 (Greenpeace 2011a), though other PFCs were also identified at that previous location. The levels of PFOA (88.7 and 112 ng/l) are above the range commonly reported in surface waters in several parts of the world, including China, though similar and even higher levels have been reported in surface waters at some locations, especially in industrialised areas (Loos *et al.* 2009, Jin *et al.* 2009). The levels found in this study are within the range reported for effluents from wastewater treatment plants, especially those which are known to receive industrial effluents for treatment.

PFCs are used in a wide range of applications, including as water and grease repellent finishes on textile and paper products and in fire fighting foams, as well as in various industrial processes, including the manufacture of electrical equipment. Most PFCs are highly persistent in the environment and able to bioaccumulate, and many have toxic properties (Hekster *et al.* 2003, Key *et al.* 1997). More information on PFOA and other PFCs, including levels reported in surface waters and effluents, and a summary of hazardous properties is provided in Box B.

## Box B. Perfluorinated chemicals (PFCs)

PFCs are man-made chemicals that are generally highly resistant to chemical, biological and thermal degradation (So *et al.* 2004). Many PFCs also have relatively low solubility in both water and oils, unique properties that have underpinned their widespread use as water, grease and stain-repellent finishes on textile and paper products, as well as for specialised solvents and surfactants used in industry and as components of cosmetics and plastic products (OECD 2002, Hekster *et al.* 2003). Their resistance to breakdown even at high temperatures has also led to their use in firefighting foams and in lubricants for high temperature applications (OSPAR 2006). However, the properties of this group of chemicals also result in one of their major environmental downsides of PFCs, namely their long persistence in the environment once they are released, whether from manufacturing or disposal operations or during the useful lifetime of a product (Key *et al.* 1997).

PFCs fall into four broad categories; Perfluorinated alkyl sulphonates (PFASs), perfluorocarboxylic acids (PFCAs), fluoropolymers and fluorotelomer alcohols (FTOH) (Dinglasan *et al.* 2004). The most widely used PFASs have been those based on perfluorooctane sulfonate (PFOS), one of the most well known PFC (Stock *et al.* 2004). Perfluorooctanoic acid (PFOA) is the most well known of the PFCAs. It has been reported that PFOA is not currently manufactured in China, but is imported to produce PFC-related formulations (FECO/MEP 2009). Other than through deliberate production, PFOA (along with other shorter and longer-chain PFCAs) can also be generated as an unintended by-product in the manufacture of perfluorinated telomer alcohols, or FTOHs (Poulsen & Jensen 2005).

PFASs (especially PFOS) and PFCAs (especially PFOA) have been reported as contaminants in almost all environmental media, including freshwater, groundwater and seawater sediments and soils (Lindstrom *et al.* 2011). PFOA is widely distributed in surface waters. In Europe, a summary of water samples from 100 rivers found average and median concentrations of 12 ng/l and 3 ng/l, respectively (Loos *et al.* 2009), though higher values for some surface waters in Europe have been reported, including 100 ng/l in the UK's River Wyre and 200 ng/l in Italy's River Po (Loos *et al.* 2009, McLachlan *et al.* 2007). Though fewer data are available for locations in China, levels have been reported for some river systems, including a median PFOA concentration of 5.4 ng/l for locations along the Yangtze River (Jin *et al.* 2009), concentrations ranging from 0.85 to 13 ng/l for stations on the Pearl River (So *et al.* 2007), ranges of 10.9-27.9 ng/l and 10.6-36.7 for the Liao River and Taihu Lake, respectively (Yang *et al.* 2011), and between 4.4 and 42 ng/l in the Haihe River with higher levels in more industrialised areas (Li *et al.* 2011). In Northern China, PFOA was found to be the most abundant PFC in a number of river systems (1.2 to 27 ng/l), with the highest mean (and highest value overall, 82 ng/l) being detected in the most industrialised of the areas investigated (Wang *et al.* 2012).

Higher PFOA concentrations (110 and 297 ng/l) have been reported at locations immediately downstream from centres of industry on the Yangtze River (Jin *et al.* 2009), and relatively high PFOA concentrations have also been found in effluents from some treatment plants receiving a high proportion of mixed industrial waste in China, including examples where industrial sectors other than textile manufacturing dominate (for example; 14-65 ng/l in the Dagu Drainage Canal, Li *et al.* 2011). Similar levels in such effluents have been reported in the US (2.5-97 ng/l) (Schulz *et al.* 2006, Sinclair & Kannan 2006), in Singapore (15.8-1057.1 ng/l) (Yu *et al.* 2009), and in Thailand (16.9 & 149.8 ng/l) (Kunacheva *et al.* 2011). Relatively high levels have also been found downstream from areas with high densities of textile manufacturing and finishing operations in Korea (26-730 ng/l; Kim *et al.* 2011), and wastewater from textile production has been noted as a source of PFOA in other countries (Bossi *et al.* 2008, Ahrens *et al.* 2009).

Though fewer data are available for other perfluorocarboxylic acids (PFCAs), including PFHxA, PFUnA and especially for PFPeA, levels in surface waters around the world are commonly lower than those of PFOA. PFHxA has been reported at many locations in Europe rivers, with average concentrations of 4 ng/l in a summary of 100 rivers, in which the highest reported value was 109 ng/l. Similarly, PFUnA was found at concentrations up to 3 ng/l (Loos *et al.* 2009). In China, PFHxA has been found in the range <0.13-2.2 ng/l and 0.15-5.3 ng/l for locations along the Pearl & Yangtze Rivers, respectively, while PFUnA concentrations were found in the range <0.13-0.40 ng/l and <0.025-3.0 ng/l respectively for these two rivers (So *et al.* 2007), with somewhat lower levels in the Liao River and Taihu Lake (Yang *et al.* 2011). As for PFOA, higher levels of PFHxA, up to 42 ng/l, were reported in the more industrialised areas of the Haihe River (Li *et al.* 2011). Similarly, higher levels of these other PFCAs have been detected in municipal and industrial wastewaters (for example, PFHxA at 14-124 ng/l in the Dagu Drainage Canal, Li *et al.* 2011). In other countries, treated industrial effluents have also been found to contain relatively high levels; FHxA (up to 77.4 ng/l) and PFUnA (up to 157.6 ng/l) in Thailand (Kunacheva *et al.* 2011), and PFHxA (71-181 ng/l) in Korea (Lin *et al.* 2010). In addition, PFOA, PFOS and other PFCs have been reported in the sediments of various rivers in China (Bao *et al.* 2010). Furthermore, the presence of PFOS and PFOA has also been reported in tap water in many cities in China (Jin *et al.* 2009, Mak *et al.* 2009).

Numerous studies have also reported the presence of PFCs in tissues of aquatic invertebrates, amphibians, fish, birds and mammals (from mice to far larger mammals including whales and polar bears) (Giesy & Kannan 2001, Houde *et al.* 2006). PFOS is generally the predominant PFC reported in the tissues analysed (Giesy & Kannan 2001, Kannan *et al.* 2005, Houde *et al.* 2006). PFOA and perfluorononanoic acid (PFNA) – or, occasionally PFUnDA - have generally been the most abundant PFCAs reported in animal tissues, particularly in top predators (Martin *et al.* 2004, Smithwick *et al.* 2005). In China, PFCs have been found in wild fish from Gaobeidian Lake near Beijing (Li *et al.* 2008), from the Yangtze River (Peng *et al.* 2010, Brigden *et. al.* 2010) and in seafood (Gulkowska *et al.* 2006). PFOS and other PFCs have also been found in human blood, cord blood and breast milk in many countries around the world, including China (Kannan *et al.* 2004, Rylander *et al.* 2010, Monroy *et al.* 2008, Tao *et al.* 2008, Yeung *et al.* 2006, 2008, Liu *et al.* 2009). In the USA, average concentrations of PFOS and PFOA in blood samples have reduced between 1999 and 2004, which may be as a result of the discontinuation of industrial production of PFOS and related chemicals in the USA in 2002 (Calafat *et al.* 2007, Olsen *et al.* 2012). Conversely, in Shenyang, China, levels of PFOS and PFOA in human blood increased between 1987 and 2002 (Jin *et al.* 2007). Research shows that food intake is the major route for exposure to PFCs in the general population (Fromme *et al.* 2009, Vestergren and Cousins 2009, Zhang *et al.* 2010), though additional exposure may occur in populations living near PFC production facilities.

