Analysis of wastewaters and associated sediments related to the manufacture of electronic products at facilities in Guadalajara, Mexico for the presence of metals and organic chemical contaminants

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# Contents

Introduction	2
Materials and methods	3
Results and Discussion	3
3.1 Sanmina SCI	5
3.2 Siemens/ Flextronics	
3.3 El Ahogado WWTP	
Conclusions	
References	
Appendix 1: Details of methodologies	25
Appendix 2: Detailed organic analytical screening data	
Appendix 3: Data for PFCs quantified in wastewater samples	

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# Introduction

A total of seven samples were received from Greenpeace Mexico for analysis at the Greenpeace Research Laboratories on 8<sup>th</sup> February 2016, including three wastewater samples and four associated sediment samples, all of which were collected on the 29<sup>th</sup> January 2016.

A sample of wastewater (MX16001) was collected from a wastewater sump in the vicinity of a Sanmina SCI facility, together with an associated sediment sample (MX16004) from the same location. It has not been confirmed that wastewater in the sump originates from the Sanmina SCI facility. Similarly, a wastewater sample (MX16002) and an associated sediment sample (MX16005) were collected from a channel into which wastewater is discharged from a Siemens facility and separately from a Flextronics facility. No other inputs to this channel from other sources were observed. In addition, a sample of treated wastewater (MX16003) was collected from the outfall of the El Ahogado Wastewater treatment plant (WWTP), together with two associated sediment samples; one of which (MX16006) was collected from within the discharge pipe and the other (MX16007) from the El Ahogado river immediate downstream of the outfall. A summary of the samples received is provided in Table 1a, with GPS coordinates for the sample collection locations in Table 1b.

All samples were analysed quantitatively for the presence of a range of metals and metalloids. For wastewater samples, concentrations of metals/metalloids in both whole and filtered water were determined in order to distinguish between metals associated with suspended matter and those present in dissolved form in the water. All samples were also analysed qualitatively for the presence of semi-volatile (solvent-extractable) organic compounds, and separately for the presence of volatile organic compounds (VOCs). In addition, for the three wastewater samples, the concentrations of a range of perfluorinated chemicals (PFCs), which cannot be identified using the technique employed for organic compounds qualitative analysis, were determined at an accredited independent laboratory.

Sample code	type	Description	
		Close to Sanmina SCI (Electrical manufacturer)	
MX16001	wastewater	collected from an open sumplemented 010m from official discharge point	
MX16004	sediment	conected from an open sump located 910m from official discharge point	
Siemens/Flextronics (Electrical manufacturers)			
MX16002	wastewater	collected from an open channel into which wastewater from both Siemens and	
MX16005	sediment	Flextronics is discharged, via separate pipes from each facility	
El Ahogado Wastewater treatment plant (WWTP)			
MX16003	wastewater	Collected from a pipe discharging treated water to the El Ahogado river	
MX16006	sediment	Collected from within the discharge pipe at its outfall to the El Ahogado river	
MX16007	sediment	Collected from the El Ahogado river immediate downstream of the outfall	

Table 1a: details of wastewater and sediment samples collected in Guadalajara, El salto, Jalisco, Mexico

Sample		N	E		
code	degree (º)	minutes (')	degree (º)	minutes (')	
MX16001	20°	30'39.0	103°	15'36.36''	
MX16002	20°	34'50.31''	103'	26'27.6"	
MX16003	20°	30'41.7	103°	15'14.2"	
MX16004	20°	30'39.4'	103°	15'36.6"	
MX16005	20°	34'50.31''	103'	26'27.6"	
MX16006	20°	30'41.7	103°	15'14.2"	
MX16007	20°	30'42.8''	103°	15'14.0"	

Table 1b: GPS coordinated of sample collection locations

# Materials and methods

All samples were collected in pre-cleaned glass or polypropylene bottles and kept cold and dark before shipment to our laboratory in the UK for analysis.

Each wastewater sample consisted of three subsamples collected in different types of bottles depending on the subsequent analyses to be carried out on each subsample. In all cases, the first 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 second sub-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 soaking in nitric acid and being rinsed thoroughly with analytical grade pentane in order to remove all heavy metal and organic residues. A third sub-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. Each sediment sample was collected in a 100 ml screw-cap glass bottle, for use in the quantitative analysis of solvent extractable (semi-volatile) organic compounds.

All samples were analysed qualitatively for semi-volatile organic compounds (sVOCs) and volatile organic chemicals (VOCs), and quantitatively for metals. Semi-volatile organic compounds were isolated from samples using solid phase extraction (SPE) with ethyl acetate, pentane and toluene (for water samples) or Accelerated Solvent Extraction (ASE) with a mixture of pentane and acetone (for sediment samples). Extracted compounds were subsequently identified as far as possible using gas chromatography/mass spectrometry (GC/MS) operated in both SCAN and SIM modes. Volatile organic chemicals (VOCs) were identified in all wastewater samples as received (with anhydrous sodium sulfate added to partition VOCs into headspace) using GC/MS with HeadSpace sample introduction technique. Metal concentrations were determined for all samples by ICP mass spectrometry (ICP-MS) following acid digestion and using appropriate intra-laboratory standards or certified reference materials. For water samples, both the total concentrations in the whole (unfiltered) sample and the concentrations of dissolved forms in a filtered water samples were determined colourimetrically using a diphenylcarbazide method. More detailed descriptions of the sample preparation and analytical procedures are presented in the Appendix 1.

PFCs in wastewater samples were quantified 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.

# **Results and Discussion**

The results for the samples are outlined in the following sections, divided into the three areas in which the samples were collected.

The semi-volatile (solvent extractable) organic chemicals identified in individual samples are summarised in Table 2. A full list of semi-volatile organic chemicals identified in each sample is provided in Appendix 2. A summary of volatile organic compounds (VOCs) identified in the samples are listed in Table 3. PFCs identified in the wastewater samples are given in Table 4, with a full list of PFCs quantified given in Appendix 3. In addition, the concentrations of metals and metalloids in sediment samples and in both filtered (dissolved metals) and in whole waters (dissolved and suspended metals) are reported Table 5.

Location	Sanmina	Sanmina SCI	Siemens/	Siemens/	El Ahogado	El Ahogado	El Ahogado
	SCI		Flextronics	Flextronics	WWTP	WWTP pipe	River
sample type	WW	Sed	WW	Sed	WW	Sed	Sed
Sample code	MX16001	MX16004	MX16002	MX16005	MX16003	MX16006	MX16007
Number of compounds isolated	30	225	28	96	101	178	147
No. of compounds identified to >90%	3	102	7	28	56	46	39
phenols:							
octylphenol					$\checkmark$		
nonylphenol		13 isomers		5 isomers	8 isomers		
bisphenol-A					$\checkmark$		
butylated hydroxytoluene (BHT)		$\checkmark$					
2,4-di-tert-butyl phenol							$\checkmark$
phenol & other alkyl-phenols		2		2	3		
phthalates & related chemicals:							
		DEHP		DEHP	DBP	DEHP	DEHP
	DBP	DBP		DBP		DBP	DBP
phthalata actors		DiBP			DiBP		DiBP
phillalate esters				BBP			
				DiNP			
	DEP		DEP		DEP / DMP		
di(2-ethylhexyl) terephthalate		~		$\checkmark$			
phosphate esters:							
triphenyl phosphate (TPP)	$\checkmark$		$\checkmark$		$\checkmark$		
phenyl phosphate					$\checkmark$		
tris(2-butoxyethyl) phosphate (TBEP)			$\checkmark$		$\checkmark$		
tris(1-chloro-2-propyl) phosphate			$\checkmark$				
other chlorinated chemicals							
dichlorobenzene		$\checkmark$			$\checkmark$		
chlorocresol					$\checkmark$		
quinones, benzophenones & related:							
2,6-di-tert-butylbenzoquinone				$\checkmark$			
Quantacure ITX				$\checkmark$			
oxybenzone (benzophenone-3)					~		
other oxygenated chemicals							
benzyl ether		~					
diphenyl ether		$\checkmark$			$\checkmark$		
Surfynol 104H			$\checkmark$				
4-tert-butylcyclohexanol					$\checkmark$	$\checkmark$	
benzoic acid			$\checkmark$				
amines & related:							
tributylamine					~		
1H-indole & derivatives		2			2		
others:							
Benzothiazole derivatives			$\checkmark$				
fragrance chemicals		2		$\checkmark$	2	$\checkmark$	
alkyl benzenes		8			2	$\checkmark$	
polycyclic aromatic hydrocarbons (PAHs)		✓		3	✓		
aliphatic hydrocarbons		34		3		34	29
long chain fatty acids & derivatives		12			7	3	$\checkmark$
other ketones				1	1	2	
dicyclopentadiene derivatives					2		
sewage associated chemicals		9		3	$\checkmark$	$\checkmark$	3
chemicals of plant based origin		12		7	12	$\checkmark$	2

Table 2: summary of organic contaminants for each wastewater (WW) and sediment (Sed) sample in which semi-volatile (solvent extractable) organic compounds were identified (to >90% reliability)

Location	Sanmina	Siemens/	El Ahogado
	SCI	Flextronics	WWTP
Sample code	MX16001	MX16002	MX16003
Number of VOCs isolated	21	1	4
No. of VOCs identified to >90%	13	0	4
halomethanes:			
dichloromethane			$\checkmark$
trichloromethane (chloroform)	$\checkmark$		$\checkmark$
bromodichloromethane			$\checkmark$
other chlorinated chemicals:			
benzene, 1,4-dichloro-	$\checkmark$		$\checkmark$
others:			
monoterpenes	4		
monoterpene alcohols/ethers	5		
alkyl benzene	$\checkmark$		
carbon disulfide	$\checkmark$		

Table 3: Volatile organic contaminants (VOCs) identified (to >90% reliability) in the wastewater samples.

