

Organic chemical and heavy metal contaminants in wastewater discharged from three textile manufacturing and washing facilities in Mexico

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Executive Summary

The manufacture of textile products employs a diverse range of techniques and processes, which in turn rely on the use of numerous process and finishing chemicals. Some of these are known to have intrinsic hazardous properties. For many of the chemicals used, however, little or no information is publicly available on their toxicology or the potential impacts of their release to the environment.

Greenpeace has recently carried out a number of investigations that have revealed the presence of a diverse range of hazardous chemicals within wastewaters discharged from manufacturing processes used by the textile industry in China. In addition, residues of some of these chemicals have been found in clothing products manufactured and sold in many countries around the world.

This study builds on recent work by further investigating releases of hazardous chemicals in effluents discharged into surface waters and generated by three individual facilities involved in the manufacture and pre-sale washing of textile products in Mexico. The three facilities were as follows: the Kaltex facility in San Juan del Río, Queretaro, the Lavamex facility located in Aguascalientes and the Lavaexport S.A DE C.V facility in Tehuacán city, Puebla. Wet processes are carried out at all these facilities, primarily involving the dyeing and washing of denim textiles.

Samples were collected from the main wastewater discharges at each of the three locations in May 2012. For the Kaltex and Lavamex facilities, two samples were collected from each facility on consecutive days, while a single sample was collected from the Lavaexport facility. The samples were not intended to provide a comprehensive understanding of the chemical makeup of discharged wastewater for each location. This is something that can vary over time. Rather, the samples were intended to provide a snapshot of the type of hazardous chemicals present in these complex industrial wastewaters. All samples were analysed at the Greenpeace Research Laboratories (University of Exeter, UK), using qualitative analysis to detect the presence (though not the concentrations) of semi-volatile and volatile organic compounds, as well as to determine the concentrations of a range of metals and metalloids.

Overall, a diverse range of chemicals was identified in the wastewater samples analysed in this study. Many of these have known hazardous properties. Some examples are toxic to aquatic life, while others are persistent and therefore will remain in the environment long after their release. Of the three facilities, the Lavamex facility was the most notable in terms of hazardous chemicals identified in wastewater samples.

For some of the chemicals identified in the various wastewater samples, little or no information is publicly available on their toxicological properties and, therefore, the consequences of their release to the environment remain unknown. Furthermore, a significant proportion of the chemicals isolated from each sample could not be reliably identified. This is not uncommon for complex industrial effluents. As a result, the properties and potential impacts of these unidentified chemicals cannot be assessed. Many of the identified chemicals either have known uses during textile manufacturing processes, or are known degradation products of such textile process chemicals. Some of the hazardous chemicals identified in this study have also been previously reported in wastewaters discharged in China, including those released from textile manufacturing facilities.

Key findings in terms of the chemicals found in the wastewater samples from each of the three facilities analysed in this study can be summarised as follows.

Lavamex facility

- Nonylphenol (NP), a well known persistent environmental contaminant with hormone disrupting properties, together with nonylphenol ethoxylates (NPEs), which are used as detergents and surfactants in textile manufacture and washing and which degrade back to NP.
- TMDD, a surfactant associated with the use of dye formulations (among other industrial applications) that is persistent in the aquatic environment and moderately toxic to aquatic life.
- Two benzotriazoles, which are commonly used as corrosion inhibitors, and are moderately toxic to aquatic organisms.
- Tributyl phosphate, a hazardous chemical used in the textile industry, and a trichloroaniline, related to the manufacture and use of dyes, which is toxic to aquatic life, were both present as minor components.

Kaltex facility

- TMDD, the surfactant identified at the Lavamex facility, which is persistent and moderately toxic in the aquatic environment, was also found here.
- HMMM, used to produce resins, which has some toxicity to aquatic organisms, together with a related chemical that could not be fully identified.
- Traces of two trichlorinated benzenes, which are widely recognised persistent toxic chemicals and are used as solvents and dye carriers. They may have originated from washing of textiles containing residues of these chemicals.
- Two phthalate esters (DEHP and DiBP) as minor components. These chemicals are reproductive toxins. They have numerous industrial uses including uses in the manufacture of textiles. For these chemicals, sources other than textile manufacture cannot be excluded.

Overall, this investigation has provided an indication of the diverse range of chemicals currently being used and/or released by the three textile manufacturing and washing facilities concerned. This study, based on a small number of samples, cannot be representative of wastewaters released from textile manufacturing and washing facilities throughout Mexico, or even of the textile manufacturing sector as a whole. It does, however, provide an illustrative snapshot of the wide array of harmful contaminants within industrial effluents and suggests that this may be a much wider problem over the country as a whole.

Information on the hazardous chemicals being used and released by individual facilities, including those engaged in the manufacture of textiles can help to bring about changes in chemical use and management by the individual companies using them. Indeed, such information is vital to highlight the nature of what is likely to be a widespread problem.

A focus on documenting and progressively reducing the upstream use of hazardous chemicals at facility and process level is key to facilitating a shift towards less hazardous or preferably non-hazardous alternatives, across all industrial sectors. Making information on the current use and release of hazardous chemicals by individual facilities publicly available will undoubtedly prove to be an important contribution towards achieving that goal.

1. Introduction

The manufacture of textile products makes use of a diverse range of techniques and processes, many of which, in turn, rely on the use of numerous process and finishing chemicals. Some of the chemicals currently employed within different parts of this sector are known to have intrinsic hazardous properties. For many others, little or no information is publicly available on their toxicological properties or on the potential hazards they pose on their release to the environment.

Greenpeace has recently conducted a number of investigations into hazardous chemicals within wastewaters discharged from parts of the textile manufacturing industry in China (Brigden et al. 2009, Greenpeace 2011a, Brigden et al. 2012b). In addition, the presence of hazardous chemical residues in various clothing products manufactured in many countries around the world has also been revealed (Greenpeace 2011b, Brigden et al. 2012a). Overall, these studies have served to highlight the ongoing use of a wide range of hazardous and potentially hazardous chemicals in parts of the textile manufacturing sector, and the resulting releases of such substances into the environment, particularly the aquatic environment.