Studies of laboratory animals indicate that some PFCs can cause adverse impacts during development and during adulthood. PFOA and PFOS have both been reported to have adverse effects on the liver in rodents and monkeys (Kawashima *et al.* 1995, Adinehzadeh *et al.* 1999, Berthiaume & Wallace 2002, Lau *et al.* 2007). Some PFCs have also been shown to act as hormone (endocrine) disruptors (Jensen & Leffers 2008). Examples of the effects PFCs have on endocrine systems include decreasing testosterone levels and increasing estradiol levels in adult rats, which can result in changes in the cells of the testis (Jensen & Leffers 2008). Other studies indicate impacts on the immune system of rodents (Yang *et al.* 2002, Lau *et al.* 2007, DeWitt *et al.* 2008). The occurrence of PFCs in biota and humans, and reported toxicological effects, has been recently reviewed (Lindstrom *et al.* 2011). There is evidence that some PFCs may impact hormone systems in humans. In the US, higher PFOA and PFOS concentrations in blood have been associated with thyroid disease in the general adult population (Melzer *et al.* 2010). High combined levels of PFOA and PFOS in men's blood in Denmark were associated with having fewer normal sperm (Joensen *et al.* 2009), while Danish women with higher blood levels of PFOA and PFOS took longer to become pregnant than those with lower levels (Fei *et al.* 2009). Furthermore, a recent study also found an association between elevated exposure to PFOS and PFOA and reduced immune response to routine childhood immunisations in children (Grandjean *et al.* 2012).

Marketing and use of PFOS is prohibited within the EU and in Canada for certain uses, although many exemptions exist (EU 2006, CEPA 2008). The above regulations do not apply to PFCAs and other PFCs. In China, there are currently no regulations of the manufacture and use of PFOS, or other PFCs. However, PFOS has recently been included among the persistent organic pollutants (POPS) regulated under the Stockholm Convention, a global treaty to protect human health and the environment, under which contracting parties must take measures to restrict the production and use of PFOS, although a wide range of uses are currently exempt (UNEP 2009).

#### 4.1.2 Metals

The concentrations of metals and metalloids included in the analysis showed little or no sign of elevation above typical background concentrations for uncontaminated surface waters.

	Shaoxing WWTP, Binhai Industrial Zone				Xiaoshan Linjiang WWTP, Linjiang Industrial Zone		Zhejiang Deou facility	
	Surface boil at outfall, Qiantang River				Wastewater lagoon, edge of Qiantang River		River adjacent to facility	
Sample type	WW/EW		WW/EW		WW/EW		RW	
Sample code	CN12008		CN12009		CN12010		CN12011	
	Filtered	Whole	Filtered	Whole	Filtered	Whole	Filtered	Whole
<b>Antimony</b>	<50	<50	<50	<50	<50	<50	<50	<50
<b>Arsenic</b>	<50	<50	<50	<50	<50	<50	<50	<50
<b>Barium</b>	33	86	21	86	139	403	34	46
<b>Cadmium</b>	<5	<5	<5	<5	<5	<5	<5	<5
<b>Chromium</b>	<20	48	<20	49	<20	<20	<20	<20
<b>Chromium (VI)</b>	<50	-	<50	-	<50	-	<50	-
<b>Cobalt</b>	<20	<20	<20	<20	<20	<20	<20	<20
<b>Copper</b>	<20	56	<20	54	<20	<20	<20	22
<b>Lead</b>	<50	<50	<50	<50	<50	<50	<50	<50
<b>Manganese</b>	93	843	52	874	182	221	310	345
<b>Mercury</b>	<2	<2	<2	<2	<2	<2	<2	<2
<b>Nickel</b>	<20	54	<20	59	<20	<20	<20	<20
<b>Selenium</b>	<200	<200	<200	<200	<200	<200	<200	<200
<b>Vanadium</b>	<20	32	<20	35	<20	<20	<20	<20
<b>Zinc</b>	59	206	36	185	126	129	38	210

Table 5: Concentrations of metals and metalloids (mg/l) in filtered and whole samples of wastewater (WW) / estuary water (EW) associated with the two communal WWTPs in Shaoxing and Xiaoshan Counties, and river water (RW) adjacent to the Zhejiang Deou Chemical Manufacture Co. facility

## 4.2 Xiaoshan Linjiang Communal WWTP within the Linjiang Industrial Zone

### 4.2.1 Organic chemical contaminants

The water sample from the lagoon of discharged wastewater (CN12010) contained a wide range of organic chemical contaminants including many with hazardous properties. From this sample, 67 organic compounds have been isolated, and 48 of them (72%) were reliably identified. Notable among these were 17 aniline derivatives (also known as benzenamines), including five N-alkylated derivatives, seven chlorinated derivatives (mono-, di-, and trichloroanilines), as well as chloromethylaniline and dichloronitroaniline, and three non-halogenated anilines (2-methoxyaniline and two propanenitrile anilines). Aniline derivatives are widely associated with the manufacture and use of dyestuffs, particularly azo dyes. Examples of chlorinated and methoxy anilines were also identified in samples collected from both other locations investigated in the current study (See Sections 4.1 and 4.3), as well as in wastewater samples analysed in a previous investigation of textile manufacturing facilities in China (Greenpeace 2011a).

Three of these compounds are known or suspected carcinogens, and as such are listed under regulations in various countries, including China and EU member states, related to the use of azo dyes in textiles (EU 2002, SAPRC 2012). These three anilines are 2-methoxy-aniline (also known as *o*-anisidine), chloromethylaniline (also known as chlorotoluidine) and chloroaniline.

The remaining anilines identified in this sample are not listed in these regulations. Nonetheless, they include some substances that are hazardous for both human health and aquatic ecosystems, including a number of di- and trichloro anilines, and N-alkyl anilines. Along with many other chlorinated anilines, di- and tri-chloro anilines are toxic to wide range of aquatic organisms, with some isomers being classified under GHS as very toxic to aquatic life with long-lasting effects (H410), toxic if swallowed, inhaled or through contact with the skin (H301, H331, H311), and may cause damage to organs through prolonged or repeated exposure (H373). 2,6-dichloro-4-nitroaniline (also known as dicloran or dichloran) is mutagenic (Shirasu *et al.* 1976), and is also toxic for freshwater fish and invertebrates (US EPA 2006). Many N-alkyl anilines are also recognised as hazardous substances, including to aquatic species. For example, N,N-diethylaniline (though identified only as a minor component in this sample) has been classified under GHS as toxic if swallowed, inhaled or through contact with the skin (H301, H331, H311) and toxic to aquatic life (H401).

The two substituted propanenitrile aniline derivatives, also known as substituted cyanoethyl anilines, are used in preparation of azo dyes, particularly those related to the dyeing of nitrogen-containing fibres. There is limited information on the toxicity of these chemicals, though they have been classified under GHS as capable of causing irritation to the eyes and skin (H315, H319).

More information on aniline derivatives is provided in Box A.

Another nitrile derivative identified in the sample as a prominent compound was methylbenzonitrile (also known as *p*-tolunitrile). *p*-Tolunitrile has use as an intermediate in the synthesis of a fungicide (Syngenta 2005, US EPA 2008b), and also has potential use in the preparation of textile related pigments (Lenz *et al.* 2001). In addition, *p*-tolunitrile is a constituent of tobacco smoke (Schlotzhauer & Chortyk 1987). Available data indicate that tolunitrile has relatively low toxicity, and is readily biodegradable, though it has been classified under GHS as irritating to eyes and skin (H315, H319).

The sample of wastewater also contained a range of chlorinated compounds, including a number of chlorinated benzenes (all three isomers of dichlorobenzene, and trace levels of tri- and penta-chlorobenzene), the chlorinated benzene derivative chloromethoxybenzene (also known as chlorinated anisole), two chloronitrobenzenes (together with nitrobenzene), 1-(4-chlorophenyl)-ethanone, and some chlorinated volatile organic compounds (VOCs).