Location	Sanmina SCI	Siemens/ Flextronics	El Ahogado WWTP
Sample code	MX16001	MX16002	MX16003
PFC	(ng/l)	(ng/l)	(ng/l)
perfluorooctanoate (PFOA)	< 10,0	82.6	12.7
Perfluorobutane sulfonate (PFBS)	23.0	< 15,0	< 15,0
perfluorobutanoate (PFBA)	< 10,0	17.3	< 11,5
perfluoropentanoate (PFPA)	11.1	14.5	< 10,0
perfluorohexanoate (PFHxA)	< 10,0	26.6	< 10,0
perfluorodecanoate (PFDA)	< 10,0	13.5	< 10,0

Table 4: Concentrations of PFCs identified in the wastewater samples (ng/l), full details provided in Appendix 3

## 3.1 Sanmina SCI

## 3.1.1 Organic chemical contaminants

Analysis of the wastewater collected near to the Sanmina facility (MX16003) identified two phthalate esters, namely di-n-butyl phthalate (DBP) and diethyl phthalate (DEP), together with a phosphate ester; triphenyl phosphate (TPP).

Phthalate esters have numerous industrial uses. DBP is toxic to reproduction in both animals and humans (Mylchreest *et al.* 2002, Swan *et al.* 2005) and within the EU has been listed as a "substances of very high concern" under the REACH Regulation (ECHA 2010). For more information see Box A.

## BOX A. Phthalate esters

Phthalates (or, more accurately, phthalate diesters) are a group of chemicals with a diversity of uses, dominated by use as plasticizers (or softeners) in plastics, especially PVC. Other applications included uses as components of inks, adhesives, sealants, surface coatings and personal care products. Phthalates have been detected in components of electronic products (Brigden *et al.* 2007a) and in wastewaters from electronic manufacturing facilities (Brigden *et al.* 2007b).

Some phthalates are discrete chemicals, such as the well-known di(2-ethylhexyl) phthalate (DEHP), while others are complex mixtures of isomers, such as diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP).

All uses of phthalates, especially the major use as PVC plasticisers, result in large-scale losses to the environment (both indoors and outdoors) during the lifetime of products, and again following disposal, principally because phthalates are not chemically bound but only physically associated to the polymer chains. Phthalates have been found to leach from food packaging materials (Fierens *et al.* 2012, Fasano *et al.* 2012); and from medical materials (Jenke *et al.* 2006, Ferri *et al.* 2012). Moreover, it has been shown that bacteria, which may grow on PVC plastics in wet conditions, may enhance DEHP leaching from plastic (Latorre *et al.* 2012). Thus, phthalates are widely found in the indoor environment, including in air and dust (Langer *et al.* 2010, Otake *et al.* 2001, Butte & Heinzow 2002, Fromme *et al.* 2004) at concentrations which commonly reflect the prevalence of plastics and certain textiles within the rooms sampled (Abb *et al.* 2009). Once plastic products are disposed to municipal landfills, phthalates may continue to leach, finally reaching groundwater (Liu *et al.* 2010).

Phthalates are commonly found in human tissues, including in blood, breast milk and, as metabolites, in urine (Colon *et al.* 2000, Blount *et al.* 2000, Silva *et al.* 2004, Guerranti *et al.* 2012), with reports of significantly higher levels of intake in children (Koch *et al.* 2006). In humans and other animals, they are relatively rapidly metabolised to their monoester forms, but these are frequently more toxic than the parent compound (Dalgaard *et al.* 2001).

Substantial concerns exist with regard to the toxicity of phthalates to wildlife and humans. For example, DEHP, one of the most widely used to date, is known to be toxic to reproductive development in mammals. DEHP is capable, in its monoester form MEHP, of interfering with development of the testes in early life, thought to be mediated through impacts on testosterone synthesis (Howdeshell *et al.* 2008, Lin *et al.* 2008). Even at low doses, exposure to mixtures of phthalates can result in cumulative effects on testicular development in rats (Martino-Andrade *et al.* 2008). In addition, adverse impacts on female reproductive success in adult rats and on development of the young have been reported following exposure to this chemical (Lovekamp-Swan & Davis 2003, Grande *et al.* 2006, Gray *et al.* 2006). A more recent study (Abdul-Ghani *et al.* 2012) has shown that both DEHP and DBP can induce gross malformations, damage to DNA and changes in behavioural development when administered to developing chick embryos. Butylbenzyl phthalate (BBP) and dibutyl phthalate (DBP) have also been reported to exert reproductive toxicity (Ema & Miyawaki 2002, Mylchreest *et al.* 2002, Aso *et al.* 2005). The review of Caldwell (2012) highlights recently discovered impacts of DEHP including chromosomal damage, increased cancer progression and changes in gene expression at increasingly lower concentrations. DEHP, DBP DiBP and BBP are all classified as "toxic to reproduction" within Europe.

Other research has revealed a correlation between phthalate exposure during pregnancy and decreased anogenital index (distance from the anus to the genitals) in male children (Swan *et al.* 2005), though it is clearly not possible to establish a cause-effect relationship from such studies.

Other commonly used phthalates, including the isomeric forms DINP and DIDP, are of concern because of observed effects on the liver and kidney, albeit at higher doses. DINP has also been found to exhibit antiandrogenic effects on reproductive development of Wistar rats (Boberg *et al.* 2011), though less prominent than DEHP, DBP and BBP.

At present, globally there are relatively few controls on the marketing and use of phthalates, despite their toxicity, the volumes used and their propensity to leach out of products throughout their lifetime. Of the controls that do exist, however, probably the best known is the ban on the use of six phthalates in children's toys and childcare articles in a number of countries, including the EU-wide which was the first to be implemented (EU 2005). More recently, the EU has included four phthalates (DEHP, BBP, DBP and DiBP) in the regulation that restricts hazardous substances in electrical and electronic equipment (RoHS), such that the sale of such equipment with components containing these phthalates above 0.1% will be banned from 22<sup>nd</sup> July 2019 (EU 2015). While these address two important exposure routes, exposures through other consumer products have so far largely escaped regulation. Furthermore, certain phthalates, including DEHP, DBP, DiBP and BBP, have been listed as Substances of Very High Concern (SVHC) under the EU REACH Regulation (ECHA 2013).

Triaryl phosphates, including TPP, are used as flame retardants, and have been used in electronic products (IPCS 1991). TPP is the most acutely toxic to aquatic life of all the triaryl phosphates in common use (IPCS 1991). For more information see Box B.

#### BOX B. Triaryl and tri-alkyl phosphates

**Triphenyl phosphate, TPP.** Triaryl phosphates, including TPP, are used as flame retardants, including in electronic products (IPCS 1991). TPP is the most acutely toxic to aquatic life of all the triaryl phosphates in common use (IPCS 1991).

TPP has been reported as a contaminant in human blood (Jonsson *et al.* 2001) and is a strong inhibitor of a key enzyme (monocyte carboxyl esterase) in human blood cells (Amini & Crescenzi 2003). Research has also indicated an ability to inhibit human androgen hormone reception in vitro (Honkakoski *et al.* 2004). Contact dermatitis following exposure to TPP has been reported by several authors, with some cases dating back to the 1960s (Carlsson *et al.* 1997 and Sanchez *et al.* 2003).

*Tris(1-chloro-2-propyl) phosphate* is one of a number of tris(monochloropropyl) phosphates (TMCPP), a group of chemicals used as flame retardants (NRC 2000). TMCPP mixtures are sold under various trade names, including Antiblaze 80, Amgard TMCP, Fyrol PCF and Hostaflam PO 820.

Tris(1-chloro-2-propyl) phosphate is not readily biodegraded under conventional wastewater treatment, though it is rapidly metabolised by certain fish (IPCS 1998). Traces of tris(1-chloro-2-propyl) phosphate have been detected in industrial and domestic effluents, but not in surface waters and sediments (IPCS 1998). The uptake of tris(1-chloro-2-propyl) phosphate has been demonstrated in a number of living organisms, including humans (Sundkvist *et al.* 2010, Greaves & Letcher 2014, Van den Eede *et a*l. 2015), and bioaccumulation has been suggested in the benthic food web (Brandsma et al. 2015).

In mammals, tris(1-chloro-2-propyl) phosphate is of low to moderate acute toxicity by oral (LD50 in rats is 101-4200 mg/kg body weight), dermal (LD50 in rats and rabbits is > 5000 mg/kg body weight) and inhalation routes (LD50 in rats is > 4.6 mg/litre) (IPCS 1998). However, acute toxicity values for other organisms in the environment are available, with LD50 values ranging from 3.6 to 180 mg/litre. Aquatic toxicity information shows no observed effect concentrations (NOEC) for algae, daphnids and fish are 6, 32 and 9.8 mg/litre, respectively (IPCS 1998). Little is known about the possible effects on human health of chronic exposure to phosphorus flame retardants like TCIPP (Van den Eede *et al.* 2015). Despite the lack of information on the carcinogenic potential of the TMCPPs identified, studies on a very similar compound, tris(2-chloroethyl) phosphate, showed that is possesses carcinogenic properties when tested on mice and rats (IPCS 1998) and recently it has been added to the list of candidates as 'substances of very high concern' under the REACH Regulation (ECHA 2013).