This study further extends the scope of the previous work carried out by investigating hazardous chemicals present in wastewaters discharged into aquatic systems from three individual facilities involved in the manufacture and pre-sale washing of textile products in Mexico.

2. Sampling programme

A total of five samples were collected in May 2012 from locations where wastewaters are discharged from each of the three facilities. Details of the samples collected are provided below, and a summary of the sample descriptions and location of sampling points is presented in Tables 1a & 1b.

Kaltex

Single samples (MX12004 and MX12005) were collected on two consecutive days, 2 May and 3 May 2012, from the same discharge channel originating from the Kaltex facility in San Juan del Río, Queretaro, Mexico. At the time of sampling, wastewater was being discharged to the channel via a pipe that was operating at high capacity. According to a previous report (Herrera 2008), in 2008 Kaltex was known to be discharging 209 litres of wastewater a second, equivalent to 18 million litres a day. The wastewater from this discharge channel finally enters the San Juan River. This facility is believed to carry out the majority of the denim washing and dyeing operations for Kaltex in Mexico.

Lavamex

Single samples (MX12006 and MX12007) were also collected on two consecutive days, 2 May and 3 May 2012, from a discharge pipe associated with the Lavamex facility of the INISA group, located in Aguascalientes, Mexico. The Lavamex facility is almost exclusively dedicated to denim washing and dyeing operations. The discharge from the Lavamex facility wastewater pipe was continuous and operating at high capacity at the time of sampling, and appeared to be the sole source of a network of streams flowing through more than 20 acres of surrounding fields. Water from these streams is used for agricultural purposes. In rainy seasons, when flow rates are naturally high, diluted wastewater from the Lavamex facility may reach the San Pedro River.

The Lavamex facility, and the Kaltex facility in San Juan del Río in particular, are considered to be among the biggest facilities carrying out denim fabric-related wet manufacturing in Mexico.

Lavaexport

A single sample (MX12008) was collected on 16 May 2012 from a pipe associated with the Lavaexport S.A DE C.V facility in Tehuacán city, Puebla, Mexico. Lavaexport is one of the many mid-size facilities operated in Tehuacán, one of the biggest centres of denim production in Mexico. It is involved exclusively in denim washing and dyeing. A flexible pipe, carrying wastewater from the Lavaexport facility, discharges directly into the surrounding fields outside the facility's boundaries. The pipe was observed to be moved from one place to another at different times, so that the discharged wastewater is dispersed and absorbed into the ground. However, during rainy seasons, the diluted wastewater stream from Lavaexport may reach the closest water body, Dren de Tehuacan, through minor water bodies.

Sample code	Collection point	Sample type	Time & Date	Description	
Kaltex	MX12004	Discharge channel	Wastewater	07.33 2 May 2012	Collected from discharge channel of Kaltex facility which enters the San Juan River
	MX12005			16.05 3 May 2012	
Lavamex	MX12006	Discharge pipe	Wastewater	22.28 2 May 2012	Collected from wastewater pipe of Lavamex facility discharging water into surrounding fields
	MX12007			09.05 3 May 2012	
Lavaexport	MX12008	Discharge pipe	Wastewater	16.02 16 May 2012	Collected from wastewater pipe of Lavaexport facility discharging water into surrounding fields

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

Sample code	North		East		
	Degree (°)	Minutes ('), Seconds (")	Degree (°)	Minutes ('), Seconds (")	
Kaltex	MX12004	20	24'10.49"	100	0'4.07"
	MX12005				
Lavamex	MX12006	21	47'56.72"	102	17'32.79"
	MX12007				
Lavaexport	MX12008	18	30'38.09"	97	30'27.44"

Table 1b: GPS coordinates of sample collection locations

Each sample consisted of two subsamples collected in different types of bottle depending on the subsequent analyses to be carried out on each subsample. One subsample was collected in a 0.5 litre screw-cap glass bottle, for use in the quantitative analysis of metals and qualitative analysis of solvent extractable (semi-volatile) organic compounds. In addition, a duplicate sample was collected in a separate 50 ml amber glass bottle with a ground-glass stopper (filled to leave no headspace) to be analysed for volatile organic chemicals (VOCs). All bottles had been pre-cleaned, which included being rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metal and organic residues. All samples were immediately chilled and kept cool and dark during transit to the Greenpeace Research Laboratories at the University of Exeter in the UK. Upon arrival, samples were stored cool and dark prior to analysis.

3. Methodology

Each sample was analysed qualitatively for the presence of semi-volatile (solvent-extractable) organic compounds, and separately for the presence of volatile organic compounds (VOCs). In addition, each sample was analysed quantitatively to determine the concentrations of a range of metals and metalloids.

Metal and metalloid concentrations were determined for all samples by ICP atomic emission spectrometry (AES) following acid digestion and using appropriate certified reference materials in addition to intra-laboratory standards. Both the total concentrations in the whole (unfiltered) sample and the concentrations of dissolved forms in a filtered sample were determined separately for each sample. Hexavalent chromium concentrations in filtered samples were determined colourimetrically using a diphenylcarbazide method.

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

4. Results and Discussion

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

Sample code	Kaltex		Lavamex		Lavaexport
	Discharge channel		Discharge pipe		Discharge pipe
	MX12004	MX12005	MX12006	MX12007	MX12008
Number of compounds isolated	22	24	87	51	93
Number of compounds identified to >90%	12	13	41	11	26
Percentage identified to >90%	55%	54%	47%	22%	24%
Nonylphenol isomers			13	8	
Nonylphenol ethoxylates (NPEs)			10	7	
HMMM	✓	✓			
TMDD	✓	✓	✓*	✓*	
Pyrazole, 4-bromo-3,5-dimethyl-	✓	✓			
Phthalate esters	2*	2*			
Trichlorinated benzenes	2 (SIM)	2 (SIM)	3 (SIM)	3 (SIM)	
1H-Benzotriazole & derivatives			2*	1	
1H-Pyrazole, 4-nitro-			✓		
Hydrazine, 1,1-dipropyl-			✓		
Indole derivatives			2		3*
Tributyl phosphate (TBP)			✓*	✓*	
2,4,6-Trichloroaniline			✓*	✓*	
2,6-Dichloro-m-cresol			✓*	✓*	
2,4-dichlorophenol			SIM	SIM	
Ethanone, 1-(2-aminophenyl)-			✓*		
Fatty alcohols and derivatives					11
2-(Dodecyloxy)ethanol					✓
2-(2-Butoxyethoxy)ethanol					✓
Monoterpene alcohols					4
Trihalomethanes (THMs)	4 (SIM)	4 (SIM)	2 (SIM)		2 (SIM)
Other organic compounds					4

Table 2. Summary of key organic volatile and semi-volatile contaminants present in samples of wastewater discharged from Kaltex, Lavamex and Lavaexport facilities, Mexico, which were identified to a high degree of reliability (>90% reliability). The number indicates, where appropriate, if more than one compound was identified for a group. SIM indicates compounds detected at trace levels only using Selected Ion Monitoring mode of analysis.