Chlorinated benzenes are widely recognised hazardous chemicals and many are well known environmental contaminants. They are persistent organic pollutants which can remain in the environment for a prolonged time after their initial release (ATSDR 2006). Di- and tri-chlorobenzenes have many industrial uses, including some related to the manufacture of textiles. All dichlorobenzenes are used as intermediates for dye manufacture, particularly 1,2-dichlorobenzene after conversion to 1,2-dichloro-4-nitrobenzene or dichloroaniline (ATSDR 2006). 1,4-dichlorobenzene is also widely used as a deodoriser and disinfectant in sanitary products, which has resulted in it becoming a well-known environmental contaminant. Trichlorinated benzenes have also been used, among other uses, as intermediates for pigments and dyes as well as dye carriers (ATSDR 2006). Dichlorobenzenes were also identified in samples from all other locations investigated in this study (Sections 4.1 & 4.3), and trichlorobenzenes were also identified in one of these locations (Section 4.3).

Pentachlorobenzene is no longer produced in the UN-ECE region (Europe, North America and parts of central and western Asia) and few data are available on production, recent or past, outside the UN-ECE region (van de Plassche *et al.* 2002). Past uses of pentachlorobenzene included as fungicide, a starting material for manufacture of other chemicals and as a dyestuff carrier (Environment Canada 2010). It may be also produced unintentionally during combustion in thermal and industrial processes and can appear as an impurity in products such as solvents or pesticides.

More information on chlorinated benzenes is presented in Box C.

Chlorinated anisoles have previously been detected in various compartments of the environment (Jaffe 1991), including in marine and fresh water organisms, sediments, and also in effluents of municipal wastewater treatment plants. However, these chemicals are not produced in industrial quantities but rather formed in the environment as a result of biotransformation from, for example, the corresponding chlorophenols (Neilson 1990). There is limited information concerning toxicity of chloroanisoles.

### **Box C. Chlorinated and brominated benzenes**

Monochlorobenzene release to the environment is expected to derive primarily from its use as a solvent, either through fugitive emissions or volatilisation from pesticides for which it has been used as a carrier. It bioaccumulates in algae, fish and aquatic invertebrates. Human exposure to monochlorobenzene can cause CNS depression and respiratory tract irritation, and animal studies have reported liver necrosis, renal toxicity and effects on the pancreas, blood and lymph and adrenal glands (Ware 1988a, Meek *et al.* 1994a).

Effects reported in humans after acute exposure to high levels of dichlorobenzenes (DCBs) include anaemia, skin lesions, vomiting, headaches, eye and respiratory tract irritation, anorexia, weight loss, yellow atrophy of the liver, blood dyscrasias, porphyria, and chromosomal breaks in blood samples (Ware 1988b). Animal experiments have recorded liver and kidney damage to be the most frequent effects, though high doses caused CNS perturbation and death through respiratory depression. The dichlorobenzenes are bioaccumulative in algae, aquatic invertebrates and fish (Ware 1988b). Laboratory animals exposed to 1,2-DCB exhibited hepatic, renal and haematological effects as well as lymphoid depletion of the thymus and spleen and multifocal mineralisation of both muscular and heart muscles (Ware 1988b, Meek *et al.* 1994b). Human toxicity data are sparse, but chromosomal aberrations, anaemia and leukemia have been reported (Meek *et al.* 1994b). 1,2-DCB is also toxic to higher plants, inducing abnormal mitosis (cell division) in onions (Ware 1988b). There is little known about 1,3-DCB toxicity in comparison to the more commercially important DCBs.

1,4-DCB is ubiquitous in the environment, having being measured in air, effluents, surface and ground water, sediments and biota. It is not persistent in air or surface water due to its volatility, but it does persist and accumulate in anaerobic sediments (McPherson *et al.* 2002). 1,4-DCB has been widely used as a deodoriser and disinfectant in sanitary products resulting in it being a widespread contaminant in the aquatic environment. In addition, uses in rooms deodorants and mothballs significantly contributed to high indoor levels of this chemical (Sakai *et al.* 2004). 1,4- DCB may be absorbed both through the inhalation of vapours, through the skin and through consumption of contaminated food. Once absorbed, 1,4-DCB is stored in the adipose tissue, and has been detected in human samples (CEC 1986, Ware 1988b). 1,4-DCB causes abnormal mitosis in higher plants. It was shown in a comparative study on the estrogenicity of DCBs (Versonnen *et al.* 2003) that 1,2-DCB was not estrogenic, while 1,3-DCB and 1,4-DCB were estrogenic *in vitro* using the yeast estrogen screen assay, with 1,4-DCB being the most potent. This compound was also shown to have estrogenic potency *in vivo* in zebrafish. 1,4-DCB is classified (US DHHS 2011) as reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity from studies in experimental animals (group 2B).

Environmental regulations have curbed the use and discharge of trichlorobenzenes to the environment, at least in Europe and the US (Harper *et al.* 1992, Bryant 1993). Not surprisingly, therefore, little research appears to have been carried out in comparison with that on some other chlorobenzenes. The general human population would probably receive their greatest exposure to trichlorobenzenes through inhalation. The toxicity of all trichlorobenzenes appears similar; they damage the liver, kidney and thyroid. There is also some indication of slight foetotoxicity at high doses. There is little evidence of mutagenicity (Giddings *et al.* 1994a). All three isomers are toxic to phytoplankton (Sicko-Goad *et al.* 1989a-d, Sicko-Goad & Andresen 1993a & b).

All isomers of tetrachlorobenzene express similar toxic effects in experimental animals (Giddings *et al.* 1994b) including damage to the liver, kidney, thyroid and lungs, with 1,2,4,5-tetrachlorobenzene being the most toxic. In addition to the effects noted above, 1,2,4,5-tetrachlorobenzene has also been found to cause changes in the spleen, thymus, lymph nodes and haematological parameters in animals (Giddings *et al.* 1994b). In rats, 1,2,3,4- and 1,2,3,5-tetrachlorobenzene caused reduction in the number of live offspring at concentrations too low to adversely affect the mother (Giddings *et al.* 1994b). An increase in chromosomal aberrations was also seen in workers exposed to 1,2,4,5-tetrachlorobenzene at a pesticide manufacturing complex (Giddings *et al.* 1994b). If released into aquatic environment, tetrachlorobenzenes may accumulate in fish, probably through absorption across the gills (Brauner *et al.* 1994).

Studies of pentachlobenzene toxicity in experimental animals demonstrated weight loss and effects on the liver, thymus, kidney, adrenal glands and digestive tract (Giddings *et al.* 1994c). Other effects included anaemia and malformation of sperm, with some indication of foetotoxicity and development toxicity.

Brominated benzenes have also been used as starting materials in preparation of dyes; for example, 1,4-dibromobenzene has been used after conversion to the corresponding amines (Sirohi *et al.* 2012). Toxic effects of dibromobenzenes investigated in experimental animals included hepatotoxicity (Szymańska *et al.* 1996), which was observed for 1,2- and 1,3-dibromobenzenes but not for 1,4-dibromobenzene; genotoxicity in terms of DNA damage *in vivo* and *in vitro*, studied for 1,4-dibromobenzene (Colacci *et al.* 1990); and nephrotoxicity, which was studied for 1,3-dibromobenzene (Sapota *et al.* 1999).

Two chloronitrobenzenes (CNBs) were identified; 3-CNB and 4-CNB. CNBs are nitroaromatic compounds, an important class of industrial chemicals widely used in the production of dyes, polymers, pesticides, and explosives, among other products (Jones *et al.* 2006, NTP 1993). 2-CNB and 4-CNB are high production volume chemicals and are produced worldwide (Jones *et al.* 2006, NTP 1993). Some chemicals that are derived from CNBs for use in dye manufacture are carcinogenic, including chloroaniline, which was identified in this sample (IARC 2012). There are also concerns about the potential carcinogenicity of 4-CNB in animals (IARC 1996, Matsumoto *et al.* 2006). *In*

*vitro* tests have also found evidence of the mutagenicity of 2-CNB and 4-CNB in *Salmonella typhimurium* (NTP 1993). Other toxicological effects for 2- and 4-CNBs have also been reported, including impacts on the immune and reproduction systems in animals (Li *et al.* 1997, 1999, NTP 1993). In addition, exposure to 4-CNB has been shown to cause methemoglobinemia and/or anaemia in either exposed workers or in experimental animals (Minami *et al.* 1990, Nair *et al.* 1986).