*Tris(2-butoxyethyl) phosphate* (TBEP) is used as a flame retardant as well as a solvent in some resins, a viscosity modifier in plastics, and also as a plasticiser in synthetic rubber, plastics and lacquers (WHO 2000). TBEP is not readily biodegraded under conventional wastewater treatment.

In the aquatic environment, TBEP is harmful to fish, with a LC50 of 24 mg/L for rainbow trout (Rhodia 2016). Studies in laboratory animals have shown that the liver is the target organ for TBEP toxicity; however, the long-term toxicity and carcinogenicity of TBEP have not been investigated (WHO 2000).

In addition, 21 volatile organic chemicals (VOCs) were isolated from this sample, of which 13 were identified, including chloroform and 1,4-dichlorobenzene.

Chloroform has industrial uses as a solvent, but can also be generated as a by-product of the disinfection processes commonly used in wastewater treatment plants, from the reaction between the disinfectant (usually chlorine or chlorine-containing chemicals) with natural organic matter present in the source water (US EPA 2012). This may be the source of chloroform for this sample. Chloroform is a hazardous chemical, and has been listed by the International Agency for Research on Cancer (IARC) in Group 2B as possibly carcinogenic to humans (IARC 2012).

Similarly, 1,4-dichlorobenzene is a well-known environmental contaminants largely due to widespread use as a deodoriser and disinfectant in sanitary products, which may be a contributory source at this location. This chemical has some hazardous properties; it is toxic to the liver and kidneys following repeated exposures (EURAR 2004) and has been listed by IARC in Group 2B as possibly carcinogenic to humans in relation to inhalation exposure (IARC 2012).

In addition, quantitative analyses were carried out for a range of PFCs in the wastewater. The only PFCs detected were perfluorobutane sulfonate (PFBS, 23.0 ng/l) and perfluoropentanoate (PFPA, 11.1 ng/l). The concentrations of PFBS and PFPA in this sample are within the range reported in municipal waste water treatment plant effluents (Ahrens *et al.* 2009, Schultz *et al.* 2006)). Similar concentrations have been reported in some surface waters, though reported concentrations in surface waters are commonly slightly lower than those found in this sample (Eschauzier *et al.* 2011, Heydebreck *et al.* 2015). The concentrations of these two PFCs could indicate use of these PFCs within this facility, though the somewhat low concentrations for industrial wastewaters, together with all other quantified PFCs being below detection limits, does not provide strong evidence for this.

## Sediment sample (MX16004)

A broad range of additional organic chemicals were identified in the sediment (MX16004) collected from the sample location from which the wastewater (MX16001) was collected. Their presence in sediment, but not in the wastewater, is likely to have arisen from their historic presence in wastewaters previously discharged *via* this location. Key substances amongst these included phthalate esters and 13 isomers of nonylphenol.

In addition to DBP, a phthalate which was identified in both the wastewater (MX16001) and the associated sediment (MX16002), two additional phthalates, di-iso-butyl phthalate (DiBP) and di(2-ethylhexyl) phthalate (DEHP), were identified in the sediment, together with a related compound, di(2-ethylhexyl) terephthalate (DEHT). As for DBP, DEHP and DiBP are toxic for reproduction and have been listed as Substances of Very High Concern (SVHC) under the EU REACH Regulation (ECHA 2013); see Box A for more information. In common with ortho-phthalates such as DBP, DiBP and DEHP, di(2-ethylhexyl) terephthalate (DEHT) is predominantly used as a plasticizer and softener for plastics. Unlike the ortho-phthalates, however, adverse effects on reproduction have not been reported for DEHT (Wirnitzer *et al.* 2011).

Nonylphenol is a group of well-known persistent environmental contaminants with hormone disrupting properties. A common source of nonylphenol is the use of nonylphenol ethoxylates (NPEs) as a detergent or surfactant, which subsequently degrades to nonylphenol either within a wastewater treatment facility or following release into the aquatic environment. In addition to being highly resistant to further degradation and therefore persistent within the environment, nonylphenol is able to bio-accumulate and is toxic, primarily due to its hormone-disrupting properties that can lead to altered sexual development in some organisms, most notably the feminisation of fish in contaminated waters (OSPAR 2004, Jobling *et al.* 1995, 1996). As a result of their hazardous properties, the manufacture, use and release of nonylphenol NPEs are regulated in some regions (OSPAR 1998, EU 2003). Additional information on nonylphenol, including hazardous properties, is available in Box C.

Other compounds identified in the sediment sample included butylated hydroxytoluene (BHT), diphenyl ether, indole, long chain fatty acids and their derivatives, alkyl benzenes, a PAH, and aliphatic hydrocarbons.

Butylated hydroxytoluene (BHT) has been commonly used as an antioxidant in a wide range of products, including plastics and other petrochemical products, cosmetics and food products (Jobling *et al.* 1995). BHT has been classified under the Globally Harmonized System of Classification and

Labelling of Chemicals (GHS)<sup>1</sup> as toxic to aquatic life with long lasting effects (H411), and irritating to the skin and eyes (H315, H319).

Diphenyl ether, also known as diphenyl oxide, has a variety of uses including in 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 is classified under GHS as toxic to aquatic life with long-lasting effects (H411), but has shown low inhalation and oral toxicity in experimental animals (US EPA 2010).

Indole has various industrial uses, but is also used as a fragrance chemical (Sullivan & Gad 2014). It has been classified under GHS as harmful if swallowed (H302), toxic in contact with skin (H311) and very toxic to aquatic life (H400).

Long chain fatty acid esters, which are present in animal or vegetable fats, oils, or waxes, are used in a variety of manufacturing processes, but can also originate from natural sources. These, and other fatty acid derivatives, can undergo partial degradation to give rise to the fatty acids themselves (IPPC 2003). Fatty acids and their derivatives are generally not of particular environmental concern due to their low toxicity and being readily biodegradable.

The occurrence of alkyl benzenes, PAHs and aliphatic hydrocarbons in the environment is often due to their presence in crude oil and petroleum products (Overton 1994). Alkylbenzenes are also produced following the degradation of the linear alkylbenzene sulphonate (LAS) detergents. Many alkylbenzenes and PAHs are highly resistant to degradation and may accumulate in sediments (Preston & Raymundo 1993). Alkylbenzenes are also useful sewage markers (Chalaux *et al.* 1995).

Also identified were two isomers of the synthetic musk fragrance chemical Galaxolide, and a number of cholesterol derivatives, which are commonly found in sewage (Homem *et al.* 2015), as well as a number of chemicals likely to be of plant origin.

## 3.1.2 Metals

The wastewater collected close to the Sanmina SCI facility (MX16001) contained concentrations of dissolved chromium (70  $\mu$ g/l) and dissolved nickel (47  $\mu$ g/l) somewhat above levels typically found in in uncontaminated surface freshwater, in which median values for chromium are commonly around 10 ug/l (ATSDR 2012) and concentrations of nickel are commonly below 20  $\mu$ g/l (ATSDR 2005, Salomons & Forstner 1984). Concentrations of copper and nickel for the whole (unfiltered) sample were approximately double the respective dissolved concentrations, indicating a similar quantity of these metals associated with suspended matter as was present in dissolved forms.

In addition, a number of other metals were present at concentrations in the whole (unfiltered) sample notably higher than the respective dissolved concentrations, including copper, iron, lanthanum,

<sup>&</sup>lt;sup>1</sup> The Globally Harmonized 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 2015). The hazard statements used for individual substances 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)

neodymium, tantalum, tin and zinc indicating their presence as part of the suspended matter within the water.

The sediment collected at the same location (MX16004) contained some metals, including cadmium, copper, tin and zinc, at concentrations between 2-5 times higher than the upper end of the ranges typically found in uncontaminated surface freshwater sediments (Salomons and Forstner 1984).