* minor component of the total ion chromatogram

Sample type	Kaltex				Lavamex				Lavaexport	
	Discharge channel				Discharge pipe				Discharge pipe	
	MX12004		MX12005		MX12006		MX12007		MX12008	
	Filtered	Whole	Filtered	Whole	Filtered	Whole	Filtered	Whole	Filtered	Whole
Antimony	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Arsenic	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Barium	<10	<10	11	17	19	24	21	25	34	44
Cadmium	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Chromium	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Chromium (VI)	<50	-	<50	-	<50	-	<50	-	<50	-
Cobalt	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Copper	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Lead	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Manganese	<10	<10	<10	<10	144	170	157	176	2180	2290
Mercury	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Nickel	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Selenium	<200	<200	<200	<200	<200	<200	<200	<200	<200	<200
Vanadium	59	60	61	62	<20	<20	<20	<20	<20	<20
Zinc	19	31	15	25	14	18	16	16	22	24

Table 3: Concentrations of metals and metalloids (mg/l) in filtered (Filt.) and whole (Wh.) wastewater samples associated with the Kaltex, Lavamex or Lavaexport facilities, Mexico.

4.1 Kaltex

4.1.1 Organic chemical contaminants

Samples (MX12004 and MX12005), collected from the Kaltex facility on two consecutive days, showed very similar patterns of organic compounds that could be reliably identified. It should be noted, however, that for these and all other samples analysed in this study, a significant proportion of the chemicals isolated from each sample could not be reliably identified. This is not uncommon in the analysis of complex industrial effluents and means that their properties and potential impacts cannot be fully assessed.

The most prominent peak in the chromatogram for both samples was identified as hexa(methoxymethyl)melamine or HMMM, a monomer used to produce methylated melamine formaldehyde resins. These are used as a cross-linker in thermo set coatings such as beverage can coatings and automotive paint finishes. It is used also as a flame retardant for polymeric materials such as epoxy resins. The mass spectral analysis of another compounds isolated from both samples suggested that it was a closely related chemical to HMMM, although it could not be reliably identified. Commercial HMMM based resins are not a single substance, but rather contain a mixture of oligomers and polymers as well as the HMMM monomer itself. This can be present within the mixture in varying amounts depending on the manufacturing process used. Commercial products usually contain about 28-50% HMMM monomer, with the balance primarily being methylated melamine-formaldehyde polymers.

The HMMM monomer has been found to be acutely toxic to fish, invertebrates and algae, but it displayed little or no toxicity in mammalian studies (EPA 2004). It was not possible to identify any categorisation for this compound according to the Globally Harmonised System (GHS)¹.

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

A number of other compounds were also identified in both samples, including a decynediol derivative known as TMDD (also called Surfynol 104), and 4-bromo-3,5-dimethylpyrazole. In addition, for both samples, two phthalate esters (often known simply as phthalates) were identified as minor components, and some chlorinated compounds were present, though at only trace levels (two trichlorinated benzenes and four trihalomethanes).

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

TMDD was also identified in previous investigations of manufacturing wastewaters in China, including those related to the manufacture of textiles (Greenpeace 2011a, Brigden et al. 2012b). TMDD is not commonly reported as an environmental contaminant. It has, however, been reported in river water in Germany and in the Netherlands (Dzikowitzky et al. 2004a&b, Guedez et al 2010, Hankemeier et al. 1999, Schwarzbauer & Heim 2005,) and in the US (Snyder et al. 2001). Once discharged to surface waters, TMDD is not readily degraded and persists in the aquatic environment (US EPA 2008a). TMDD has been found to be moderately toxic to aquatic organisms in laboratory experiments on fish (fathead minnows and carp), aquatic invertebrates (*Daphnia magna*), and green algae (*Selenastrum capricornutum*) (US EPA 2002). Further, this substance has been classified under the GHS as harmful to aquatic life with long lasting effects (H412).

4-Bromo-3,5-dimethylpyrazole is a halogenated heterocyclic compound which is primarily used in the synthesis of other chemicals. This substance has been classified under the GHS as irritating to eyes and skin (H315, H319) and as having the potential to cause respiratory irritation (H335). No additional information could be found related to the hazardous properties of this chemical, nor any connection to use in the manufacture of textiles

The two phthalates, di-(2-ethylhexyl) phthalate (DEHP) and di-iso-butylphthalate (DiBP), were present in both wastewater samples, though only as minor components. Both DEHP and DiBP have uses in the manufacture of textiles, though these phthalates have numerous other uses, primarily are plasticisers in PVC and other plastics. Other applications include their use as components of inks, adhesives, surface coatings and personal care products. DEHP and DiBP are common environmental contaminants, primarily due to losses from products in which they have been incorporated (Fromme et al. 2002).

The presence of these two phthalates in the wastewater may be due to their use during textile manufacturing. However, given the widespread use of these compounds, which were present as only as minor components of the mix of chemicals isolated from the wastewater, other sources cannot be excluded, including leaching from plasticised materials with which the wastewater had been in contact.