Nitrobenzene is a high production volume industrial chemical, primarily used to manufacture aniline (ATSDR 1990, WHO 2003b), a substance subsequently used in the manufacture of dyes, amongst many other uses (Khalid *et al.* 2009). Nitrobenzene can also be generated during the degradation of some dyes (Zhao & Hardin 2007). Animal experiments have shown nitrobenzene to be carcinogenic in rodents (Cattley *et al.* 1994, CIIT 1993). In addition, a metabolite of nitrobenzene (aniline) is a potential human carcinogen (US EPA 1994). Nitrobenzene has been classified as reasonably anticipated to be a human carcinogen by the US Department of Health and Human Service (DHSS 2011). A range of other toxicological effects have also been reported, including impacts on fertility (Kawashima *et al.* 1995b), and impacts on other organs including the liver and kidneys (Morgan *et al.* 1985, Bond *et al.* 1981).

Nitrobenzene and chloronitrobenzenes are classified under GHS as toxic to aquatic life with long-lasting effects (H411), able to cause damage to organs through prolonged or repeated exposure (H372) and suspected of being able to cause cancer (H351), in addition to being toxic if swallowed, inhaled or through contact with the skin (H301, H331, H311). In addition, the chloronitrobenzenes are classified as suspected of damaging fertility (H361).

1-(4-Chlorophenyl)-ethanone, also known as *p*-chloroacetophenone, has a variety of uses in organic compound synthesis, including as an intermediate for manufacture of heteroaryl thiazole dyes (Yen and Chen 2010). This chemical is highly irritating to eyes and mucous membranes. It has been used as a component of self-defence sprays (Recer *et al.* 2002), including tear gases (Brone *et al.* 2008), owing to its incapacitating effects by causing instant pain and irritation of the eyes resulting in excessive tears and cramp of the eyelids (blepharospasm).

In addition to the semi-volatile (solvent extractable) organic chemical contaminants identified above, analysis also identified a range of common volatile organic compounds (VOCs) in the sample (see Table 4). The predominant VOCs were chloroethane (81 mg/l) and 1,2-dichloroethane (EDC) (22 mg/l) followed by dichloromethane (6 mg/l) and two other VOCs detected at 2mg/l (hexachlorobutadiene and chloroform).

Chloroethane, also known as ethyl chloride, is a chlorinated solvent that has been used in production of ethyl cellulose, dyes, medicinal drugs and the gasoline additive tetraethyl lead, among other commercial chemicals, as well as receiving some use as a refrigerant (ATSDR 1998). Chloroethane has been classified under GHS as harmful to aquatic life with long-lasting effects (H412), and as suspected of causing cancer (H351), though the International Agency for Research on Cancer (IARC) has listed chloroethane as not classifiable as to its carcinogenicity to humans (Group 3) (IARC 1999b).

1,2-Dichloroethane (also known as ethylene dichloride) is a hazardous chlorinated volatile compound primarily used in the manufacture of PVC. The concentration detected in sample CN12010 (22 mg/l) is twice the level proposed as an Annual Average Environmental Quality Standard (AA-EQS) for internal waters within the EU (10 mg/l) under the Water Framework Directive (EU 2000, EC 2006) (no maximum allowable concentration has been set up for this chemical within Directive). Environmental levels of 1,2-dichloroethane reported for fresh river water and sea water are commonly about 0.010 mg/l (Chary and Fernandes-Alba 2012), more than 1000 times lower than that found in the sample of wastewater from the lagoon. The International Agency Research on Cancer has classified this compound as possibly carcinogenic to humans (Group 2B) (IARC 1999b).

Hexachlorobutadiene (HCBD) was identified in sample CN12010 at 2 mg/l, significantly above an environmental concern level of 0.1 µg/litre (WHO 1994), which is the same for AA-EQS for internal waters within the EU, as well as a maximum allowable concentration at any one time of 0.6 ug/l for internal waters within the EU, under the EU Water Framework Directive (EU 2000, EC 2006). This hazardous chemical is mainly produced as a by-product during the manufacture of certain chlorinated hydrocarbons. More information on HCBD is presented in Box D.

Chloroform (trichloromethane) and dichloromethane were also identified in sample CN12010 at low levels, 2 and 6 mg/l respectively. These hazardous compounds have uses as solvents; however, chloroform can also be formed as a by-product during water disinfection using chlorine-containing compounds, which is a common practice at many WWTPs and, therefore, may be the source for this sample.

A number of other compounds also identified in the wastewater are indicative of contamination by oil or other petrochemicals, including naphthalene and alkyl naphthalene derivatives, three other polycyclic aromatic hydrocarbons (PAHs), dibenzofuran and benzothiophene, as well as 1,1'-biphenyl and its methyl derivatives (Overton 1994). However, 1,1'-biphenyl has also received some deliberate use as a dyestuff carrier for textile manufacture (among other industrial uses) (IPCS 1999).

## **Box D. Hexachlorobutadiene**

Hexachlorobutadiene (HCBD) is a synthetic chemical that is not found naturally in the environment. HCBD is mainly produced as a by-product during the manufacture of certain chlorinated hydrocarbons, such as tetrachloroethylene, trichloroethylene, carbon tetrachloride and related products (van der Gon *et al.* 2007). Commercially manufactured HCBD has several minor uses, e.g. as a chemical intermediate in the manufacture of rubber compounds, a solvent and a fluid for gyroscopes (Lerche *et al.* 2002). HCBD residues have been detected in many environmental compartments, including river water (Fatta *et al.* 2007), sediments (Lee *et al.* 2005, Schwarzbauer *et al.* 2000), fish tissues (Pere-Trepaut *et al.* 2006) and soils from industrial sites contaminated with chlorinated hydrocarbons (Röhres *et al.* 2002).

Hexachlorobutadiene toxicity has been extensively studied in rats and to a lesser degree in other laboratory animals. It has been shown that HCBD is toxic to the kidneys in rats, causing damage to the proximal tubules (US EPA 2003, Pahler *et al.* 1997, Rosner *et al.* 1998, Nakagawa *et al.* 1998). Several oral studies in rats have suggested that HCBD-induced cytotoxicity may lead to kidney tumour formation (US EPA 2003). There is limited evidence for the genotoxicity of HCBD in animals, and insufficient evidence for its classification in humans. HCBD has been classified by IARC as a Group 3 carcinogen (IARC 1999c). Limited information is available on human health effects associated with exposure to HCBD. However, human *in vitro* data suggest that the metabolism of hexachlorobutadiene in humans is similar to that observed in animals (Green *et al.* 2003, WHO 1994). HCBD vapour is considered to be irritating to the mucous membranes of humans, and the liquid is corrosive. It has also been generally observed that existing nephropathy or age-related kidney degeneration can exacerbate the nephrotoxicity and increase the risk of renal injury from HBCD exposure in humans (WHO 1991).

Environmental toxicity of HCBD has mainly been described in aquatic organisms, with crustaceans and fish being the most sensitive groups. An environmental concern level of 0.1 µg/litre was established for HCBD by the World Health Organisation (WHO 1994), and the same value has since been proposed as an Annual Average Environmental Quality Standard (AA-EQS) for internal waters under the EU Water Framework Directive (EU 2000, EC 2006). A maximum allowable concentration at any one time of 0.6 µg/l has also been established under the WFD. In common with mercury and cadmium, HBCD is also identified within the EU as a “priority hazardous substance” under this Directive, such that a target of phase-out or cessation of emissions, discharges and losses will apply. HBCD is highly bioaccumulative, such that the consumption of benthic or aquatic organisms in polluted surface water by other species may give cause for concern relating to transfer through the food web.

In addition to the organic chemicals identified using qualitative chemical screening, as described above, a number of PFCs were also identified and their concentrations quantified in the sample. Perfluorooctanoic acid (PFOA) was present at 93.2 ng/l (0.0932 mg/l), similar to levels found in the samples associated with a communal WWTP within the Binhai Industrial Zone (Section 4.1), and also in textile manufacturing wastewaters analysed in a previous study in 2011 (Greenpeace 2011a).

