Analysis of wastewater and solid waste generated at a Flextronics manufacturing facility at Jalisco, Mexico for the presence of metals and organic chemical contaminants

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Introduction

A total of three samples were received from Greenpeace Mexico for analysis at the Greenpeace Research Laboratories on 4th July 2016, including two wastewater samples and one associated solid waste sample, all of which were collected on the 24th June 2016 from a Flextronics facility located in Zapopan, Jalisco, Mexico.

The two wastewater samples (MX16022 & MX16023) were collected from tanks in which wastewater was being treated. Both wastewater samples had visibly high levels of suspended solids. The solid waste sample (MX16021) was collected from a storage container in which the waste was stored following separation from wastewater. The fate of the solid waste and the treated wastewater is not known. All samples were collected from GPS location 20º44'20.9''N, 103º26'29.6''E. A summary of the samples received is provided in Table 1.

Sample code	type	Description
MX16021	solid waste	Collected from a solid waste storage container. Solid waste entering the container had been separated from wastewater in the tanks from which wastewater samples were collected
MX16022	wastewater	Viscous, black wastewater collected from a wastewater treatment tank labelled "digester". Mixing was occurring, though no apparent aeration
MX16023	wastewater	Viscous, dark brown wastewater collected from the larger wastewater treatment tank in which active aeration was occurring.

Table 1: details of wastewater and solid waste samples collected at a Flextronics facility, Zapopan, Jalisco, Mexico

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. In addition to quantification for the solid waste sample, filtered solids from one of the wastewater samples (MX16022) were separately analysed quantitatively for metals and metalloids. The solid waste sample (MX16021) was also analysed qualitatively for the presence of semi-volatile (solvent-extractable) organic compounds, as was a filtered portion of each wastewater sample. In addition, an unfiltered portion of each wastewater samples was analysed qualitatively for the presence of volatile organic compounds (VOCs).

Materials and methods

All samples were collected in pre-cleaned glass bottles and kept cold and dark during shipment to our laboratory in the UK for analysis. Each wastewater sample consisted of two subsamples collected in different types of bottles depending on the subsequent analyses to be carried out on each subsample. In both 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. The solid waste sample was collected in a 100 ml 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.

All samples were analysed qualitatively for semi-volatile organic compounds (sVOCs) and quantitatively for metals. Wastewater samples were also analysed qualitatively for volatile organic chemicals (VOCs).

Semi-volatile organic compounds were isolated from samples using solid phase extraction (SPE), eluting with ethyl acetate, pentane and toluene (for filtered wastewater samples) or using Accelerated Solvent Extraction (ASE) with a mixture of pentane and acetone (for the solid 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 a whole (unfiltered) subsample and the concentrations of dissolved forms in a filtered subsample were determined separately for each sample. Numerous metals are used in the electronics manufacturing sector, and so the analysis quantified a wide range of metals including rare earth metals. Hexavalent chromium concentrations in 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.

Results and Discussion

The semi-volatile (solvent extractable) organic chemicals identified in individual samples, together with volatile organic compounds (VOCs) identified in wastewater samples, are summarised in Table 2. A full list of semi-volatile organic chemicals identified in each sample is provided in Appendix 2. In addition, the concentrations of metals and metalloids in the solid waste sample, in the filtered solid from one wastewater sample (MX16022), and in both filtered (dissolved metals) and whole (dissolved and suspended metals) wastewater samples are reported Table 3.

Organic chemical contaminants

A number of organic chemicals were identified in the solid waste sample (MX16021). Key substances amongst these included isomers of nonylphenol, isomers of diisopropylbiphenyl, a number of alkyl benzenes, and 2,6-di-tert-butyl,4-methylphenol which is also known as butylated hydroxyl toluene (BHT).

The composition of organic chemicals in the filtered suspended solids from each of the two wastewater samples (MX16022 & MX16023) had an almost identical GC-MS profile to that of the solid waste sample (MX16021), and are therefore not presented in Table 2.. The one difference was the presence of nonylphenol in the solid waste (MX16021), which was not found in the suspended solid fraction of MX16022 or MX16023.

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 and NPEs are regulated in some regions (OSPAR 1998, EU 2003, ECHA 2013). Additional information on nonylphenol, including hazardous properties, is available in Box A.