DEHP and DiBP are toxic substances, particularly due to their ability to exert toxic effects on reproductive systems in animals and humans (Howdeshell et al. 2008, Lin et al. 2008, Swan et al. 2005). As a result, DEHP and DiBP have been classified as “toxic to reproduction” within Europe, and both have been listed as “substances of very high concern” under the European REACH Regulation, together with some other phthalates (ECHA 2011). Furthermore, both DEHP and DiBP have been classified as having the potential to damage fertility or the unborn child (H360DF). Additional information on phthalates is provided in Box A.

Additionally, the samples contained trace levels of several halogenated compounds (detected only using the more sensitive Selected Ion Monitoring or “SIM” analysis mode), including two trichlorinated benzenes and some trihalomethanes (THMs), including chloroform, bromoform, bromodichloro- and dibromochloromethane which most often arise as a result of chlorination of water for disinfection purposes.

The two trichlorinated benzenes (TCBs) identified were 1,2,3-TCB and 1,2,4-TCB. TCBs have many industrial uses, primarily as solvents and chemical intermediates. In relation to the textile sector, 1,2,3-TCB and 1,2,4-TCB are used as dye carriers and also in the production of pigments and dyes (ATSDR 2010, OSPAR 2005). Given the trace levels of TCBs in the samples, their presence may be due to having been washed out from fabric containing residues of TCBs brought to this facility, rather than the direct use of TCBs within the facility.

TCBs are widely recognised hazardous chemicals. They are not readily biodegradable and are, therefore, persistent pollutants that can remain in the environment for a prolonged time after their initial release, primarily in soils and sediments. TCBs also have the potential to bioaccumulate in aquatic organisms (ATSDR 2010, OSPAR 2005). TCBs are toxic to many aquatic organisms (EU 2003a, OSPAR 2005), while studies on mammals indicate that all TCBs have effects on the liver and the blood system (ATSDR 2010, OSPAR 2005). Within the EU, TCBs have been included as priority substances under the Water Framework Directive, a regulation designed to improve the quality of water within the EU (EU 2001). Classifications for TCBs under the GHS include being toxic or very toxic to aquatic life with long lasting effects (H410), harmful if swallowed (H302) and irritating to skin (H315).

Box A. Phthalate esters (phthalates)

Phthalates (or, more accurately, phthalate diesters) are chemicals with a diversity of uses, dominated by use as plasticisers (or softeners) in plastics, especially PVC. Other applications include uses as components of inks, adhesives, sealants, surface coatings and personal care products. Specifically related to textiles, phthalates were recently reported within plastisol prints on textile products manufactured and sold around the world, with very high levels of certain phthalates in some products, including DEHP (Brigden et al. 2012).

Some phthalates are discrete chemicals, such as the well known di(2-ethylhexyl) phthalate (DEHP), while others are complex mixtures of isomers, such as diisononyl phthalate (DiNP). All uses of phthalates, especially the major use as PVC plasticisers, result in large-scale losses to the environment (both indoors and outdoors) during the lifetime of products, and again following disposal, principally because phthalates are not chemically bound but only physically associated to the polymer chains. For example, phthalates have been found to leach from food packaging materials and contaminate corresponding food products (Fierens et al. 2012, Fasano et al. 2012); from tubing material used for drug products manufacturing (Jenke et al. 2006) and from PVC blood bags that primarily contained DEHP (Ferri et al. 2012). Moreover, it has been shown that bacteria, which may grow on PVC plastics in wet conditions (e.g., shower curtains), may enhance DEHP leaching from plastic (Latorre et al. 2012). Phthalates, including DEHP are widespread within the environment, including the aquatic environment (Fromme et al. 2002). Phthalates are also 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 that 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, including DiBP, 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 phthalates, is known to be toxic to reproductive development in mammals, capable (in its monoester form MEHP) of interfering with development of the testes in early life, thought to be mediated through impacts on testosterone synthesis (Howdeshell et al. 2008, Lin et al. 2008). Even at low doses, exposure to mixtures of phthalates can result in cumulative effects on testicular development in rats (Martino-Andrade et al. 2008). In addition, adverse impacts on female reproductive success in adult rats and on development of the young have been reported following exposure to this chemical (Lovekamp-Swan & Davis 2003, Grande et al. 2006, Gray et al. 2006). Other research has revealed a correlation between exposure to certain phthalates during pregnancy, including DiBP and DnBP, and decreased ano-genital index (distance from the anus to the genitals) in male human children (Swan et al. 2005). A more recent study (Abdul-Ghani et al. 2012) has shown that both DEHP and DnBP (di-n-butyl phthalate) 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. Certain phthalates, including DEHP and DiBP are classified as “toxic to reproduction” within Europe.

At present, there are relatively few controls on the marketing and use of phthalates, despite their toxicity, the volumes used and their propensity to leach out of products throughout their lifetime. Of the controls which do exist, however, probably the best known is the EU-wide ban on the use of six phthalates in children’s toys and childcare articles (EC 2005). While this addresses one important exposure route, exposures through other consumer products have so far largely escaped regulation both within the EU and elsewhere. However, within Europe, certain phthalates, including DEHP, DiBP, DnBP and BBP, have been included into the list of candidates as “substances of very high concern” under the REACH Regulation (ECHA 2011).

Within the EU, DEHP is also listed as a priority substance under the Water Framework directive, a regulation designed to improve the quality of water within the EU (EU 2008). DEHP and DnBP have also been identified as substances for priority action under the OSPAR convention, under which signatory countries have agreed a target of cessation of discharges, emissions and losses of all hazardous substances to the marine environment of the North-East Atlantic by 2020, the “one generation” cessation target (OSPAR 1998). In August 2012, despite a European Commission ruling from June 2012 (ENDS 2012), the Danish Ministry of Environment announced plan to introduce a wider ban on marketing and use for four hormone-disrupting phthalates; DEHP, DnBP, BBP and DiBP (DMOE 2012).

All four trihalomethanes (THMs), which include chloroform, bromoform, bromodichloromethane, and dibromochloromethane, were detected in both samples at trace levels. Their simultaneous presence in the water samples suggests that the most likely source of these chemicals is from disinfection processes commonly used in water treatment plants. THMs are formed as by-products of reactions between the disinfectant (usually chlorine or chlorine-containing chemicals) with bromide and/or natural organic matter present in the source water, such as decaying vegetation (US EPA 2012).