sample type	wastewater (µg/l)						sediments	(mg/kg)		continental crust * (mg/kg)	
location	Sanmi	na SCI	Siem Flexti	iens/ ronics	El Aho WV	ogado VTP	Sanmina SCI	Siemens/ Flextronics	El Ahogado WWTP pipe	El Ahogado River	
Sample code	MX1	6001	MX1	6002	MX1	6003	MX16004	MX16005	MX16006	MX16007	
	filt.	wh	filt.	wh	filt.	wh	-	-	-	-	-
Antimony	0.6	0.9	0.5	0.5	0.6	0.6	2.2	0.4	0.4	0.5	0.2
Arsenic	7	10	13	13	7	7	7.2	1.2	4.3	3.4	1.8
Barium	69	98	61	66	29	36	123	16	511	133	425
Beryllium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.56	0.25	5.60	1.4	2.8
Cadmium	0.17	0.39	0.06	0.06	0.06	0.25	1.15	0.21	0.13	0.08	0.2
Chromium	70	175	0.79	0.82	3.63	5.59	47.8	2.83	17.9	8.51	100
Chromium (VI)	<50	<50	<50	<50	<50	<50	-	-	-	-	
Cobalt	0.5	1.0	0.3	0.3	<0.1	1.2	6.26	0.85	12.6	6.69	25
Copper	9	38	5	6	6	10	140	7.0	13.0	12.0	55
Erbium	0.02	0.08	< 0.01	<0.01	0.01	0.02	0.54	0.50	4.12	1.85	2.8
Gadolinium	0.03	0.13	< 0.01	0.01	0.01	0.02	0.93	0.91	6.18	3.33	5
Gallium	<0.2	0.4	<0.2	<0.2	<0.2	<0.2	3.5	2.2	23.7	6.6	15
Holmium	< 0.01	0.03	< 0.01	<0.01	< 0.01	<0.01	0.19	0.18	1.38	0.65	1.2
Iron	119	727	286	329	145	202	12600	4220	22250	12800	50000
Lanthanum	0.03	0.56	0.04	0.05	0.01	0.07	5.37	5.83	22.8	15.4	30
Lead	1.2	4.1	1.6	2.0	0.5	0.5	17	13	17	12	13
Lutetium	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.07	0.06	0.55	0.22	0.5
Manganese	145	167	42	43	126	140	116	52	659	232	950
Mercury	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.4	<0.1	<0.1	<0.1	0.08
Neodymium	0.03	0.45	0.03	0.05	0.02	0.07	4.52	4.82	24.0	15.9	28
Nickel	47	76	<2	<2	19	20	62	1	17	11	75
Praseodymium	< 0.01	0.12	< 0.01	0.01	< 0.01	0.02	1.23	1.39	6.33	4.26	8.2
Samarium	< 0.01	0.11	< 0.01	<0.01	< 0.01	0.02	0.96	1.00	5.90	3.55	6
Selenium	<1	<1	<1	<1	<1	<1	0.8	0.5	3.9	1.9	0.05
Strontium	404	411	141	140	367	371	63.2	8.5	54.9	36.9	375
Tantalum	<2	22	<2	<2	<2	3.15	<0.5	<0.5	<0.5	<0.5	2
Thulium	<0.01	0.02	<0.01	<0.01	< 0.01	<0.01	0.08	0.07	0.62	0.27	0.5
Tin	2	9	1	1	2	4	37	8	3	2	2
Vanadium	4.5	10.3	2.8	2.7	8.2	8.3	27.9	6.6	41.2	33.8	135
Yttrium	<20	<20	<20	<20	<20	<20	8	7	49	21	33
Zinc	35	166	26	27	11	13	323	61	46	32	70

Table 5: Concentrations of metals and metalloids in filtered (filt.) and whole (wh.) wastewater samples ([g/l]), and in sediment samples (mg/kg dry weight), \*together with reported average concentrations for the Earth's continental crust (Krauskopf & Bird 1994).

## **3.2 Siemens/ Flextronics**

## 3.2.1 Organic contaminants

For the sample of wastewater from the channel that receives inputs from Siemens and Flextronics (MX16002), 29 organic chemicals were isolated (28 semi volatile compounds and 1 volatile organic compound), of which 7 could be identified. These included three organophosphate compounds, a decynediol derivative and the phthalate ester diethyl phthalate (DEP).

The three organophosphate esters identified were all triarylphosphates, namely triphenyl phosphate (TPP), which was also identified in the wastewater associated with Sanmina SCI (MX16001), as well as tris(2-butoxyethyl) phosphate (TBEP) and tris(1-chloro-2-propyl) phosphate. TBEP and tris(1-chloro-2-propyl) phosphate are known to be used as flame retardants. They are not readily biodegraded under conventional wastewater treatment, and can cause impacts on aquatic organisms at relatively low concentrations. For more information on these organophosphate esters, see Box B.

The decynediol derivative was 2,4,7,9-tetramethyl-5-decyne-4,7-diol, also known as TMDD, which is produced and used in large quantities, primarily as an industrial defoaming surfactant under the trade name Surfynol 104 (NZ 2016). TMDD has been found to be toxic to aquatic organisms in laboratory experiments on fish (fathead minnows), aquatic invertebrates (*Daphnia magna*), and green algae (*Selenastrum capricornutum*) (NZ EPA 2016).

Separately, the quantification of PFCs in the wastewater (MX16002) detected five compounds. The predominant compound was perfluorooctanoic acid (PFOA, 82.6 ng/l), with four other PFCs at concentrations between 13.5-26.6 ng/l, namely PFBA, PFPA, PFHxA, and PFDA. The concentrations in the samples were somewhat higher than concentration commonly reported in surface waters (Eschauzier *et al.* 2011, Heydebreck *et al.* 2015), though are within the ranges reported in municipal waste water treatment plant effluents (eg, Ahrens *et al.* 2009, Schultz *et al.* 2006). These data may indicate uses of PFCs within one or both of these facilities, though notably higher concentrations of PFCs have been reported in other industrial effluents.

A number of additional organic chemicals were identified in the sediment sample collected from this sample location (MX16005), which are likely to have arisen from their presence in historic discharged wastewater, or within ongoing periodic discharges at other times. These included four phthalates, nonylphenol, and two photoinitiator related chemicals, as well as other chemicals likely to have arisen from sewage inputs or of plant origin.

The four phthalates identified included DEHP, which was also identified in the wastewater, together with di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP) and di-isononyl phthalate (DINP), as well as the related chemical di(2-ethylhexyl) terephthalate (DEHT). DBP and DEHT are discussed above in section 3.1. BBP has been reported to exert reproductive toxicity (Ema & Miyawaki 2002, Aso *et al.* 2005), and within the European Union BBP has been listed as a Substance of Very High Concern (SVHC) under the EU REACH Regulation (ECHA 2013). DINP is of concern because of observed effects on the liver and kidney, albeit at higher doses, and DINP has also been found to exhibit anti-androgenic effects on reproductive toxicant within the EU (Denmark 2015). See Box A for more information.

Nonylphenol, of which 5 isomers were identified, is a well-known toxic and persistent environmental contaminant. Additional information on nonylphenol, which was also identified in sediment associated with the Sanmina SCI facility (MX16004), is given in Section 3.1 and in Box C.

#### Box C. Alkyl phenols (AP); Nonylphenol (NP) and Octylphenol (OP)

Nonylphenol (NP) is a group of related (isomeric) chemicals that are manufactured primarily for use in producing nonylphenol ethoxylates (NPEs), a group of non-ionic surfactants. NP is also used directly for a range of specialised industrial uses. NPEs are the most widely used type of a broader group of substances known as alkylphenol ethoxylates (APEs). Similarly, the APE octylphenol (OP) has direct uses but is also used to manufacture octylphenol ethoxylates (OPEs).

NPEs and OPEs have been used as surfactants, emulsifiers, dispersants and/or wetting agents in a variety of industrial and consumer applications. Assessments in the early 2000s noted that the largest share were then used in industrial and institutional cleaning products (detergents), with smaller amounts used as emulsifiers, textile and leather finishers, and as components of pesticides and other agricultural products, and water-based paints (OSPAR 2004, Guenther et al 2002).

Once released to the environment, APEs can degrade back to the parent alkylphenol (e.g. NP or OP), which are persistent, bio-accumulative, and toxic to aquatic life. APs, especially NP, are widely distributed in fresh and marine waters, and – in particular – sediments, in which persistent APs tend to accumulate (Ying *et al.* 2002, Jonkers *et al.* 2005, David *et al.* 2009, Shue *et al.* 2010). Because of their releases to water, APEs and APs are also common components of sewage effluents and sludge (Micic & Hofmann 2009, Ying et al 2009, Yu et al 2009), including that applied to land. NP has been detected in rain and snow in Europe (Fries & Püttmann 2004, Peters *et al.* 2008), and residues of both NP and OP have been reported as contaminants in house dust (Butte & Heinzow 2002, Rudel *et al.* 2003) and indoor air (Rudel *et al.* 2003, Saito *et al.* 2004).

Research into levels in wildlife remains limited, although there have been reports of significant levels in both invertebrates and fish in the vicinity of sites of manufacture and/or use of APEs, and close to sewer outfalls (Lye *et al.* 1999, Rice *et al.* 2003, Mayer *et al.* 2008). Both NP and OP are known to accumulate in the tissues of fish and other organisms, and have been found as common contaminants of seafood in some locations (OSPAR 2004, Basheer *et al.* 2004, Brigden *et al.* 2010b). NPs have also been reported as contaminants in human tissues (Lopez-Espinosa *et al.* 2009).

The most widely recognised hazard associated with APs (both NP and OP) is their estrogenic activity, i.e. their ability to mimic natural estrogen hormones. This can lead to altered sexual development in some organisms, most notably the feminisation of fish (Jobling *et al.* 1995, 1996). Atienzar *et al.* (2002) described direct effects of NP on DNA structure and function in barnacle larvae, a mechanism that may be responsible for the hormone disruption effects seen in whole organisms. In rodents, exposure to OP caused adverse effects on male and female reproductive systems, including lower sperm production and increased sperm abnormalities (Blake *et al.* 2004). Chitra *et al.* (2002) and Adeoya-Osiguwa *et al.* (2003) describe effects on mammalian sperm function, while DNA damage in human lymphocytes has also been documented (Harreus *et al.* 2002), although some have challenged the significance of these findings. Impacts on immune system cells in vitro have also been described (Iwata *et al.* 2004). NP is classified under the GHS for classification and labelling of chemicals as 'toxic to reproduction, category 2' (H361FD), and both NP and OP are classified as very toxic to aquatic life, with the potential for long-lasting effects (H400, H410).