Sample type	SW	WW	WW
Sample code	MX16021	MX16022	MX16023
Number of compounds isolated	55	41	44
Number of compounds identified to >90%	34	27	20
phenols:			
nonylphenol isomers	10		
phenol		1	1
phenol, 4-methyl		1	1
phenol, 2,3,5-trimethyl		1	
butylated hydroxyl toluene (BHT)	1		
Phthalate esters:			
di(2-ethylhexyl) phthalate (DEHP)		1	1
di-n-butyl phthalate (DBP)		1	1
di-iso-butyl phthalate (DiBP)		1	1
diethyl phthalate (DEP)		1	1
dimethyl phthalate (DMP)		1	1
alcohols:			
2-ethyl-1-hexanol		1	1
benzyl alcohol			1
TMDD (Surfynol 104H)		1	
amines & related:			
1H-indole		1	1
tributyl amine			1
chlorinated chemicals:			
Dichloroaniline		1	
Benzene, 1,4-dichloro-		SIM	
hydrocarbons:			
Diisopropylbiphenyl isomers	8		
Benzene			SIM
styrene		SIM	
o-xylene		SIM	
other alkyl benzenes	9	6	6
aliphatic hydrocarbons	1	5	2
others:			
sewage associated chemicals	3		
Sesquiterpenes	2		
Dimethyl trisulfide		1	

Table 2: summary of organic contaminants for each wastewater (WW) and solid waste (SW) sample in which volatile and semi-volatile (solvent extractable) organic compounds were identified (to >90% reliability). SIM – volatile compound (VOC) identified in Selective Ion Monitoring (SIM) mode

Diisopropylbiphenyl has been used, in the past at least, as a replacement for polychlorinated biphenyls (PCBs) in capacitors (Tulp et al. 1978, Addison 1983), and one isomer, 4,4'-diisopropylbiphenyl, is listed being used as a plasticiser in electrical or electronic equipment (Oeko-Institut 2014). Diisopropylbiphenyl is also used as a heat transfer fluid in heating and cooling systems, and some commercial formulations contain a range of isomers of diisopropylbiphenyl (Eastman 2015, 2016). The commercial mixture of diisopropylbiphenyl isomers has been classified under GHS as May be fatal if swallowed and enters airways (H304), May cause damage to organs through prolonged or repeated exposure (H373) and May cause long-lasting harmful effects to aquatic life (H413) (Eastman 2015).

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 a widely used type of a broader group of substances known as alkylphenol ethoxylates (APEs).

NPEs have been used as surfactants, emulsifiers, dispersants and/or wetting agents in a variety of industrial and consumer applications. Assessments in the early 2000 decade noted that the largest share were 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 alkyl phenol (eg NP), 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 NP 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).

There are numerous studies of NP in biota, particularly in fish and other aquatic organisms (Soares et al. 2008), as well as in humans (Asimakopoulos et al. 2012). There have also been reports of significant levels of NP 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). NPs 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 in human tissues (Lopez-Espinosa *et al.* 2009).

The most widely recognised hazard associated with NPs 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. 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 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 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. Almost 20 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). 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). Even before their listing under this Directive, however, the widely recognised environmental hazards presented by NP and its 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). However, the precise extent to which this measure was effective is unclear. 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).

Butylated hydroxytoluene (BHT) has been widely 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)[1] as toxic to aquatic life with long lasting effects (H411), and irritating to the skin and eyes (H315, H319).

A number of closely related alkyl benzenes were identified, all with branched side chains of between 10 and 12 carbon atoms length (C10-C12). The occurrence of alkyl benzenes and aliphatic hydrocarbons may be due to their presence in crude oil and petroleum products (Overton 1994). However, alkylbenzenes are also used in the manufacture of linear alkylbenzene sulphonate (LAS) detergents, which can contain unreacted alkylbenzenes, and this source would be consistent with the type of alkyl benzenes identified (Macias-Zamora & Ramirez-Alvarez 2004). Many alkylbenzenes are highly resistant to degradation and may accumulate in sediments (Preston & Raymundo 1993). Alkylbenzenes have been used as markers of sewage pollution (Chalaux *et al.* 1995), because of their association with urban wastewater run-off and industrial discharges to sewers.

Although this wastewater was primarily industrial in origin, analysis also identified some chemicals which are commonly found in household sewage (Homem *et al.* 2015), as well as two chemicals likely to be of plant origin.