4.1.2 Metals

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

4.2 Lavamex

4.2.1 Organic chemical contaminants

As with samples from the Kaltex facility, most identified compounds were found in both samples collected from the wastewater discharge pipe of the Lavamex facility on two consecutive days (MX12006 and MX12007). Similarly to the Kaltex facility, the majority of the chemicals isolated from each sample could not be reliably identified, such that their properties and potential impacts cannot be fully assessed.

Overall, more organic compounds were identified in sample MX12006 than in sample MX12007 collected on the following day, most probably reflecting the complexity of the waste stream which may vary significantly depending on the specific operating process undertaken at the facility at any particular time. Though samples from the Lavamex facility had several compounds that were also present in the wastewater samples from Kaltex facility (TMDD, as a minor component, traces of three trichlorinated benzenes in both samples, and traces of two THMs in MX12006), a wider range of organic compounds was detected in wastewater samples from the Lavamex facility than from Kaltex.

TMDD (also known as Surfynol 104), used primarily as an industrial defoaming surfactant, is moderately toxic to aquatic organisms but can have long-lasting effects due to its persistence in the aquatic environment (US EPA 2002, 2008a). Trichlorinated benzenes (TCBs) are primarily used as solvents and chemical intermediates, and within the textile sector are also used as dye carriers. As with the TCBs identified in wastewater from the Kaltex facility, their presence in these samples at only trace levels suggests that their presence may be due to having been washed out from fabric at this facility, rather than the direct use of TCBs within the facility. TCBs are widely recognised hazardous chemicals that do not readily breakdown in the environment; they are toxic to aquatic life and can have long lasting effects. More information on these substances (TMDD and TCBs) is given in Section 4.1.

The two THMs, chloroform and bromodichloromethane, detected at trace levels in one sample (MX12006) most likely originated as by-products of disinfection processes, as mentioned in Section 4.1 for this group of chemicals.

The most prominent compound identified in both MX12006 and MX12007 samples was 4-methyl-1H-benzotriazole, a tolyltriazole. Tolyltriazoles, as well as the parent compound 1H-benzotriazole (identified in sample MX12006 only), are commonly used as corrosion inhibitors in antifreeze mixtures, coolant formulations and surface coatings. Both benzotriazoles that were identified in the samples exhibit toxicity to aquatic organisms (Pillard et al. 2001), and are classified under the GHS as harmful to aquatic organisms causing long-term adverse effects (H412). They are also considered harmful if swallowed or inhaled (H302, H332) and are capable of causing serious eye irritation (H319).

Less prominent, though probably more significant, was the identification of nonylphenol (NP) and nonylphenol ethoxylates (NPEs) in both samples from the Lavamex facility. Samples MX12006 and MX12007 contained 13 and 8 isomers of NP respectively, together with 10 and 7 isomers of NPEs respectively. NP is a group of closely related compounds mainly produced for use in the manufacture of the NPEs, which are widely used as detergents and surfactants in many industrial sectors, including the manufacture of textiles. Within wastewater treatment facilities, or following release into the aquatic environment, NPEs readily degrade back to NP, which are highly resistant to further degradation and therefore persistent within the environment. In addition, these compounds are able to bioaccumulate and are toxic. Toxicity is primarily due to their hormone-disrupting properties which 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 NPEs and NP are regulated in some regions (OSPAR 1998, EU 2003b). Additional information on NPEs and NP, including information on their hazardous properties, is given in Box B.

Two other compounds identified in one of the samples from this facility (MX12006) have possible connections to textile manufacture; 4-nitro-1H-pyrazole and 1,1-dipropylhydrazine. The first of these is a nitropyrazole. This is one of a group of compounds that have been used as starting material for azo dyes synthesis. The nitropyrazole in this sample has been classified under the GHS as harmful if swallowed and able to cause serious damage to eyes (H302, H318). 1,1-dipropylhydrazine belongs to a class of hydrazine derivatives that are a group of compounds known to be used as colour stabilisers for aniline-based dyes.

Box B. Nonylphenol ethoxylates (NPEs) and nonylphenol (NP)

Nonylphenol (NP) describes group of related (isomeric) chemicals that are manufactured for use in producing nonylphenol ethoxylates (APEs), 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). NPEs have been used as surfactants, emulsifiers, dispersants and/or wetting agents in a variety of industrial and consumer applications including the manufacture of textiles, the largest share in industrial and institutional cleaning products (detergents), with smaller amounts used as emulsifiers, textile and leather finishers and as components of pesticides and other agricultural products and water-based paints (OSPAR 2004, Guenther et al. 2002).

Once released to the environment, NPEs can degrade back to NP, which are persistent, bioaccumulative and toxic to aquatic life. Both NPEs and NPs are widely distributed in fresh and marine waters and, in particular, sediments, in which these persistent compounds accumulate (Ying et al. 2002, Jonkers et al. 2005, David et al. 2009, Shue et al. 2010). Because of their releases to water, NPEs and NPs 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 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 NPEs 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. 2010). NPs have also been recently reported in human tissues (Lopez-Espinosa et al. 2009).

The most widely recognised hazard associated with NP 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 as toxic to reproduction (category 2) (H361FD), harmful if swallowed (H302) and 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. More than 10 years ago, the Ministerial Meeting under the OSPAR Convention agreed on the target of cessation of discharges, emissions and losses of hazardous substances to the marine environment 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, another AP (tert-octylphenol, t-OP) was also listed under this category in 2000 (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). Octylphenols (OP) have been designated as "priority substances" 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). However, the precise extent to which this measure was effective is unclear. Furthermore, 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 after January 2005, with some minor exceptions principally for "closed-loop" industrial systems (EU 2003b). Restrictions on the sale of textile products containing residues of NPEs within the EU do not currently exist, though such a regulation is currently under development within the EU (KEMI 2012). In addition, Germany has recently announced its intention to propose both NP and t-OP as substances of very high concern (SVHC) under the EU REACH Regulation (ECHA 2012a).