In addition to PFOA, three other perfluorinated carboxylic acids (PFCAs) were also detected, though at lower concentrations than PFOA (between 10.2 and 13.0 ng/l); namely perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA) and perfluoroundecanoic acid (PFUnA). Both PFHxA and PFUnA were also identified in wastewaters sampled from another location related to textile manufacturing in 2011 (Greenpeace 2011a), though in that case at somewhat lower concentrations (3.4-4.4 ng/l and 0.28-2.9 ng/l respectively).

As noted in Section 4.1, the concentration of PFOA is above the range commonly reported in surface waters, and is within the range reported for effluents from industrial and municipal wastewater treatment plants. Similarly, the concentrations of the other PFCAs that were detected were above the range typical reported in surface waters, although even higher levels have been reported for surface waters at some industrialised locations. Treated industrial and municipal effluents commonly contain higher concentrations of these PFCAs than those found in this study, though it must be kept in mind that the wastewater sampled in the current study almost certainly consisted of a mix of effluents from a number of industrial sources. More information on PFOA and other PFCAs, including levels reported in the environment and in discharged effluents, is provided in Box B.

### **4.2.2 Metals**

The concentrations of metals and metalloids included in the analysis showed little or no sign of elevation above typical background concentrations for uncontaminated surface waters, with the exception of zinc. This sample contained dissolved zinc at 126 mg/l, somewhat higher than background concentrations of zinc expected for uncontaminated surface waters, which are generally below 50 mg/l, with median values commonly below 10 mg/l (ATSDR 2005a, Comber *et al.* 2008).

Zinc and zinc compounds have numerous industrial uses across a wide range of different sectors, including uses of zinc compounds in textile manufacture, such as in some printing processes and as mordants in dyeing (ATSDR 2005). 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).

## 4.3 River adjacent to the Zhejiang Deou Chemical Manufacture Co.

### 4.3.1 Organic chemical contaminants

The predominant organic chemicals in the sample of river water (CN12011) were substituted anilines (also known as benzenamines), in particular N-ethyl-4-methyl-aniline. A closely related aniline (N,N-diethyl-4-methyl-aniline) was also identified. In addition, three brominated anilines were identified in the sample (dibromoaniline, methyl-dibromoaniline and 2,4,6-tribromoaniline), as well as dichloroaniline as a minor component.

N-ethyl-4-methyl-aniline, also known as N-ethyl-p-toluidine, is a toxic chemical and has been classified under GHS as fatal by inhalation, in contact with skin and if swallowed (H300, H310, H33); it also causes skin and eye irritation (H315, H319) as well as being harmful to aquatic life, with long-lasting effects (H402, H412). There is no available information on the toxicity of the related compound N,N-diethyl-p-toluidine, and only limited information on the application of both these toluidine derivatives. As noted in previous sections, substituted anilines are used as dye intermediates, including for certain azo dyes.

Brominated anilines, similarly to chlorinated derivatives, are used in many applications, including as intermediates in the manufacture of dyes. They may arise in manufactured colour additives and also in industrial wastewaters as a result of incomplete reaction of starting materials or low grade of starting materials. As is the case for many halogenated anilines, brominated anilines are toxic chemicals; for example, dibromoaniline is classified under the Globally Harmonised System (GHS) as harmful if swallowed, inhaled or in contact with the skin (H302, H332, H312) and irritating to the eyes and skin (H315, H319). 2,4,6-tribromoaniline is classified under GHS as toxic if swallowed or in contact with the skin (H301, H311), harmful if inhaled (H332), irritating to the eyes and skin (H315, H319) and may cause damage to organs through prolonged or repeated exposure (H373). So far it has not been possible to identify any hazardous properties for methyl-dibromoaniline.

Dichloroaniline, which was detected as minor component in the sample, is toxic to wide range of aquatic organisms with the potential for long lasting effects, along with many other chlorinated anilines. However, as for the N-alkyl anilines, the brominated and chlorinated anilines identified in this sample are not amongst the carcinogenic amines listed by legislation in various countries regulating the use of azo dyes in textiles (EU 2002, SAPRC 2012), nor are they listed by the International Agency for Research on Cancer (IARC 2012). More information on aniline derivatives in general is provided in Box A.

Aniline derivatives (including chlorinated and N-alkyl derivatives) were also identified in samples collected from other locations investigated in the current study (See Sections 4.1 and 4.2), as well as in wastewater samples analysed in a previous investigation of textile manufacturing facilities in China (Greenpeace 2011a). However, the N-alkyl anilines identified in sample CN12011 were different from that found in sample CN12010.

In addition to the anilines, a range of halogenated benzenes and derivatives, as well as three ethers were also identified in the water sample.

The range of halogenated benzenes included 1,4-dibromo-2-methyl-benzene (classified under GHS as irritating to the eyes and skin; H315, H319), and two compounds identified as minor constituents; dibromobenzene, classified under GHS as toxic to aquatic life (H401) and irritating to the eyes and skin (H315, H319), and 1-bromo-4-chloro-2-methyl-benzene, classified under GHS as irritating to the eyes and skin (H315, H319). In addition, a range of chlorinated benzenes were identified, though these were all present at only trace levels. These included chlorobenzene, three dichlorobenzenes, three trichlorobenzenes and a tetrachlorobenzene. Dichlorobenzenes were also identified in samples from all other locations investigated in this study (Sections 4.1 & 4.2), and trichlorobenzenes were also identified in one of these locations (Section 4.2).

The three ethers identified in the wastewater sample were diphenyl ether, 1,2-dimethoxybenzene and benzyl methyl ether. Diphenyl ether, also known as diphenyl oxide, has a variety of uses including pesticide and other agricultural chemical manufacturing, other basic organic chemical manufacturing, soap and cleaning compound manufacturing, chemical product and preparation manufacturing and food manufacturing. This chemical has shown low inhalation and oral toxicity in experimental animals and is slightly to severely irritating to rabbit skin and slightly irritating to rabbit eyes (US EPA 2010). It is also classified under GHS as toxic to aquatic life with long-lasting effects (H411).

1,2-dimethoxybenzene, also known as veratrole, is primarily used as an intermediate in chemical synthesis, including in the formulation of the insecticide Verbutin (Breda *et al.* 2006) (in its acrylated form acetoveratrole). It is also used in production of dimethoxypropiophenones (Yadav and More 2012) and of 3,4-dimethoxyacetophenone, the latter being widely used in manufacture of pharmaceuticals, insecticides, dyes and other commercial products (Revathi *et al.* 2008). There is limited information on the toxicity of this compound, although it has been classified under GHS as harmful if swallowed (H302).

There is also limited information regarding the toxicity of benzyl methyl ether, which is used in organic compounds synthesis with some application in photochemistry (d'Alessandro et al. 1991) and for which no hazard phrases have been assigned other than being flammable.

#### 4.3.2 Metals

The concentrations of metals and metalloids included in the analysis showed little or no sign of elevation above typical background concentrations for uncontaminated surface waters.

### 5. Conclusions

All samples collected and analysed for this study contained a diverse range of chemicals, many of which have known hazardous properties. For some other chemicals identified, little or no information is publicly available on their toxicology, such that the consequences of their release to the environment remain unknown. In addition, a significant proportion and, in some cases, most of the chemicals isolated from each sample could not be reliably identified, not uncommon for complex industrial effluents or surface waters contaminated with them, such that their properties and potential impacts cannot be assessed.

A large proportion of the chemicals that could be identified are related to the manufacture of textiles, and in particular can arise from the manufacture and use of dyes or dye formulations. Their presence in the wastewaters sampled is consistent with the presence of many textile manufacturing and related facilities within the two industrial zones investigated in this study. However, many of identified chemicals, including certain dye-related compounds, also have other industrial uses, while others have no known connection to the manufacture of textiles. Even for those chemicals commonly associated with textile manufacture, the possibility that other types of industrial activities contributed to presence within the waters sampled in this study cannot, therefore, be excluded.

Results from analysis of this small number of samples clearly cannot be taken as representative of wastewaters released from industrial zones throughout China, or even of textile manufacturing facilities in general. However, these case studies do provide an illustrative snapshot of what is likely to be a much wider problem.