A wider range of organic chemicals were identified in the two filtered wastewater samples, compared to the solid waste sample. A similar profile of chemicals was found for the two wastewater samples (MX16022 & MX16023), though the chemical groups identified were different to those for the solid waste sample (MX16021), as may be expected from differential partitioning based on solubility in aqueous or organic-rich waste materials, with the exception that examples of alkyl benzenes and aliphatic hydrocarbons were identified in both types of material.

Key substances amongst these included phthalate esters, phenols, alcohols, amines, chlorinated chemicals, alkyl benzenes and aliphatic hydrocarbons.

The same five phthalate esters (commonly called phthalates) were identified in both wastewater samples (MX16022 & MX16023), namely di(2-ethylhexyl) phthalate (DEHP), di-n-butyl phthalate (DBP), di-iso-butyl phthalate (DiBP), diethyl phthalate (DEP) and dimethyl phthalate (DMP). Phthalate esters have numerous industrial uses, with the use as plasticizers (softeners) in plastics dominating for many phthalates. DEHP, DBP, and DiBP are toxic for reproduction in mammals (Howdeshell et al. 2008, Lin et al. 2008, Mylchreest et al. 2002, Swan et al. 2005), and within the EU have been listed as Substances of Very High Concern (SVHC) under the REACH Regulation (ECHA 2013). For more information on phthalate esters, see Box B.

Phenol and 4-methylphenol were identified in both wastewaters, with another alkylphenol (2,3,5-trimethylphenol) identified only in MX16022. 4-methylphenol (also known as *p*-cresol) has many uses including the manufacture of certain antioxidants, in disinfectant and preservative formulations. Both *p*-cresol and 2,3,5-trimethylphenol (also known as isopseudocumenol) do have some natural sources (ATSDR 2008, Khatoon et al. 2015). Nonetheless, both have been classified under GHS as toxic if swallowed or in contact with the skin (H301, H311), and isopseudocumenol has also been classified as toxic to aquatic life with long lasting effects (H411).

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[1] 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)

BOX B. 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 previously been detected in components of electronic products (Brigden *et al.* 2007a) and in wastewaters from electronic manufacturing facilities (Brigden *et al.* 2007b), among many other products and environmental samples.

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. 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 classified as "toxic to reproduction" within Europe.

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). Other research has revealed a correlation between phthalate exposure during pregnancy and decreased ano-genital index (distance from the anus to the genitals) in male children (Swan *et al.* 2005), 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 anti-androgenic effects on reproductive development of Wistar rats (Boberg *et al.* 2011), though less prominently than DEHP, DBP and BBP.

Diethyl phthalate (DEP) is used in a diverse array of cosmetic and other personal care products (SCCNFP 2003, Koniecki *et al.* 2011). As for other phthalates, once released into the environment, DEP is a subject to biodegradation by microorganisms (Chang et al. 2004, Yuan et al. 2002). Evidence for adverse effects of DEP remains limited relative to that available for certain other phthalates. Recent studies indicate that DEP exerts toxicity to aquatic organisms through oxidative stress, and has reproductive endocrine disrupting properties affecting steroid biosynthesis (Mankidy et al. 2013, Sohn et al. 2016). DEP is also a minimal to mild skin and eye irritant in animals (Labunska & Santillo 2004). As for other phthalates, concerns also exist due to due to its widespread distribution in the environment (WHO 2003, Blount et al. 2000, Gao & Wen 2016), including in dusts in the indoor environment (Mitro et al. 2016).

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 which 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 22nd July 2019 (EU 2015). While these address two important exposure routes, exposures through other consumer products have so far largely escaped regulation. Certain phthalates, including DEHP, DBP, DiBP and BBP, have now been listed as Substances of Very High Concern (SVHC) under the EU REACH Regulation (ECHA 2013).

Surfynol 104H is a decynediol derivative (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 (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).

Of the two alcohols identified, 2-ethyl-1-hexanol has known uses in electronics manufacture (Baldwin et al. 1996). This alcohol, however, is also a metabolite of one of the phthalates also identified in the wastewater (DEHP), and this could be a contributing source of 2-ethyl-1-hexanol in this case (WHO 1992). This chemical is classified under the GHS as harmful if inhaled (H332) and capable of causing skin and eye irritation (H315 & H319). The other alcohol, benzyl alcohol, is a high volume chemical with many uses, including in the manufacture of epoxy resins and has been classified under GHS as harmful if swallowed (H302) (REACH 2016).