For two other compounds identified in this sample, 1H-Indole-2,3-dione and a derivative of this, indolo[2,1-b]quinazoline-6,12-dione (also known as tryptanthrine), no information could be found on their use or release from textile manufacturing. 1H-Indole-2,3-dione is classified under the GHS as irritating to eyes and skin (H315, H319) and having the potential to cause respiratory irritation (H335), while for the derivative tryptanthrine it was not possible to identify any classification according to the GHS.

Some other compounds were identified as minor components in both samples. These included tributyl phosphate (TBP), a trichloroaniline and a dichlorocresol, together with a trace level of a related dichlorophenol (detected only using the more sensitive Selected Ion Monitoring or "SIM" analysis mode). In addition, 1-(2-aminophenyl)-ethanone was identified as a minor component in one sample (MX12006).

Tributyl phosphate (TBP) has various industrial application including use as a solvent, a flame retardant in hydraulic fluids, a carrier for certain dyes, a plasticiser in plastics and textiles, and as an antifoaming agent (WHO 1991, UNEP 2001, ATSDR 2009). TBP does not occur naturally in the environment (WHO 1991) but has been commonly detected in surface waters (Reemtsma et al. 2008, ATSDR 2009, Regnery & Puttmann 2010), and freshwater sediments (Ishikawa et al. 1985). TBP has also been detected in wastewaters discharged to surface waters from treatment facilities (Reemtsma et al. 2008, ATSDR 2009), and was recently reported in wastewater discharged from a textile manufacturing facility in China (Greenpeace 2011a).

The biodegradation of TBP is moderate to slow depending on conditions, and TBP can also be photochemically degraded in aquatic environments (Regnery & Puttmann 2010). TBP has been estimated to have a moderate potential to bioaccumulate in aquatic organisms (Sasaki et al. 1981), and has been detected in fish and in liver samples from seabirds (Evenset et al. 2009). TBP toxicity has been reported for a range of aquatic organisms and (WHO 1991, UNEP 2001, Verbruggen et al. 2005), and also in rodents. The acute toxicity to fish (LC50) ranges from 4.2 to 11.8 mg/litre (WHO 1991), with the lowest reported no effect “no observed effect concentration” (NOEC) for fish of 0.82 mg/L (UNEP 2001). A maximum permissible concentration of 66 µg/l has been derived for TBP in freshwaters to protect all species from adverse effects (Verbruggen et al. 2005). It has also been shown that TBP is toxic to certain protozoan species (Bowen et al. 2006). In rodents, long term exposure to TBP has been associated with effects on the liver in mice, including increased incidence of benign liver tumours and an increase in liver weights (Auletta et al. 1998), and effects on the bladder of rats (Arnold et al. 1997). Only limited data exist on the toxic effect of TBP on humans; an in vitro study reported that TBP has a slight inhibitory effect on human plasma cholinesterase (WHO 1991). TBP has been classified under GHS as harmful if swallowed (H302), irritating to skin (H315) and suspected of causing cancer (H351). In the EU, TBP is included on the Community Rolling Action Plan (CoRAP) list of substances for evaluation to clarify the initial suspicion that its manufacture and/or use could pose a risk to human health or the environment (ECHA 2012b)

Trichloroanilines (also known as trichlorobenzenamines) are a type of aniline derivative. These form a broad group of substances often associated with dyestuff manufacture and use, though other industrial uses exist (Stellman et al. 1998, Lacasse & Baumann 2004). Aniline derivatives can be released into the environment directly in industrial effluents from the textile industry (Pinheiro et al. 2004). Many aniline derivatives, including the compound identified in this sample (2,4,6-trichloroaniline) were recently reported by Greenpeace as present in mixed wastewaters discharged in China, which had originated in part from textile manufacturing facilities (Brigden et al. 2012b).

Many chlorinated anilines are toxic to a wide range of aquatic organisms (Dom et al. 2010, Abe et al. 2001). 2,4,6-trichloroaniline has been classified under the GHS as being very toxic to aquatic life with long lasting effects (H410), toxic if swallowed, inhaled or in contact with skin (H301, H311, H331) and has the potential to cause damage to organs through prolonged or repeated exposure (H373).

Some aniline derivatives, including certain chlorinated anilines, are listed under regulations in some countries related to the use of azo dyes in textiles due to the compound being a known or suspected carcinogen (EU 2002, SAPRC 2012). However, the chlorinated aniline detected in this sample (2,4,6-trichloroaniline) is not among those listed.

Information on the use of the dichlorocresol (2,6-dichloro-m-cresol) and 2,4-dichlorophenol in textile manufacture could not be found. A number of possible sources exist. Both these compounds can be produced from the reaction of chloramines, chemicals commonly used as water disinfectants, with either cresol or phenol respectively, chemicals which occur naturally and can be commonly found in surface waters (Heasley et al. 2004).

2,4-dichlorophenol has also been detected in bleaching effluents from pulp mills and textile plants (Krijgsheld & Van der Gen 1986), and can also be formed as a metabolite of herbicides manufactured from this dichlorophenol (Smith 1985, ATSDR 1999).

The other minor component in MX12006, 1-(2-aminophenyl)-ethanone also known as 2'-aminoacetophenone, is classified under the GHS as irritating to eyes and skin (H315, H319) and as having the potential to cause respiratory irritation (H335). No other information could be found on the properties of this compound or on the use or release from textile manufacturing.

4.2.2 Metals

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

4.3 Lavaexport

4.3.1 Organic chemical contaminants

The pattern of organic compounds identified in the single wastewater sample from the Lavaexport facility (MX12008) was very different from that in samples from the other two facilities considered in this study (Kaltex and Lavamex). The only similarities were the two THMs and two indole-based chemicals (1H-indole-2,3-dione and indolo[2,1-b]quinazoline-6,12-dione) which were minor components in MX12008 and were also identified in one sample (MX12006) from the Lavamex facility. As noted in Section 4.2, one of the indoles, 1H-Indole-2,3-dione, is classified under the GHS as irritating to eyes and skin (H315, H319) and having the potential to cause respiratory irritation (H335). No information could be found on the use or release of the identified indoles from textile manufacturing.

The two THMs (chloroform and bromodichloromethane) that were detected at trace levels in sample MX12008, and also in all samples from other facilities investigated in this study, are most likely to originate as by-products of water and sewage disinfection processes, as mentioned in Section 4.1 for this group of chemicals.