In Mexico, the manufacture, use and release of NP and NPEs, and the related OP/OPEs are not currently regulated. Outside Mexico, regulations addressing the manufacture, use and release of NP and NPEs, together with certain other APE/APs, do exist in some regions. More than 15 years ago, the Ministerial Meeting under the OSPAR Convention agreed on the target of cessation of discharges, emissions and losses of hazardous substances to the marine environment of the north-east Atlantic by 2020, and included NP/NPEs on the first list of chemicals for priority action towards this target (OSPAR 1998). Subsequently, in 2000, OP was also listed under this category (OSPAR 2006). Since then, NP has been included as a "priority hazardous substance" under the EU Water Framework Directive, such that action to prevent releases to water will be required throughout Europe within 20 years of adoption of the regulation (EU 2001). OP has been designated as a "priority substance" under the Water Framework Directive. Even before their listing under this Directive, however, the widely recognised environmental hazards presented by NP and OP and their ethoxylates have led to some long-standing restrictions on their use in many countries. Among these, a Recommendation agreed by the Paris Commission (now part of the OSPAR Commission) in 1992, required the phase-out of NPEs from domestic cleaning agents by 1995 and industrial cleaning agents by the year 2000 (PARCOM 1992). Furthermore, since January 2005 within the EU, products (formulations used by industry) containing greater than 0.1% NP or NPEs may no longer be placed on the market within Europe, with some minor exceptions principally for "closed loop" industrial systems (EU 2003). In addition, both NP and NPEs have been listed as Substances of Very High Concern (SVHC) under the EU REACH Regulation (ECHA 2013).

The two photoinitiator related chemicals identified were 2-isopropylthioxanthone (Quantacure ITX) and 2,6-di-tert-butylbenzoquinone (DBQ). Photoinitiators are additives that use ultraviolet (UV) or visible light to induce polymerisation, or to cure materials, for example in coatings and inks. Photoinitiators have extensive applications in the manufacture of printed circuits, encapsulation of electronic components, decorative coating, surface coating, etc. Photoinitiators are sold under various trade names including Quantacure, Irgacure, Darocure, Photocure, Vicure and others.

Quantacure ITX has been widely used as a photoinitiator in inks in the flexographic printing industry (USEPA 2002). There is little information available on the properties of this chemical, though it has been shown that thioxanthone-based compounds, including isomers of isopropylthioxanthone, are known to be of high aquatic hazard and capable of causing long-term effects in aquatic organisms even at relatively low concentrations of less than 0.1 mg/l (USEPA 2002). Thioxanthones, the chemical group to which Quantacure ITX belongs, are often used in conjunction with other photoinitiators to design cost effective synergistic photoinitiator blends (Cho *et al.* 2003, Segurola *et al.* 1999, Andersen *et al.* 1996).

Benzoquinone derivatives, including DBQ, can be used as photoinitiators 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-ditert-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).

In addition, chemicals were identified in the sediment that can arise from their presence in petroleum products, or be generated as products of incomplete combustion. These were the polycyclic aromatic hydrocarbons (PAHs) fluoranthene, naphthalene and pyrene (Overton 1994). Other chemicals included those commonly found in sewage, including squalene and cholesterol derivatives, as well as some chemicals of plant origin.

## 3.2.2 Metals

The wastewater from the channel into which discharges from the Siemens facility and the Flextronics facility are discharged (MX16002), and sediment from the same location (MX16004), did not contain any of the quantified metals/metalloids at concentrations above levels typically found in uncontaminated surface freshwater & associated sediments.

## 3.3 El Ahogado WWTP

## 3.3.1 Organic contaminants

Compared to the other wastewater samples, a greater number of organic chemicals were isolated from the wastewater collected from the El Ahogado WWTP wastewater outfall, as it discharges to the El Ahogado River (MX16003). 101 compounds were isolated, of which 56 were identified, consisting of a wide range of different chemical groups.

Key substances amongst these included nonylphenol and octylphenol, four phthalates, three phosphate esters, bisphenol-A, two chlorinated chemicals and a number of petroleum derived chemicals (alkyl benzenes and a PAH). Other chemicals detected included diphenyl ether,

tributylamine and indole, as well as chemicals likely to have arisen from sewage inputs or of plant origin.

Eight isomers of the persistent environmental contaminant nonylphenol were identified, together with a single isomer of octylphenol. Nonylphenol was also identified in sediment associated with the Sanmina SCI facility (MX16004) and that associated with the Siemens/ Flextronics facilities (MX16005), and is discussed in section 3.1 and Box C. Octylphenol is a closely related chemical with similar hazardous properties (See Box C).

The phthalates identified were DBP, DiBP, DEP & dimethyl phthalate (DMP). For information on these see sections above and Box A.

The three phosphate esters were triphenyl phosphate (TPP) and tris(2-butoxyethyl) phosphate (TBEP), both of which were also identified in the wastewater from Siemens/ Flextronics wastewater (MX16002) and discussed in Section 3.2, together with phenyl phosphate, which is an irritant but of lesser concern.

Bisphenol-A (BPA) is a high production chemical predominantly used in the manufacture of polycarbonate plastic and epoxy resins, including for use in components in electronic equipment (Huang *et al.* 2012, Michałowicz 2014). BPA is an endocrine disrupting chemical that can cause adverse effects on reproduction in animals (Oehlmann *et al.* 2009) and is suspected of being detrimental to reproduction and development in humans (Rubin & Soto 2009, Michałowicz 2014). For more information see Box D.

Amongst the other chemicals detected, tributylamine is used in a wide variety of industrial processes and has been classified under GHS as toxic to aquatic life (H401) and toxic in contact with skin (H311). Diphenyl ether has industrial uses, including as a heat transfer fluid, and has been classified under GHS as toxic to aquatic life with long lasting effects (H411). Indole has various industrial uses, but is also used as a fragrance chemical (Sullivan & Gad 2014). It has been classified under GHS as harmful if swallowed (H302), toxic in contact with skin (H311) and very toxic to aquatic life (H400).

As discussed above, alkyl benzenes and PAHs may be present due to their presence in crude oil and petroleum products, though alkylbenzenes are also produced following the degradation of the linear alkylbenzene sulphonate (LAS) detergents, and have been used as markers of sewage pollution (Chalaux *et al.* 1995, Overton 1994, Preston & Raymundo 1993).

The two chlorinated chemicals were dichlorobenzene (See Section 3.1) and chlorocresol, the latter of which is used as a preservative in skin ointments (Gómez de la Fuente *et al.* 2013), and so may arise from sewage inputs. Other chemicals identified, and which are commonly found in sewage, included squalene, the two synthetic musks Galaxolide and Versalide (Homem *et al.* 2015), and a benzophenone derivative (oxybenzone), which is used as UV stabiliser in sunscreens/cosmetics (Garcia *et al.* 2011).

The only PFC detected in the wastewater (MX16003) was perfluorooctanoic acid (PFOA) at a trace concentration (12.7 ng/l, 0.012  $\mu$ g/l). As noted above, the concentration of PFOA in this sample is with the range commonly reported in surface waters in several parts of the world (Ahrens 2011, Loos *et al.* 2009, Jin *et al.* 2009, So *et al.* 2007). This presence of this relatively low concentration of PFOA, and the fact that all other quantified PFCs were below detection limits, means that we have no strong evidence for specific use of PFCs within facilities that discharge their wastewater for treatment at this WWTP.

#### Box D. Bisphenol A (BPA)

Bisphenol A (BPA) is a very high production volume chemical (one of the highest global production volumes of any man-made chemical), manufactured globally for a variety of uses, which are dominated by the manufacture of polycarbonate plastic and various epoxy resins and including widespread use in food-contact applications (Michałowicz 2014). Despite its polymeric form, repeated use and wear of polycarbonate plastics, especially at high temperatures, can result in significant hydrolysis of the plastic, releasing free bisphenol A (Brede *et al.* 2003, Kubwabo *et al.* 2009). As a result of the widespread use of polycarbonate and other bisphenol A-derivatives, human exposure to bisphenol A is ubiquitous (Michałowicz 2014). The US Centre for Disease Control (CDC) reported detectable 'conjugated' residues of BPA in 93% of human urine samples (Calafat *et al.* 2008). Furthermore, its occurrence in more biologically-active 'unconjugated' form in human blood also appears to be common, at levels which are thought already to exceed the presumed 'safe daily exposure' dose (Vandenberg *et al.* 2007), challenging long-held assumptions that BPA is rapidly metabolized and, therefore, detoxified in the human body.