Given the lack of information on the individual sources of effluent directed to the communal WWTPs within the industrial zones, it is not possible to know which facility or facilities may be responsible for each of the various hazardous chemicals identified within mixed wastewaters discharged from the communal WWTPs. This situation is further exacerbated by the lack of publicly available information on the location of outfalls through which wastewaters are discharged to the environment, even for large outfalls carrying mixed effluents from communal WWTPs within major industrial zones.

Progressively replacing hazardous substances with less hazardous, and preferably non-hazardous, alternatives will help bring about rapid reductions and ultimate cessation in their discharges, emissions and losses, and ultimately reduce the burden of hazardous substances the local and global environment. Making information on the current use and release of hazardous chemicals by individual facilities publicly available will be an important contribution towards that goal.

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## Appendix 1: Details of methodologies

### Analysis for Volatile Organic Compounds (VOCs)

#### Methods

VOCs were analysed using an Agilent 6890 gas chromatograph with an Rtx-624 column (30m, 0.25mm ID, 1.4 $\mu$ m 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 350°C (held for 4min), rising to 550°C at 50°C/min, and then to 2100°C at 150°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. Chlorinated VOCs quantified in the water samples with limits of quantification are presented in Table A1 below.

#### Quality control

Method detection limits (MDL) and limits of quantification (LOQ) were obtained using data of 9 replicas of standard solution analysis. 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.

Compound	MDL	LOQ
<b>Methane, tribromo-</b>	0.3	1.0
<b>Methane, tetrachloro-</b>	0.3	1.1
<b>Methane, dichloro-</b>	0.2	0.7
<b>Methane, dibromochloro-</b>	0.4	1.5
<b>Methane, dibromo-</b>	0.3	1.0
<b>Methane, bromochloro-</b>	0.5	1.7
<b>Ethene, trichloro-</b>	0.5	1.7
<b>Ethene, tetrachloro-</b>	0.6	2.0
<b>Ethene, 1,2-dichloro-, trans-</b>	0.3	0.9
<b>Ethene, 1,2-dichloro-, cis-</b>	0.2	0.8
<b>Ethene, 1,1-dichloro-</b>	0.2	0.7
<b>Ethane, dibromo-</b>	0.5	1.6
<b>Ethane, 1,2-dichloro-</b>	1.1	3.8
<b>Ethane, 1,1-dichloro-</b>	0.4	1.3
<b>Ethane, 1,1,2,2-tetrachloro-</b>	0.2	0.7
<b>Ethane, 1,1,1-trichloro-</b>	0.4	1.3
<b>Ethane, 1,1,1,2-tetrachloro-</b>	0.4	1.5
<b>Chloroform</b>	0.2	0.7
<b>1,3-Butadiene, 1,1,2,3,4,4-hexachloro-</b>	0.3	1.1

Table A1. Method detection limits (MDL) and limits of quantification (LOQ).

## **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. Water samples (500ml) were prepared using solid phase extraction technique with Dionex AutoTrace workstation, eluting with ethyl acetate followed by a mixture of pentane and toluene (95:5). Obtained extracts were concentrated to a volume of 3ml with a stream of clean nitrogen and cleaned up prior to analysis.

For the clean-up stage, each extract was 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 1ml 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 6890 Series II GC with Restek Rtx-XLB column (30m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5973 Inert 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 350°C, held for 2 minutes, raised to 2600°C at 100°C/min, then to 3200°C at 60°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.

### *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. Any background contaminants detected in blanks are subtracted from the chromatograms obtained for the samples before mass spectra are interpreted.

## **Analysis for metals and metalloids**

### *Preparation*

To obtain total metal concentrations, a representative portion of each whole water sample was acidified by the addition of concentrated nitric acid to give a final concentration of 10% v/v. Separately, a portion of each whole sample was filtered through a 0.45 micron filter and then acidified in the same way to enable determination of dissolved metal concentrations. 50 ml of each acidified sample was digested firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 180°C over 15 minutes followed by holding at 180°C for a further 15 minutes. Cooled digests were filtered and made up to 50 ml 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 0.5, 1.0, 2.5 and 5.0 mg/l respectively, 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 µg/l and 100 µg/l, matrix matched to the samples.

Concentrations of chromium (VI) were determined colorimetric for each water sample following filtration. 0.5 ml of a 1,5-diphenylcarbazide testing solution (freshly prepared from 0.4 g of 1,5-diphenylcarbazide, 20 ml acetone, 20 ml ethanol, 20 ml orthophosphoric acid solution and 20 ml of demineralised water) was added to 9.5 ml of each filtered sample. The solution was mixed and let to stand for 10 minutes to allow full colour development. Concentrations were determined using a spectrophotometer at 540 nm, correcting with a blank prepared from deionised water,

using standards freshly prepared from potassium dichromate at concentrations of 0, 50, 100, 200 and 500 µg/l respectively. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

#### *Quality control*

Two samples were prepared for ICP analysis 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 4 mg/l for each metal, 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 4 mg/l and 0.4 mg/l (water samples) prepared in an identical manner but 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.

For chromium (VI) determination, two samples were prepared and analysed in duplicate, along with a blank sample, and two quality control solutions of 100 and 400 µg/l prepared in an identical manor to the samples.

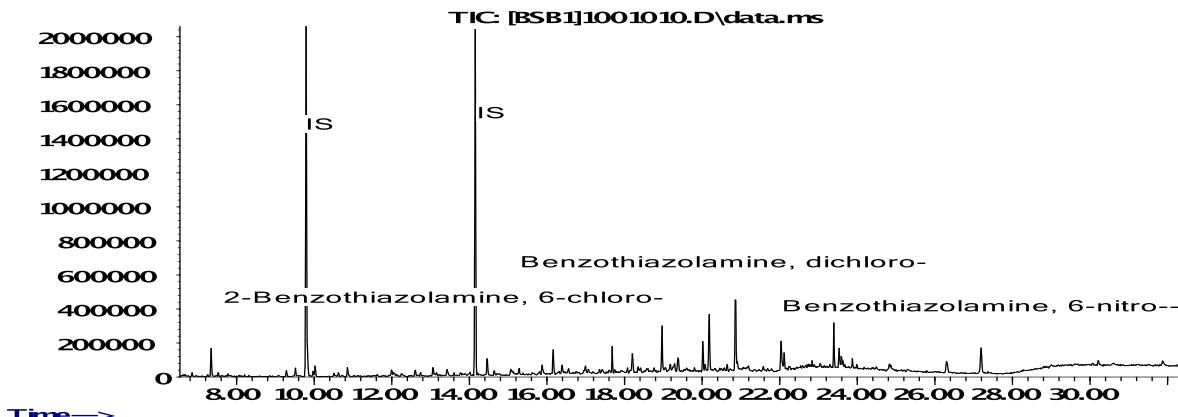
Further details of the methods employed can be provided on request.

## Appendix 2: Detailed semi-volatile organic analytical screening data

Detailed screening data arising from GC-MS analysis of solvent extracts of each of the samples are presented below. These data list only those semi-volatile organic compounds identified following solvent extraction and do not include any volatile organic compounds (VOCs) identified through separate headspace GC-MS analysis of sub-samples; the VOCs identified in each sample are listed in Table 3 in the main body of the report. Only those semi-volatile substances identified to greater than 90% quality match (following verification by expert interpretation) are listed here. On the chromatograms, "IS" indicates internal standard.