Among the other compounds identified in sample MX12008, the majority (11 compounds) were fatty alcohols, of which 1-dodecanol was the principle compound detected. Four monoterpene alcohols, naturally occurring compounds present in many plant oils, were also identified.

In general, fatty alcohols are used as starting materials in the synthesis of alcohol ethoxylates (AEs), which are widely used as non-ionic surfactants and detergents, and can be substitutes for NPEs in many applications. Although both AEs and NPEs have similar toxicity to aquatic organisms, AEs are far more readily biodegradable than NPES. The biodegradation intermediates of AEs (fatty alcohols) are less toxic than the parent surfactants and are also readily biodegradable themselves. The opposite is the case for NPEs, where the biodegradation intermediates (nonyl phenol) are far more toxic than NPEs, as well as being persistent and bioaccumulative – see Box B. The Predicted No-Effect Concentration (PNEC) for AEs is over two orders of magnitude less than that for NP (Campbell 2002). Their use as surfactants, detergents, wetting and dispersing agents is widespread in industries such as paper manufacture, oil refining, as well as textiles. Other more minor uses are as pigment dispersants in decorative emulsion paints and water-based inks as well as in cosmetics and agrochemicals.

1-Dodecanol, the principal fatty alcohol detected, is a high production volume chemical primarily used for the production of dodecyl ethoxylates and dodecyl sulfates. Although 1-dodecanol exhibits toxicity to aquatic organisms at concentrations of about 1 mg/l (IPCS 1998), it is readily degradable (Federle & Itrich 2006), as are other fatty acid alcohols such as hexadecanol, and does not give rise to environmental concerns. 1-Dodecanol has also been found to be practically non-toxic in experiments with laboratory animals as well as a result of human use experiences (IPCS 1998).

A related compound was also identified, namely 2-(dodecyloxy)ethanol, which is also known as ethylene glycol monododecyl ether. This is a metabolite of alcohol ethoxylates (AEs), and is itself readily degraded (Lajoie et al. 1997). It was not possible to identify a classification according to the GHS.

One other glycol ether was also detected; 2-(2-butoxyethoxy)ethanol, also known as diethylene glycol mono-n-butyl ether (DGMBE) or butyl diglycol. This compound is widely used as a solvent, especially in lacquers, paints and printing inks, and also as a component of water-based cleaning agents and polishes (Goen et al. 2002, Gijsbers et al. 2004). As with many other glycol ethers, this compound is readily miscible with water. Animal studies indicate that DPGME has low acute toxicity, though irritation of the lung can result in exposed workers from repeated inhalation exposure (EU 2000). DGMBE is classified under the GHS as seriously irritating to eyes (H319).

In addition, two derivatives of a long chain fatty acid (stearic acid) were identified. Esters of this type of fatty acid are present in animal or vegetable fats, oils, or wax. These substances are used in a variety of textile manufacturing processes, including use as defoaming and dispersing agents in dye formulations, and as sizing agents (IPPC 2003). They are not of particular environmental concern due to their low toxicity and being readily biodegradable, but may contribute to oxygen demands placed upon receiving waters.

As noted in Sections 4.1 and 4.2, it is noteworthy that the majority of the chemicals isolated from the sample collected from this location, including four major components, could not be reliably identified, such that their properties and potential impacts cannot be assessed.

4.3.2 Metals

The concentrations of analysed metals showed little or no sign of elevation above typical background concentrations for uncontaminated surface waters, with the exception of manganese. The sample contained dissolved manganese at 2180 mg/l, while concentrations in uncontaminated surface waters are commonly less than 200 µg/l (Salomons & Forstner 1984, ATSDR 2008).

The source of manganese in this instance is not clear as this metal is not recognised as commonly used in the textile industry (IPPC 2003). Manganese is an essential trace metal, although exposure to high levels can result in toxic effects upon for humans and animals, including serious neurotoxic effects in humans (ATSDR 2008, Michalke et al. 2007).

5. Conclusions

Overall, a diverse range of chemicals was identified in each of the samples of wastewaters collected from the three facilities investigated in this study. In some, though not all cases, the mix of chemicals included many with known hazardous properties. For some chemicals that were identified little or no information is publicly available on their toxicological properties. Accordingly, the consequences of their release to the environment remain unknown. It is also noteworthy that a significant proportion, and in some cases most, of the chemicals isolated from each sample could not be reliably identified. This is not uncommon for complex industrial effluents. As a result, the properties and potential impacts of these unidentified chemicals cannot be assessed.

For one facility (Lavamex), certain compounds identified in the wastewaters (NPEs and nonylphenol) are regulated in some regions with respect to their manufacture, use and release. This is due to the toxicity, persistence and bioaccumulative potential of nonylphenol. The use of conventional wastewater treatment processes cannot effectively address the presence of these compounds in effluents. The presence of these compounds, together with other hazardous chemicals identified in samples of wastewater discharged from this facility provide a clear example of the use and consequent release of hazardous chemicals from textile manufacturing.

Similarly, for the Kaltex facility, a number of hazardous or potentially hazardous chemicals were present in the wastewater samples. The mix of chemicals identified did not include examples that are known to be currently regulated in terms of their manufacture and use either in Mexico or elsewhere. Nonetheless, their release to the environment in wastewaters discharged from this facility does give cause for concern, particularly in light of the very large volumes of wastewater that are reported to be discharged from this facility on an ongoing basis.

Although the single sample from the Lavaexport facilities provided fewer examples of hazardous substances in the discharged wastewater compared to the other two facilities, a small number of chemicals were identified that provide additional examples of substances with known hazardous properties being released into the local environment.

This study involved the analysis of a small number of samples and, therefore, provides only a snapshot of the types of hazardous chemicals present in wastewaters discharged from these facilities. It is feasible, and even likely, that the composition of wastewaters discharged from each of these three facilities could vary over time in terms of the individual chemicals present. It may well be that compounds additional to those identified in this study are discharged in wastewaters from each of these three facilities at other times.