Bisphenol A was recognized as a potent synthetic oestrogen (and therefore potential endocrine disruptor) as long ago as the 1930s, well before the polymerization to epoxies and polycarbonate became commercially significant (Dodds 1936). Observed impacts of low dose BPA exposure in animals include decreased daily sperm production in rats (Sakaue et al. 2001), changes in maternal behaviour in mice (Palanza et al. 2002) and anomalous brain development in both rodents and primates (MacLusky et al. 2005, Leranth et al. 2007, 2008), themselves linked to aspects of sexual differentiation. Soto et al. (2008) summarise evidence for low dose BPA effects on the development of reproductive organs in rodents. Low dose exposure has also recently been found to interfere with insulin secretion in mice (Ropero et al. 2008), raising the concern that BPA exposure could be a contributory factor in the rise in type 2 diabetes in some parts of the world. Associations have also been reported between BPA levels in urine and the prevalence of certain other common medical conditions in humans in the US (Lang et al. 2008). Other useful reviews of the mammalian toxicology of BPA are provided by Wellshons et al. (2006) and Crain et al. (2007), and, more recently, Michałowicz (2014) recently reviewed sources, toxicity and biotransformation of bisphenol-A. Another recent review concluded that, based on emerging research since 2007, BPA should be classified as a reproductive toxicant on the basis that can impact on female reproduction and has the potential to affect male reproductive systems in animals and possibly in humans (Peretz et al. 2014). Other recent studies indicate that BPA could impair the immune system of foetuses and young children at lower exposure levels than previously considered (Menard et al. 2014a & b, RIVM 2015).

Bisphenol A is also of great concern in the aquatic environment, to which it is estimated around 90% of emissions to the environment primarily occur (whether from industrial operations, discharges via sewers or leachates from landfills and waste dumps). BPA is widely distributed in freshwater systems (Fromme et al. 2002, Rodriguez-Mazaz et al. 2004, RIVM 2015), at concentrations which, though generally low away from industrial point sources, are nonetheless toxicologically relevant to a range of aquatic organisms, including through mechanisms of endocrine disruption (Kang et al. 2007, RIVM 2014, 2015). Although degradation of the parent compound can occur quite rapidly under aerobic conditions, some of its partial breakdown products are more environmentally persistent and can themselves show some oestrogenic activity (Suzuki et al. 2004). Furthermore, under conditions of low oxygen tension, including in sediments, degradation of BPA is considerably slower, allowing the compound to accumulate to higher levels (Planelló et al. 2008). Endocrine disrupting effects of BPA, often at environmentally relevant concentrations, have been reported in reptiles (Stoker et al. 2003), amphibians (Levy et al. 2004) and fish (Sohoni et al. 2001, Jurgella et al. 2006), as well as in molluscs (Oehlmann et al. 2006) and a range of other invertebrates (see Segner et al. 2003, Michałowicz 2014 and RIVM 2015 for review). In the sediment-dwelling larvae of chironomid flies, for example (a keystone species in many aquatic systems), BPA interferes with the hormone ecdysone, which controls moulting and structural development (Planelló et al. 2008), indicating that impacts on steroid hormone systems may be common across much of the animal kingdom.

In recent years a number of regulatory measured have been introduced or proposed. Canada was the first country to introduce controls on the use of BPA in consumer goods (Health Canada 2009), in response to the concerns relating to human exposure to BPA through use of polycarbonate products, though other have now followed this example. Within the EU, BPA has recently been classified as toxic for reproduction (category 1B) (EU 2016). As a result of the recent reports by the Dutch National Institute for Public Health and the Environment (RIVM 2104, 2015), the European Food Safety Authority (EFSA) has announced that it will reassess the hazards of BPA (EFSA 2016). In addition, France has proposed BPA as a substance of very high concern (SVHC) under the EU REACH regulations due to its reproductive toxicity (ECHA 2016) and there have also been calls for a total ban on BPA in all food contact materials within the EU (Häusling 2016).

A similar range of chemicals was identified in each of the two sediment samples; the sediment collected from within the discharge pipe at its outfall to the El Ahogado River (MX16006) and the sediment collected from the El Ahogado River itself (MX16007), immediately downstream from the outfall.

Amongst the chemicals detected in these two sediment samples were examples that were also identified in the wastewater from the El Ahogado WWTP (MX16003), including two phthalates (DEHP and DBP).

Overall, the chemicals identified in both sediment samples were dominated by aliphatic hydrocarbons, as well as long chain fatty acids and their derivatives. As in the case of the wastewater, chemicals likely to have arisen from sewage inputs or of natural origin were also identified in both sediment samples. As discussed in section 3.1, the occurrence of aliphatic hydrocarbons in the environment often arises from their presence in petroleum products, while long chain fatty acids and their derivatives can originate from natural sources, though some are used in a variety of manufacturing processes.

## 3.3.2 Metals

The wastewater from the El Ahogado WWTP (MX16003) did not contain any of the quantified metals/metalloids at concentrations above levels typically found in uncontaminated surface freshwater.

The sediment collected within the WWTP discharge pipe (MX16006) and that collected from El Ahogado River immediately downstream of the WWTP discharge pipe (MX16007) did not contain notable concentrations of metals, with the possible exception of barium and beryllium and selenium which were present at concentrations slightly elevated over levels typically found in freshwater sediments.

## Conclusions

The results of this study demonstrate the complexity of industrial wastewater discharges from parts of the electronics manufacturing sector. These discharges are acting as point sources of a number of chemicals of clear concern for the environment and human health.

The complexity of the wastewaters was illustrated by the presence of a broad range of organic chemical contaminants in the samples collected and analysed in this study. For both the wastewater samples, that collected close to the Sanmina SCI facility, and that from a channel which receives wastewater from both Siemens and Flextronics, only a relative small fraction of the isolated chemicals could be reliably identified; 10% for the wastewater associated with Sanmina SCI, and 25% for the Siemens / Flextronics wastewater. The identity and properties of the unidentifiable chemicals remain unknown.

Some of the chemicals identified in wastewaters from both these locations are known to be used by the electronics manufacturing sector. Due to the locations from which the latter sample was collected, however, it is not possible to know whether each of the chemicals identified arose from the Siemens or from the Flextronics facility (or both). Similarly, without confirmation that the wastewater collected from a sump close to the Sanmina SCI facility did originate from that facility, it is clearly not possible to determine whether the chemicals identified also arose from the Sanmina SCI facility.

A greater number, and even broader range, of organic chemicals were identified in the treated wastewater from the El Ahogado Wastewater treatment plant (WWTP), which may reflect the multiple sources that send their wastewaters to this facility for treatment.

For all three locations, but especially for the Sanmina SCI and Siemens / Flextronics outfalls, additional organic chemicals were identified in the sediment sample which were not found in the wastewater sample collected from the same location. The presence of these chemicals in sediment, but not in the associated wastewater, indicates their less frequent or perhaps historic discharge within wastewaters at each location.

For some of the chemical pollutants identified in either wastewater samples or associated sediments (especially nonylphenol and octylphenol), the use of conventional wastewater treatment is unable to address effectively their presence within wastewaters. At best such treatment can scavenge persistent substances into treatment plant sludges, thereby creating an additional contaminated waste stream.

Taken together, the results from this study indicate that parts of the electronics manufacturing sector act as point sources of hazardous chemicals to the wider environment via the discharge of wastewaters.

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## **Appendix 1: Details of methodologies**

## Analysis for Volatile Organic Compounds (VOCs)

### Methods

VOCs were analysed using an Agilent 7890B gas chromatograph with a Restek Rxi-624Sil column (30m, 0.25mm ID, 1.4µm film thickness) connected to an Agilent 7697A Headspace Sampler and linked to an Agilent 5977A MSD operated in EI mode. The GC oven temperature program included an initial temperature of 43°C (held for 4min), rising to 55°C at 5°C/min, and then to 210°C at 15°C/min (held for 2.5min). The carrier gas was helium, supplied at 1.5 ml/min. From each sample, a 10ml portions was sub-sampled into a 20ml headspace vial with 3g of anhydrous sodium sulfate (analytical reagent grade). It 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. At the same time, the sample was also analysed with the GC-MS in selective ion monitoring (SIM) mode to match against those obtained during GC-MS analysis of standard mixtures containing a range of aromatic volatile organic compounds and haloalkanes volatile organic compounds.

## **Quality control**

A blank of laboratory air capped at the time that sub-sampling had taken place was also analysed, alongside a sample of the ultra-pure reagent water with the same amount of anhydrous sodium sulfate added. Any background contaminants detected in blanks are subtracted from the chromatograms obtained for the samples before mass spectra are interpreted.

#### Analysis for extractable organic compounds

#### Preparation

For water samples, 20 µg of deuterated naphthalene was added as an Internal Standard (IS) to each portion of sample that was subject to extraction. Water samples (400ml) 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 solid samples, approximately 10 g of each sample (wet weight) was extracted employing an Accelerated Solvent Extraction (ASE) technique, using a Dionex ASE-350, with a mixture of pentane and acetone in a ratio of 3:1, and at a temperature of 100oC. 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 7890B GC with Restek Rxi-17Sil column (30m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5977A 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 40°C, raised to 260°C at 10°C/min, then to 295°C at 50°C/min (held for 15 min), and finally to 320°C at 50°C/min (held for 12 min). The carrier gas was helium, supplied at 1ml/min. Identification of compounds was carried out by matching spectra against both the Wiley 10N11 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

#### Preparation

Water samples: 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. 25 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  $180^{\circ}$ C over 15 minutes followed by holding at  $180^{\circ}$ C for a further 15 minutes. Cooled digests were filtered and made up to 25 ml with deionised water.

Sediment samples: A representative portion of each sample was dried at 30°C to constant weight, homogenised, and then ground to a powder using a pestle and mortar. Approximately 0.25 g of the dried and ground sample was digested with 1 ml concentrated hydrochloric acid and 4 ml concentrated nitric acid, firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 180°C over 20 minutes followed by holding at 180°C for a further 20 minutes. Following cooling, the digest was filtered and made up to 25 ml with deionised water.