Sample code	CN12008
Location	Outfall of Shaoxing communal WWTP, Binhai Industrial Zone, Shaoxing County
Sample type	Wastewater / surface water
Date & time	28/05/2012; 12.30
Description	Collected from the surface boil located above the outfall of the submerged discharge pipe from the Shaoxing WWTP within the Binhai Industrial Zone

Abundance



Time—>

Number of compounds isolated: 60

Compounds identified to better than 90%:

CAS# Name

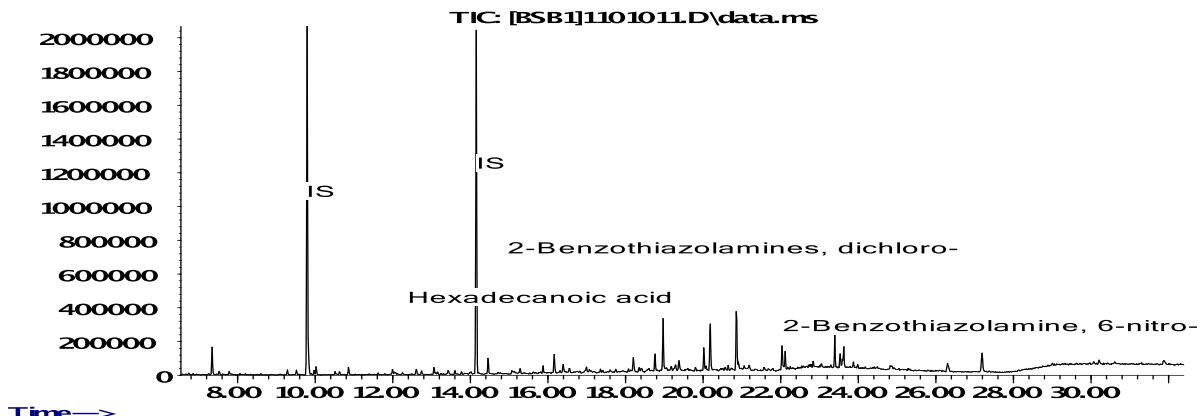
000095-50-1	Benzene, 1,2-dichloro-	(SIM)
000106-46-7	Benzene, 1,4-dichloro-	(SIM)
006285-57-0	6-Nitro-2-benzothiazolamine	
000000-00-0	Dichloro-2-benzothiazolamines, 2 isomers	
001477-42-5	* 4-Methyl-2-benzothiazolamine	
000095-24-9	6-Chloro-2-benzothiazolamine	
000126-86-3	*2,4,7,9-Tetramethyl-5-decyne-4,7-diol	
000719-22-2	*2,6-di-tert-butylbenzoquinone	
000634-93-5	*Aniline, 2,4,6-trichloro-	
000626-43-7	Aniline, 3,5-dichloro-	
000121-50-6	*Aniline, 2-chloro-5-(trifluoromethyl)-	
000084-74-2	*1,2-Benzenedicarboxylic acid, dibutyl ester	
000112-88-9	1-Octadecene	
000057-10-3	Hexadecanoic acid	
000112-39-0	Hexadecanoic acid, methyl ester	
000058-90-2	Phenol, 2,3,4,6-tetrachloro-	(SIM)
001660-94-2	Phosphonic acid, methylenebis-, tetraethyl ester	
001613-34-9	Quinoline, 2-ethyl-	

SIM indicates detection at trace levels only using Selected Ion Monitoring mode of analysis.

\* indicates a minor component of the total ion chromatogram

Sample code	CN12009
Location	Outfall of Shaoxing communal WWTP, Binhai Industrial Zone, Shaoxing County
Sample type	Wastewater / surface water
Date & time	28/05/2012; 12.30
Description	Collected from the surface boil located above the outfall of the submerged discharge pipe from the Shaoxing WWTP within the Binhai Industrial Zone

#### Abundance



Number of compounds isolated: 41

Compounds identified to better than 90%:

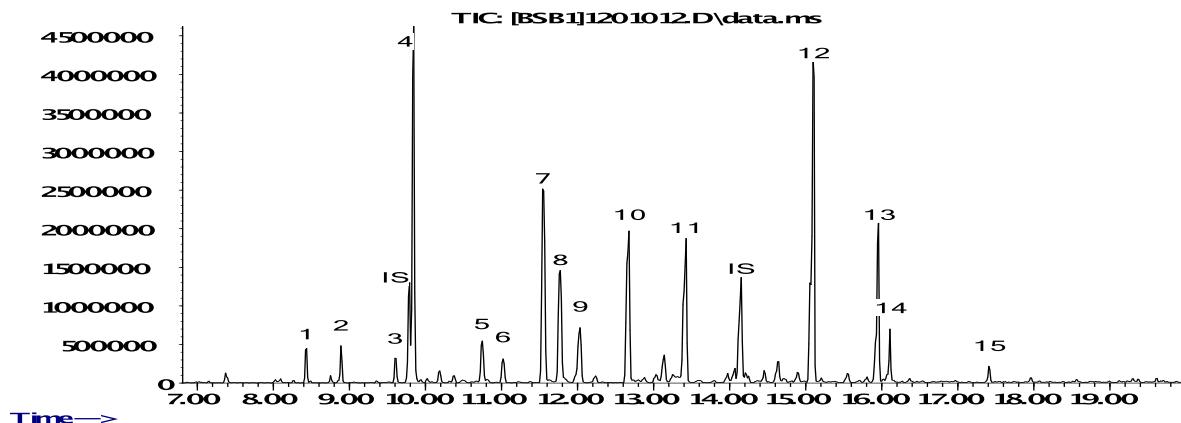
CAS#	Name	
000095-50-1	Benzene, 1,2-dichloro-	(SIM)
000106-46-7	Benzene, 1,4-dichloro-	(SIM)
006285-57-0	6-Nitro-2-benzothiazolamine	
000000-00-0	Dichloro-2-benzothiazolamines, 2 isomers	
001477-42-5	* 4-Methyl-2-benzothiazolamine	
000095-24-9	6-Chloro-2-benzothiazolamine	
000126-86-3	2,4,7,9-Tetramethyl-5-decyne-4,7-diol	
000719-22-2	*2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-	
000626-43-7	Aniline, 3,5-dichloro-	
000121-50-6	*Aniline, 2-chloro-5-(trifluoromethyl)-	
000057-10-3	Hexadecanoic acid	
000112-39-0	Hexadecanoic acid, methyl ester	
000112-61-8	Octadecanoic acid, methyl ester	
001660-94-2	Phosphonic acid, methylenebis-, tetraethyl ester	
001613-34-9	Quinoline, 2-ethyl-	

SIM indicates detection at trace levels only using Selected Ion Monitoring mode of analysis.

\* indicates a minor component of the total ion chromatogram

Sample code	CN12010
Location	Lagoon of wastewater above outfall of the Xiaoshan Linjiang communal WWTP, Linjiang Industrial Zone, Xiaoshan County
Sample type	Wastewater / surface water
Date & time	28/05/2012; 13.30
Description	Collected from a lagoon of wastewater located on the bank of the Qiantang River, above the submerged discharge pipe from the Xiaoshan Linjiang WWTP within the Linjiang Industrial Zone

Abundance



Compounds ID on chromatogram:

No.	RT, min	Compound	No.	RT, min	Compound
1	8.437	Benzene, nitro-	9	12.033	Aniline, dichloro-
2	8.902	Aniline, N-ethyl-	10	12.675	1,1'-Biphenyl
3	9.613	Aniline, 2-methoxy-	11	13.427	Aniline, dichloro-
4	9.845	Naphthalene	12	15.109	Propanenitrile, 3-(ethylphenylamino)-
5	10.747	Benzene, 1-chloro-3-nitro-	13	15.957	Propanenitrile, 3-[ethyl(3-methylphenyl)amino]-
6	11.021	Benzene, 1-chloro-4-nitro-	14	16.108	1,3,5-Triazine-2,4,6(1H,3H,5H)-trione, 1,3,5-tri-2-propenyl-
7	11.554	Naphthalene, 2-methyl-	15	17.421	Aniline, 2,6-dichloro-4-nitro-
8	11.773	Naphthalene, 1-methyl-			

Number of compounds isolated: 67

Compounds identified to better than 90%:

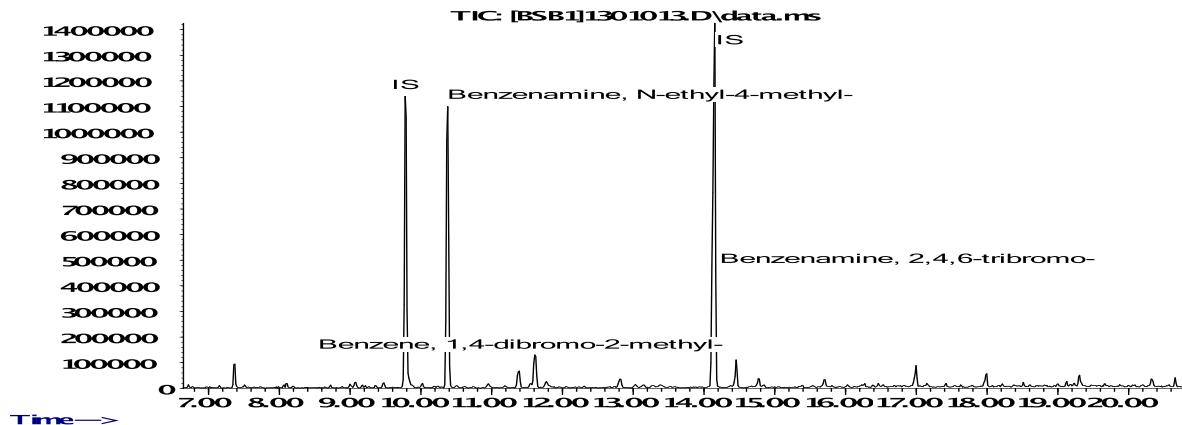
CAS#	Name
000092-52-4	1,1'-Biphenyl
000000-00-0	1,1'-Biphenyl, methyl-, 3 isomers
001025-15-6	1,3,5-Triazine-2,4,6(1H,3H,5H)-trione, 1,3,5-tri-2-propenyl-
000769-59-5	2-Butanone, 3-phenyl-
000083-32-9	Acenaphthene
000099-30-9	Aniline, 2,6-dichloro-4-nitro-
000090-04-0	Aniline, 2-methoxy-
000000-00-0	*Aniline, chloro-
000000-00-0	Aniline, dichloro-, 5 isomers
000000-00-0	*Aniline, chloromethyl-
000103-69-5	Aniline, N-ethyl-
000091-66-7	*Aniline, N,N-diethyl-
000121-69-7	*Aniline, N,N-dimethyl-
000613-97-8	*Aniline, N-ethyl-N-methyl-
000000-00-0	*Aniline, N-ethylmethyl-
000000-00-0	*Aniline, trichloro-
000095-50-1	Benzene, 1,2-dichloro-
000106-46-7	Benzene, 1,4-dichloro-
000541-73-1	Benzene, 1,3-dichloro- (SIM)
000108-70-3	Benzene, 1,3,5-trichloro- (SIM)
000120-82-1	Benzene, 1,2,4-trichloro- (SIM)
000608-93-5	Benzene, pentachloro- (SIM)
000766-51-8	Benzene, 1-chloro-2-methoxy-
000121-73-3	Benzene, 1-chloro-3-nitro-
000100-00-5	Benzene, 1-chloro-4-nitro-
000098-95-3	Benzene, nitro-
000000-00-0	Benzonitrile, methyl-
000270-82-6	*Benzo[c]thiophene
000087-68-3	Butadiene, hexachloro- (SIM)
000132-64-9	Dibenzofuran
000099-91-2	*Ethanone, 1-(4-chlorophenyl)-
000086-73-7	Fluorene
000091-20-3	Naphthalene
000090-12-0	Naphthalene, 1-methyl-
000091-57-6	Naphthalene, 2-methyl-
000148-87-8	Propanenitrile, 3-(ethylphenylamino)-
000148-69-6	Propanenitrile, 3-[ethyl(3-methylphenyl)amino]-
002489-86-3	Naphthalene, 1-(2-propenyl)-
000000-00-0	Naphthalene, dimethyl-, 2 isomers
000000-00-0	Naphthalene, ethyl-
000085-01-8	Phenanthrene

SIM indicates detection at trace levels only using Selected Ion Monitoring mode of analysis.

\* indicates a minor component of the total ion chromatogram

Sample code	CN12011
Location	River adjacent to the Zhejiang Deou Chemical Manufacture Co.
Sample type	River water
Date & time	10/05/2012; 00.30
Description	Collected from a river adjacent to the facility into which an accidental release of wastewater occurred

Abundance



Number of compounds isolated: 29

Compounds identified to better than 90%:

CAS#	Name
000147-82-0	Aniline, 2,4,6-tribromo-
000622-57-1	Aniline, N-ethyl-4-methyl-
000000-00-0	Aniline, dibromo-
000000-00-0	Aniline, dibromomethyl-
000613-48-9	Aniline, N,N-diethyl-4-methyl-
000000-00-0	*Aniline, dichloro-
000615-59-8	Benzene, 1,4-dibromo-2-methyl-
000538-86-3	Benzyl methyl ether
000101-84-8	Benzene, 1,1'-oxybis- [diphenyl ether]
000091-16-7	Benzene, 1,2-dimethoxy-
014495-51-3	*Benzene, 1-bromo-4-chloro-2-methyl-
000000-00-0	*Benzene, dibromo-
000095-50-1	Benzene, 1,2-dichloro- (SIM)
000541-73-1	Benzene, 1,3-dichloro- (SIM)
000106-46-7	Benzene, 1,4-dichloro- (SIM)
000087-61-6	Benzene, 1,2,3-trichloro- (SIM)
000120-82-1	Benzene, 1,2,4-trichloro- (SIM)
000108-70-3	Benzene, 1,3,5-trichloro- (SIM)
000634-90-2	Benzene, 1,2,3,5-tetrachloro- (SIM)
000112-95-8	Eicosane
000629-78-7	Heptadecane
000090-12-0	*Naphthalene, 1-methyl-
000091-57-6	*Naphthalene, 2-methyl-
000629-92-5	Nonadecane
000593-45-3	Octadecane
000646-31-1	Tetracosane

SIM indicates detection at trace levels only using Selected Ion Monitoring mode of analysis.

\* indicates a minor component of the total ion chromatogram

### Appendix 3: Data for all PFCs quantified in CN12008, CN12009 & CN12010

Sample code	Surface boil above submerged outfall of the Shaoxing WWTP; Binhai Industrial Zone		Wastewater lagoon above submerged outfall of the Xiaoshan Linjiang WWTP; Linjiang Industrial Industrial Zone
	CN12008 (ng/l)	CN12009 (ng/l)	CN12010 (ng/l)
<b>Perfluorobutanoic acid (PFBA)</b>	< 3	< 3	< 3
<b>Perfluoropentane acid (PFPeA)</b>	< 3	< 3	13.0
<b>Perfluorohexanoic acid (PFHxA)</b>	< 10	< 10	10.7
<b>Perfluorheptanoic acid (PFHpA)</b>	< 3	< 10	< 3
<b>Perfluorooctanoic acid (PFOA)</b>	88.7	112	93.2
<b>Perfluorononanoic acid (PFNA)</b>	< 10	< 10	< 3
<b>Perfluorodecanoic acid (PFDA)</b>	< 10	< 3	< 3
<b>Perfluoroundecanoic acid (PFUnA)</b>	< 3	< 3	10.2
<b>Perfluorododecane acid (PFDoA)</b>	< 3	< 3	< 3
<b>Perfluorotridecane acid (PFTrA)</b>	< 3	< 3	< 3
<b>Perfluorotetradecane acid (PFTA)</b>	< 3	< 3	< 3
<b>Perfluorbutansulfonate (PFBS)</b>	< 5	< 5	< 5
<b>Perfluorohexane sulfonate (PFHxS)</b>	< 5	< 5	< 5
<b>Perfluoroheptane sulphonate (PFHpS)</b>	< 5	< 5	< 5
<b>Perfluorooctane sulfonate (PFOS)</b>	< 3	< 3	< 3
<b>Perfluorodecane sulphonate (PFDS)</b>	< 5	< 5	< 5
<b>Perfluorooctane-sulfonamide (PFOSA)</b>	< 3	< 3	< 3
<b>7H-Dodecafluoroheptanoic acid (HPFHpA)</b>	< 7	< 7	< 7
<b>2H,2H-Perfluorodecane acid (H2PFDA)</b>	< 7	< 7	< 7
<b>2H,2H,3H,3H-Perfluoroundecane acid (H4PFUnA)</b>	< 7	< 7	< 7
<b>4:2 Fluorotelomer sulfonate (FTS)</b>	< 7	< 7	< 7
<b>6:2 Fluorotelomer sulfonate (FTS)</b>	< 5	< 5	< 5
<b>8:2 Fluorotelomer sulfonate (FTS)</b>	< 7	< 7	< 7

Table A3: Concentrations of PFCs quantified in wastewater/estuary water samples collected from the vicinity of a wastewater discharge from communal wastewater treatment plants (WWTPs) within the Binhai Industrial Zone (CN12008 & CN12009) and the Linjiang Industrial Zone (CN12010)