Of the two amines 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). Indole also 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).

Two chlorinated chemicals were identified in only one of the wastewater samples (MX16022); 1,4-dichlorobenzene (at a trace level) and dichloroaniline. 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). It was not possible to identify which isomer of dichloroaniline was present. Substituted anilines, including chlorinated anilines, have various industrial uses, including use as dye intermediates. Various chlorinated anilines are toxic to a wide range of organisms, including aquatic organisms (Dom et al. 2010, Monteiro et al. 2006). Two isomers, 3,5-dichloroaniline and 2,4-dichloroaniline, are 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), though clearly it was not possible to determine if either were present in the sample MX16022.

The type of alkyl benzenes identified in the filtered wastewater samples were the same type as those found in the solid waste sample (MX16021). As mentioned above, their presence in the samples may be due to their presence in crude oil and petroleum products (Overton 1994) or associated with the use of linear alkylbenzene sulphonates (LAS).

Analysis of volatile chemicals in the wastewater samples also identified benzene, styrene and o-xylene, though these were present at only trace levels, and were detected using the more sensitive Selective Ion Monitoring (SIM) method.

Metals and metalloids

For each of the wastewater samples, the filtered portion did not contain any of the quantified metals at concentrations notably higher than those typically found in uncontaminated surface waters. In contrast, the whole (unfiltered) portion of each sample contained a number of metals at high concentrations, indicating their presence in undissolved forms within the sample. Both samples contained notably high concentrations in the unfiltered sample of copper, lead, molybdenum, silver, tin and zinc, as well as arsenic in one sample (MX16022) and barium in the other (MX16023).

sample type	**wastewater (µg/l)**				**Solid waste (mg/kg)**		**continental crust * (mg/kg)**
Sample code	**MX16022**		**MX16023**		**MX16021**	**MX16022 (solid)**	
	filt.	wh	filt.	wh	-	-	-
Antimony (Sb)	<0.2	16.6	<0.2	8.9	0.4	0.5	0.2
Arsenic (As)	15	297	2	40	8.4	6.8	1.8
Barium (Ba)	5	83	13	1350	67.9	58.3	425
Beryllium (Be)	<2	6	<2	2	<1	<1	2.8
Cadmium (Cd)	<0.1	12.9	<0.1	3.9	0.56	0.44	0.2
Cerium (Ce)	<0.1	143	<0.1	131	4.93	5.07	60
Chromium (Cr)	1.0	753	1.1	190	33.7	28.6	100
Chromium VI (Cr VI)	<50	-	<50	-	-	-	-
Cobalt (Co)	2.5	43	0.8	21	1.6	1.4	25
Copper (Cu)	13	8140	7	2890	318	269	55
Dysprosium (Dy)	<0.1	12.6	<0.1	10.4	0.36	0.33	3
Erbium (Er)	<0.1	7.1	<0.1	5.8	0.19	0.19	2.8
Europium (Eu)	<0.1	1.8	<0.1	2.3	0.07	0.06	1.2
Gadolinium (Gd)	<0.1	13.7	<0.1	11.6	1.8	1.7	5
Gallium (Ga)	<0.5	55	<0.5	38	0.39	0.38	15
Holmium (Ho)	<0.1	2.5	<0.1	2.1	0.07	0.07	1.2
Lanthanum (La)	<0.1	58.5	<0.1	59.7	2.3	2.28	30
Lead (Pb)	0.8	970	0.8	760	38.7	42.9	13
Lutetium (Lu)	<0.5	1.0	<0.5	0.8	<0.2	<0.2	0.5
Manganese (Mn)	15.3	1660	66.2	762	56.2	48	950
Mercury (Hg)	<0.1	<0.1	<0.1	2.7	0.45	0.42	0.08
Molybdenum (Mo)	42	2900	24	573	130	105	1.5
Neodymium (Nd)	<0.1	60.9	<0.1	54.0	1.96	1.87	28
Nickel (Ni)	<5	350	<5	123	13	10	75
Praseodymium (Pr)	<0.1	15.4	<0.1	13.8	0.53	0.51	8.2
Selenium (Se)	<5	22	<5	27	2	2	
Samarium (Sm)	<0.1	13.5	<0.1	11.8	0.44	0.36	6
Silver (Ag)	<0.5	112	<0.5	84	3.4	3.2	0.07
Strontium (Sr)	39	1030	68	604	26.9	23.2	375
Thulium (Tm)	<0.1	1.1	<0.1	0.9	<0.05	<0.05	0.5
Tin (Sn)	1.4	2200	5.2	3220	137	140	2
Vanadium (V)	2.8	1400	1.4	442	51.3	43.5	135
Ytterbium (Yb)	<0.1	7.0	<0.1	5.6	0.19	0.19	3.4
Zinc (Zn)	16	22900	7	6220	825	682	70