## Analysis

Prepared sample digests were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using an Agilent 7900 Spectrometer utilizing a collision cell with helium as the collision gas to minimize polyatomic interferences. Multi-element standards, matrix matched to the samples, at concentrations of 1, 10, 100 and 1000  $\mu$ g/l respectively, other than for mercury (0.5, 5, 50  $\mu$ g/l respectively) were used for instrument calibration. Analysis employed in-line addition of an internal standard mix at 1000  $\mu$ g/l (Scandium, Germanium, Yttrium, Indium and Terbium).

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  $\mu$ g/l respectively. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

## **Quality control**

One water sample and one sediment sample were prepared for ICP analysis in duplicate and analysed to verify method reproducibility, along with a blank sample for both water and sediment procedures. For water samples, two mixed metal quality control solution of 80 and 800  $\mu$ g/l for each metal, other than mercury at 4 and 16  $\mu$ g/l, were digested and analysed. For sediment samples, two certified reference material (CRM) sample was prepared in an identical manner; GBW07311, stream sediment certified by the China National Analysis Centre for Iron and Steel, Beijing, China; and LGC6187, leachable metals in river sediment certified by the Laboratory of the Government Chemist, UK. All control samples were prepared in an identical manor to the samples.

Calibration of the ICP-MS was validated by the use of quality control standards at 80  $\mu$ g/l and 800  $\mu$ g/l (4  $\mu$ g/l and 16  $\mu$ g/l for mercury) prepared in an identical manner but from different reagent stocks to the instrument calibration standards.

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

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

## Appendix 2: Detailed organic analytical screening data

Detailed screening data arising from GC-MS analysis of each of the samples are presented below. These data list those semi-volatile organic compounds identified following solvent extraction, and for wastewater samples also included volatile organic compounds (VOCs) identified through separate headspace GC-MS analysis of sub-samples. Only those substances identified to greater than 90% quality match (following verification by expert interpretation) are listed here.





## Number of semi-volatile compounds isolated: 30

## Compounds identified to better than 90%: 3

CAS#	Name
000084-66-2	Diethyl phthalate (DEP)
000084-74-2	Di-n-butyl phthalate (DBP)
000115-86-6	Triphenyl phosphate (TPP)

## Number of volatile organic compounds (VOCs) isolated: 21

CAS#	Name
000075-15-0	Carbon disulfide
000067-66-3	Chloroform
000000-00-0	Octene, dimethyl-
000080-56-8	2-Pinene
000079-92-5	Camphene
00000-00-0	7-Oxabicyclo[2.2.1]heptane, 1-iso
000138-86-3	Cyclohexene, 1-methyl-4-(1-methyethenyl)-
000000-00-0	Benzene, 1-methyl-1-methylethyl

 000541-73-1
 Benzene, 1,4-dichloro 

 000470-82-6
 Eucalyptol (Cineole)

 000000-00-0
 fenchol

 000000-00-0
 Neomenthol

 000098-55-5
 .alpha.-Terpineol

## MX16002



## Number of semi-volatile compounds isolated: 28

## Compounds identified to better than 90%: 7

CAS#	Name
000065-85-0	Benzoic acid
000126-86-3	2,4,7,9-Tetramethyl-5-decyne-4,7-diol (Surfynol 104H)
000084-66-2	Diethyl phthalate (DEP)
000615-22-5	Benzothiazole, 2-(methylthio)-
013674-84-5	2-Propanol, 1-chloro-, phosphate (3:1) (Hostaflam OP 820)
000078-51-3	Tris(2-butoxyethyl) phosphate
000115-86-6	Triphenyl phosphate (TPP)

## Number of volatile organic compounds (VOCs) isolated: 1



## Number of semi-volatile compounds isolated: 101

CAS#	Name
00000-00-0	<i>p</i> -Menthane, 1,8-epoxy- (Eucalyptol)
00000-00-0	limonene or bornylene
000104-76-7	1-Hexanol, 2-ethyl-
00000-00-0	m-/o-/p-Cymene
018479-58-8	7-Octen-2-ol, 2,6-dimethyl-
00000-00-0	Benzene, dichloro-
00000-00-0	.alphaterpinolene or isoterpimolene
000102-82-9	Tributylamine
000078-70-6	1,6-Octadien-3-ol, 3,7-dimethyl- (Linalol)
0001632-73-1	fenchol
00000-00-0	Cresol (2 isomers)
00000-00-0	Cresol, chloro-
000138-87-4	Cyclohexanol, 1-methyl-4-(1-methylethenyl)- (p-Menth-8-en-1-ol)
00000-00-0	Menthol
00000-00-0	Borneol or isoborneol
00000-00-0	Camphor
00000-00-0	Terpineol (2-isomers)
000098-52-2	4-tert-Butylcyclohexanol
00000-00-0	Bornyl acetate
000334-48-5	n-Decanoic acid
000089-83-8	Phenol, 5-methyl-2-(1-methylethyl)- (Thymol)
037275-49-3	4,7-Methano-1H-indenol, hexahydro-
014888-58-5	4,7-Methano-5H-inden-5-one, 3,3a,4,6,7,7a-hexahydro-
000120-72-9	1H-indole
000101-84-8	Diphenyl ether
000143-07-7	Dodecanoic acid
00000-00-0	1H-Indole, methyl-
000093-04-9	Naphthalene, 2-methoxy-
000131-11-3	Dimethyl phtalate (DMP)
00000-00-0	4-Methylindoline or Oxindole or o-Tolyl isocyanate

- 000544-63-8 Tetradecanoic acid
- 024851-98-7 Methyl (3-oxo-2-pentylcyclopentyl) acetate
- 000084-66-2 Diethyl phthalate (DEP)
- 000057-10-3 Hexadecanoic acid
- 000000-00-0 Galaxolide (2 products)
- 000084-74-2 Di-n-butyl phthalate (DBP)
- 000131-57-7 Oxybenzone
- 000078-51-3 Tri(2-butoxyethyl) phosphate
- 000080-05-7 Phenol, 4,4'-(1-methylethylidene)bis- (Bisphenol-A)
- 000111-02-4 Squalene
- 000115-86-6 Phenyl phosphate
- 000000-00-0 Nonylphenol (8 isomers)
- 001806-26-4 Octylphenol
- 000084-69-5 Diisobutyl phthalate (DiBP)
- 000127-51-5 Cetone alpha

## Number of volatile organic compounds (VOCs) isolated: 4

## Compounds identified to better than 90%: 4

CAS#	Name
000075-09-2	Methane, dichloro-
000075-27-4	Chloroform
000075-27-4	Methane, bromodichloro-
000106-46-7	Benzene, 1,4-dichloro-





#### Number of semi-volatile compounds isolated: 225

CAS#	Name
017829-53-7	.alphaBergamotene
000495-61-4	.betaBisabolene
007616-22-0	.gammaTocopherol

000117-81-7 1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester 000084-74-2 1,2-Benzenedicarboxylic acid, dibutyl ester 000084-69-5 1,2-Benzenedicarboxylic acid, diisobutyl ester 1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-000099-85-4 003452-07-1 1-Eicosene 000506-52-5 1-Hexacosanol 1-Octadecanethiol 002885-00-9 000112-88-9 1-Octadecene 000112-72-1 1-Tetradecanol 000120-72-9 1H-Indole 000614-96-0 1H-Indole, 5-methyl-2-Heptadecanone 002922-51-2 002345-28-0 2-Pentadecanone 000000-00-0 S-Methylcholesterol 000119-13-1 2H-1-Benzopyran-6-ol, 3,4-dihydro-013466-78-9 3-Carene 034303-81-6 3-Hexadecene, (z)-035507-09-6 7-Hexadecene, (z)-000469-38-5 9,19-Cyclolanost-24-en-3-ol, (3.beta.)-000112-80-1 9-Octadecenoic acid (z)-022393-85-7 9-Octadecenoic acid (z)-, tetradecyl ester 000120-12-7 Anthracene 004537-15-9 Benzene, (1-butylheptyl)-002719-63-3 Benzene, (1-butyloctyl)-004536-86-1 Benzene, (1-propyloctyl)-000101-84-8 Benzene, 1,1'-oxybis-000106-46-7 Benzene, 1,4-dichloro-000099-87-6 Benzene, 1-methyl-4-(1-methylethyl)-000934-80-5 Benzene, 4-ethyl-1,2-dimethyl-001077-16-3 Benzene, hexyl-000538-68-1 Benzene, pentyl-Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, octadecyl ester 002082-79-3 000076-49-3 Bicyclo[2.2.1]heptan-2-ol, 1,7,7-trimethyl-, acetate, endo-006422-86-2 Bis(2-ethylhexyl) terephthalate 000128-37-0 Butylated hydroxytoluene 000087-44-5 Caryophyllene 028338-69-4 Cholest-3-ene, (5.alpha.)-7 000747-90-0 Cholesta-3,5-diene 000080-97-7 Cholestanol 000057-88-5 Cholesterol 000294-62-2 Cyclododecane 000295-65-8 Cyclohexadecane 000586-62-9 Cyclohexene, 1-methyl-4-(1-methylethylidene)-000295-17-0 Cyclotetradecane 005989-27-5 d-Limonene 000080-97-7 Dihydrocholesterol 000629-97-0 Docosane 000112-40-3 Dodecane Dodecane, 2,6,11-trimethyl-031295-56-4 061141-72-8 Dodecane, 4,6-dimethyl-003658-44-4 Dodecanoic acid, undecyl ester