Table 3: Concentrations of metals and metalloids in filtered (filt.) and whole (wh.) wastewater samples (µg/l), and in the solid waste samples (mg/kg dry weight), *together with reported average concentrations for the Earth's continental crust (Krauskopf & Bird 1994).

For each metal, the concentration in the solid material that was separated from one of the wastewater samples (MX16022) was very similar to that found in the solid waste sample (MX16021). These data indicate that, in terms of metals content, the solid waste material collected from a storage contained (MX16021) is almost identical to be solid material suspended within the wastewater generated at this facility.

These two solid materials contained high concentrations of a number of metals, including copper, lead, molybdenum, silver, tin and zinc. These results are consistent with the high concentrations of these metals in the unfiltered water samples arising from undissolved forms within the sample. Though not directly comparable, average concentrations of these metals in the Earth's continental crust are presented in Table 3 to provide a comparison with the concentrations in the solid samples.

Concentrations of molybdenum, selenium, silver, tin and zinc were notably higher than average concentrations of these metals in the Earth's continental crust, and to a lesser extent so were those of copper, lead, and arsenic.

In Mexico, the regulation addressing the content of metals/metalloids in hazardous waste in Mexico sets limits for 8 elements; arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver (SEMARNAT 2006). This regulation sets limits for the concentration of each element in an extract from the waste, rather than the total concentration of the element in the waste, and, therefore, the concentrations determined in this study cannot be directly compared with limits in this regulation. The concentrations of these elements in the solid waste samples (MX16021 & MX16022) would, however, give an extract with concentrations of elements below the limits set under the hazardous waste regulation (SEMARNAT 2006).

Conclusions

This study has demonstrated that industrial wastewater collected within this Flextronics manufacturing facility contains a complex mix of industrial chemicals, including examples that would be a clear concern for the environment and human health should they be released into the environment. Some of the chemicals identified in the wastewater samples are known to have uses in the electronics manufacturing sector.

Both the organic chemical data and metals data strongly suggest that the solid waste material stored at the site is solid material isolated from the wastewater without, or with only limited, further treatment.

It should be noted that the fate of wastewater and solid waste sampled within the facility is not known, and therefore any implications resulting from the presence of organic chemicals and certain metals at higher concentrations in the industrial wastewater and/or solid waste are similarly unknown at present. Many of the contaminants of greatest concern identified in these samples, however, would not be amenable to effective degradation in conventional wastewater treatment facilities, such that their presence is of concern even though samples were collected while treatment was still ongoing. Any release of these waste streams into the environment should, therefore, be avoided.

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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 43^0C (held for 4min), rising to 55^0C at 5^0C/min, and then to 210^0C at 15^0C/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) 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 40^0C , raised to 260^0C at

10^{0}C/min, then to 295^{0}C at 50^{0}C/min (held for 15 min), and finally to 320^{0}C at 50^{0}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^{o}C over 15 minutes followed by holding at 180^{o}C for a further 15 minutes. Cooled digests were filtered and made up to 25 ml with deionised water.

Solid 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^{o}C over 20 minutes followed by holding at 180^{o}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 μg/l respectively, other than for mercury (1, 2, 5, 20 μg/l respectively) were used for instrument calibration. Analysis employed in-line addition of an internal standard mix at 100 μg/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 μg/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 μg/l for each metal, other than mercury at 4 and 16 μg/l, were digested and analysed. For sediment samples, a certified reference material (CRM) sample was prepared in an identical manner; GBW07406, soil from the National Research Center for Certified Reference Materials, China. 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 μg/l and 800 μg/l (4 μg/l and 16 μg/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 μg/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.