- 000544-85-4 Dotriacontane
- 055527-92-9 Ergost-22-en-3-ol, (3.alpha.,5.beta.)-
- 000000-00-0 Farnesol isomer A
- 001222-05-5 Galaxolide, 2 isomers
- 000629-94-7 Heneicosane
- 000630-04-6 Hentriacontane
- 000593-49-7 Heptacosane
- 000629-78-7 Heptadecane
- 000630-01-3 Hexacosane
- 000544-76-3 Hexadecane
- 002598-99-4 Hexadecanoic acid, octadecyl ester
- 000060-33-3 Linoleic acid
- 000475-20-7 Longifolene
- 001490-04-6 Menthol
- 000630-03-5 Nonacosane
- 000629-92-5 Nonadecane
- 000630-02-4 Octacosane
- 000593-45-3 Octadecane
- 002778-96-3 Octadecanoic acid, octadecyl ester
- 000629-99-2 Pentacosane
- 000629-62-9 Pentadecane
- 000108-95-2 Phenol
- 000106-44-5 Phenol, 4-methyl-
- 084852-15-3 Phenol, nonyl-, mix of 13 isomers
- 054411-87-9 Pregn-20-en-3-ol, 20-methyl-, (3.beta.,5.alpha.)-
- 000111-02-4 Squalene
- 019466-47-8 Stigmastanol
- 000646-31-1 Tetracosane
- 000629-59-4 Tetradecane
- 025117-24-2 Tetradecane, 4-methyl-
- 000638-68-6 Triacontane
- 000638-67-5 Tricosane
- 000629-50-5 Tridecane
- 000630-05-7 Tritriacontane
- 001120-21-4 Undecane

## <u>MX16005</u>





## Number of semi-volatile compounds isolated: 96

## Compounds identified to better than 90%: 28

CAS#	Name
000495-61-4	.betaBisabolene
013877-93-5	.betaCaryophyllene
000117-81-7	Bis(2-ethylhexyl)phthalate (DEHP)
000084-74-2	Di-n-butyl phthalate (DBP)
000085-68-7	Benzylbutyl phthalate (BBP)
028553-12-0	
071549-78-5	Di-i-nonyl phthalate (DiNP), mixture of 15 isomers
014103-61-8	-
068515-48-0	
006422-86-2	Bis(2-ethylhexyl) terephthalate
018435-45-5	1-Nonadecene
006971-40-0	17-Pentatriacontene
000719-22-2	2,6-Di-tert-butylbenzoquinone
000141-79-7	3-Penten-2-one, 4-methyl-
000080-97-7	5.alphaCholestan-3.betaol
036441-74-4	Baccharane
000474-62-4	Campesterol
000057-88-5	Cholest-5-en-3-ol (3.beta.)-
000297-03-0	Cyclotetracosane
000206-44-0	Fluoranthene
000091-20-3	Naphthalene
000108-95-2	Phenol
000106-44-5	Phenol, 4-methyl-
084852-15-3	Phenol, nonyl-, mixture of 5 isomers
000504-20-1	Phorone
000129-00-0	Pyrene
005495-84-1	2-Isopropylthioxanthone (Quantacure ITX)
000000-00-0	Sitosterol
000111-02-4	Squalene
000083-48-7	Stigmasta-5,22-dien-3-ol

019466-47-8 Stigmastanol



## Number of semi-volatile compounds isolated: 178

CAS#	Name
000117-81-7	Bis(2-ethylhexyl)phthalate (DEHP)
000084-74-2	Di-n-butyl phthalate (DBP)
000872-05-9	1-Decene
001599-67-3	1-Docosene
002922-51-2	2-Heptadecanone
000123-42-2	2-Pentanone, 4-hydroxy-4-methyl-
000141-79-7	3-Penten-2-one, 4-methyl-
019689-18-0	4-Decene
002807-33-2	4-Nonene, 5-methyl-, (Z)-
074685-30-6	5-Eicosene, (E)-
000100-41-4	Benzene, ethyl-
000080-97-7	Cholestanol
000295-65-8	Cyclohexadecane
016631-62-2	Cyclohexene, 3-ethylidene-
016631-66-6	Cyclohexene, 4-ethylidene-
000295-17-0	Cyclotetradecane
000629-97-0	Docosane
003891-98-3	Dodecane, 2,6,10-trimethyl-
061141-72-8	Dodecane, 4,6-dimethyl-
000544-85-4	Dotriacontane
000112-95-8	Eicosane
000629-94-7	Heneicosane
000630-04-6	Hentriacontane
000593-49-7	Heptacosane
000629-78-7	Heptadecane
007225-64-1	Heptadecane, 9-octyl-
000630-01-3	Hexacosane
000544-76-3	Hexadecane
000112-61-8	Methyl stearate
000630-03-5	Nonacosane
000629-92-5	Nonadecane
000630-02-4	Octacosane
000557-61-9	Octacosanol
000593-45-3	Octadecane
000629-99-2	Pentacosane
000629-62-9	Pentadecane
000096-76-4	Phenol, 2,4-di-tert-butyl-
000504-20-1	Phorone
000083-48-7	Stigmasterol
000646-31-1	Tetracosane
000629-59-4	Tetradecane
014167-59-0	Tetratriacontane
000638-68-6	Triacontane
000638-67-5	Tricosane
001120-21-4	Undecane





### Compounds identified to better than 90%:

CAS#	Name
000084-74-2	1,2-Benzenedicarboxylic acid, dibutyl ester
000084-69-5	1,2-Benzenedicarboxylic acid, diisobutyl ester
000117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester
000112-41-4	1-Dodecene
018435-45-5	1-Nonadecene
000112-88-9	1-Octadecene
029833-69-0	1-Pentadecene, 2-methyl-
001120-36-1	1-Tetradecene
074685-30-6	5-Eicosene, (e)-
041446-61-1	6-Tetradecene, (z)-
035507-09-6	7-Hexadecene
000057-88-5	Cholest-5-en-3-ol (3.beta.)-
114174-10-6	Cholesta-5,22-dien-3-ol, 23-ethyl-
000080-97-7	Cholestanol
000295-65-8	Cyclohexadecane
000629-97-0	Docosane
055401-55-3	Docosane, 11-decyl-
000544-85-4	Dotriacontane
000112-95-8	Eicosane
000629-94-7	Heneicosane
000593-49-7	Heptacosane
000629-78-7	Heptadecane
000630-01-3	Hexacosane
000544-76-3	Hexadecane
000112-61-8	Methyl stearate

000630-03-5 Nonacosane

- 000629-92-5 Nonadecane
- 000630-02-4 Octacosane
- 000593-45-3 Octadecane
- 000629-99-2 Pentacosane
- 000629-62-9 Pentadecane
- 000096-76-4 Phenol, 2,4-bis(1,1-dimethylethyl)-
- 000150-86-7 Phytol
- 019466-47-8 Stigmastanol
- 000646-31-1 Tetracosane
- 000629-59-4 Tetradecane
- 000638-68-6 Triacontane
- 000638-67-5 Tricosane
- 000410-61-6 Z-5-nonadecene

## Appendix 3: Data for PFCs quantified in wastewater samples

Location	Sanmina SCI	Siemens/ Flextronics	El Ahogado WWTP
Sample code	MX16001	MX16002	MX16003
	(ng/l)	(ng/l)	(ng/l)
Perfluorooctane sulfonate (PFOS)	< 10,0	< 10,0	< 10,0
Perfluorooctanoate (PFOA)	< 10,0	82.6	12.7
Perfluorbutansulfonate (PFBS)	23.0	< 15,0	< 15,0
Perfluorobutanoate (PFBA)	< 10,0	17.3	< 11,5
Perfluoropentanoate (PFPA)	11.1	14.5	< 10,0
Perfluorohexane sulfonate (PFHxS)	< 15,0	< 15,0	< 15,0
Perfluorohexanoate (PFHxA)	< 10,0	26.6	< 10,0
Perfluoroheptane sulphonate (PFHpS)	< 15,0	< 15,0	< 15,0
Perfluorheptanoate (PFHpA)	< 10,0	< 10,0	< 10,0
Perfluorooctane-sulfonamide (PFOSA)	< 10,0	< 10,0	< 10,0
Perfluorononanoate (PFNA)	< 10,0	< 10,0	< 10,0
Perfluorodecane sulphonate (PFDS)	< 15,0	< 15,0	< 15,0
Perfluordecanoate (PFDA)	< 10,0	13.5	< 10,0
Perfluoroundecanoate (PFUnA)	< 10,0	< 10,0	< 10,0
Perfluorododecanoate (PFDoA)	< 10,0	< 10,0	< 10,0
Perfluorotridecanoate (PFTrA)	< 10,0	< 10,0	< 10,0
Perfluorotetradecanoate (PFTA)	< 10,0	< 10,0	< 10,0
Perfluor-3,7-dimethyloctanoate (PF-3,7-DMOA)	< 20,0	< 20,0	< 20,0
7H-Dodecafluoroheptanoate (HPFHpA)	< 20,0	< 20,0	< 20,0
1H,1H,2H,2H-Perfluoroctansulfonate (H4PFOS)	< 15,0	< 15,0	< 15,0

Table A3: Concentrations of PFCs (ng/l) quantified in wastewater samples