MX16021

Number of semi-volatile compounds isolated: 55
Compounds identified to better than 90%:

CAS#	Name
004537-15-9	Benzene, (1-butylheptyl)-
004537-11-5	Benzene, (1-butylhexyl)-
002719-63-3	Benzene, (1-butyloctyl)-
002400-00-2	Benzene, (1-ethyldecyl)-
002719-62-2	Benzene, (1-pentylheptyl)-
004537-14-8	Benzene, (1-pentylhexyl)-
004534-49-0	Benzene, (1-pentyloctyl)-
002719-64-4	Benzene, (1-propylnonyl)-
004536-86-1	Benzene, (1-propyloctyl)-
017699-05-7	Bicyclo[3.1.1]hept-2-ene, 2,6-dimethyl-6-(4-methyl-3-pentenyl)-
000087-44-5	Caryophyllene
000747-90-0	Cholesta-3,5-diene
000765-27-7	Cholestane-3.beta.-thiol
000000-00-0	Diisopropylbiphenyl, 8 isomers
000630-03-5	Nonacosane
000128-37-0	Phenol, 2,6-bis(1,1-dimethylethyl), 4-methyl- (Butylated hydroxyl toluene, BHT)
084852-15-3	Phenol, nonyl-, mixture of 10 isomers
000111-02-4	Squalene

MX16022

Number of semi-volatile compounds isolated: 38
Compounds identified to better than 90%:

CAS#	Name
000117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP)
000084-66-2	1,2-Benzenedicarboxylic acid, diethyl ester (DEP)
000131-11-3	1,2-Benzenedicarboxylic acid, dimethyl ester (DMP)
000084-69-5	1,2-Benzenedicarboxylic acid, diisobutyl ester (DiBP)
000084-74-2	1,2-Benzenedicarboxylic acid, dibutyl ester (DBP)
000104-76-7	2-Ethyl-1-hexanol
000120-72-9	1H-Indole
000126-86-3	5-Decyne-4,7-diol, 2,4,7,9-tetramethyl- (Surfynol 104H)
000000-00-0	Benzenamine, dichloro- (dichloroaniline)
004537-15-9	Benzene, (1-butylheptyl)-

002719-63-3	Benzene, (1-butyloctyl)-
002400-00-2	Benzene, (1-ethyldecyl)-
002719-62-2	Benzene, (1-pentylheptyl)-
002719-64-4	Benzene, (1-propylnonyl)-
004536-86-1	Benzene, (1-propyloctyl)-
003658-80-8	Dimethyl trisulfide
000112-40-3	Dodecane
000629-78-7	Heptadecane
000544-76-3	Hexadecane
000629-62-9	Pentadecane
000108-95-2	Phenol
000697-82-5	Phenol, 2,3,5-trimethyl-
000106-44-5	Phenol, 4-methyl-
001120-21-4	Undecane

Number of volatile organic compounds (VOCs) isolated:
Compounds identified to better than 90%: 3

CAS#	Name
000106-46-7	Benzene, 1,4-dichloro- (SIM)
000095-47-6	o-Xylene (SIM)
000100-42-5	Styrene (SIM)

MX16023

Number of semi-volatile compounds isolated: 43
Compounds identified to better than 90%:

CAS#	Name
000117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester (DEHP)
000084-66-2	1,2-Benzenedicarboxylic acid, diethyl ester (DEP)
000131-11-3	1,2-Benzenedicarboxylic acid, dimethyl ester (DMP)
000084-69-5	1,2-Benzenedicarboxylic acid, diisobutyl ester (DiBP)
000084-74-2	1,2-Benzenedicarboxylic acid, dibutyl ester (DBP)
000102-82-9	1-Butanamine, N,N-dibutyl- (tributyl amine)
000104-76-7	2-Ethyl-1-hexanol
000120-72-9	1H-Indole
004537-15-9	Benzene, (1-butylheptyl)-
002719-63-3	Benzene, (1-butyloctyl)-
002400-00-2	Benzene, (1-ethyldecyl)-
002719-62-2	Benzene, (1-pentylheptyl)-
002719-64-4	Benzene, (1-propylnonyl)-
004536-86-1	Benzene, (1-propyloctyl)-
000100-51-6	Benzyl alcohol
000629-78-7	Heptadecane
000629-62-9	Pentadecane
000108-95-2	Phenol
000106-44-5	Phenol, 4-methyl-

Number of volatile organic compounds (VOCs) isolated:
Compounds identified to better than 90%: 1

CAS#	**Name**
000071-43-2	Benzene (SIM)