Due to the small number of samples analysed for this study, the results cannot be taken to be representative of all wastewaters from textile manufacturing and washing facilities in Mexico, or more broadly from these type of facilities in general. However, the three case studies do provide a snapshot that illustrates what is likely to be a much wider problem regarding the ongoing use and release of hazardous chemicals by the textile manufacturing sector in Mexico, and indeed elsewhere.

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

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Appendix 1: Details of methodologies

Analysis for Volatile Organic Compounds (VOCs)

Methods

VOCs were analysed using an Agilent 6890 gas chromatograph with an Rtx-624 column (30m, 0.25mm ID, 1.4µm film thickness) connected to an Agilent 7694 Headspace Sampler and linked to an Agilent 5973N MSD operated in EI mode. The GC oven temperature program included an initial temperature of 350°C (held for 4min), rising to 550°C at 50°C/min, and then to 2100°C at 150°C/min. The carrier gas was helium, supplied at 1ml/min. From each sample, three 10ml portions were sub-sampled into 20 ml headspace vials. One sub-sample was analysed with the GC-MS in total ion monitoring (SCAN) mode to identify as many of the volatile organic compounds present as possible. Additionally, Selected Ion Monitoring (SIM) analysis was performed simultaneously with SCAN analysis to identify the presence of the selected VOCs listed below in Table A1. Identification of compounds was carried out by matching spectra against the Wiley7N Library, employing expert judgment in order to avoid misidentifications. The two remaining sub-samples were then stored for duplicate quantitative analysis, if required, for any VOCs that had been detected in the samples through screening.

Compound	Compound
Benzene	Ethene, tetrachloro-
Benzene, 1,2,3-trichloro-	Ethene, trichloro-
Benzene, 1,2,4-trichloro-	Hexachlorobutadiene
Benzene, 1,2,4-trimethyl-	<i>m</i> - & <i>p</i> -Xylene
Benzene, 1,2-dichloro-	Methane, bromo-
Benzene, 1,3,5-trichloro-	Methane, bromochloro-
Benzene, 1,3,5-trimethyl-	Methane, bromodichloro-
Benzene, 1,3-dichloro-	Methane, chloro-
Benzene, 1,4-dichloro-	Methane, dibromo-
Benzene, bromo-	Methane, dibromochloro-
Benzene, chloro-	Methane, dichloro-
Benzene, tert-butyl-	Methane, dichlorodifluoro-
Bromoform	Methane, tetrachloro-
Chloroform	Naphthalene
Ethane, 1,1,1,2-tetrachloro-	<i>o</i> -Xylene
Ethane, 1,1,1-trichloro-	Propane, 1,2,3-trichloro-
Ethane, 1,1,2,2-tetrachloro-	Propane, 1,2-dibromo-3-chloro-
Ethane, 1,1-dichloro-	Propane, 1,3-dichloro-
Ethane, 1,2-dibromo-	Propene, 1,3-dichloro-, trans-
Ethane, 1,2-dichloro-	Styrene
Ethane, chloro-	Toluene
Ethane, hexachloro-	Toluene, 2-chloro-
Ethene, 1,1-dichloro-	Toluene, 4-chloro-
Ethene, 1,2-dichloro-, cis-	Vinyl chloride
Ethene, 1,2-dichloro-, trans-	Ethene, tetrachloro-

Table A1. List of VOC compounds for SIM analysis.

Quality control

A number of blanks of laboratory air capped at the time that sub-sampling had taken place were also analysed, alongside samples of the ultra pure reagent water which was used for the preparation of standard calibration solutions.

Analysis for extractable organic compounds

Preparation

20 µg of deuterated naphthalene was added as an Internal Standard (IS) to each portion of sample that was subject to extraction. Water samples (500 ml) 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 3 ml with a stream of clean nitrogen and cleaned up prior to analysis.

For the clean-up stage, each extract was shaken with 3 ml isopropyl alcohol and 3 ml 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 1 ml as before. 20 µg of bromonaphthalene was added to each extract as a second IS prior to GC-MS analysis.

Analysis

For the total organic compounds screening, samples were analysed using an Agilent 6890 Series II GC with Restek Rtx-XLB column (30 m, 0.25 mm ID, 0.25 µm film thickness) linked to an Agilent 5973 Inert MSD operated in EI mode and interfaced with an Agilent Enhanced Chem Station data system. The GC oven temperature program employed was as follows: an initial temperature of 350°C, held for 2 minutes, raised to 2600°C at 100°C/min, then to 3200°C at 60°C/min (held for 8 minutes). The carrier gas was helium, supplied at 1 ml/min. Identification of compounds was carried out by matching spectra against both the Wiley 7N and Pesticides Libraries, using expert judgment as necessary in order to avoid misidentifications. Additionally, both the spectra and retention times of compounds isolated from the samples were matched against those obtained during GC-MS analysis of standard mixtures containing a range of chlorinated benzenes, phenols and pesticides, polychlorinated biphenyls (PCBs), phthalates, polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons.

Quality control

A number of extraction and solvent blanks were also analysed to ensure the detection of any possible contamination resulting from sample handling in the laboratory. Any background contaminants detected in blanks are subtracted from the chromatograms obtained for the samples before mass spectra are interpreted.

Analysis for metals

Preparation

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

Analysis

Prepared sample digests were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Varian MPX Simultaneous Spectrometer. Multi-element standards at concentrations of 0.5, 1.0, 2.5 and 5.0 mg/l respectively, and matrix matched to the samples, were used for instrument calibration. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed. Analysis of the mercury content in the samples was carried out separately. Mercury (Hg) was determined using cold vapour generation ICP-AES. Ionic mercury, Hg (II), was reduced to elemental mercury, Hg (0), through reaction of the sample with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The elemental mercury vapour was carried in a stream of argon into the spectrometer. Two calibration standards were prepared, at 10 µg/l and 100 µg/l, matrix matched to the samples.

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

Concentrations were determined using a spectrophotometer at 540 nm, correcting with a blank prepared from deionised water, using standards freshly prepared from potassium dichromate at concentrations of 0, 50, 100, 200 and 500 µg/l respectively. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Quality control

Two samples were prepared for ICP analysis in duplicate and analysed to verify method reproducibility, along with a blank sample (10% v/v nitric acid in deionised water), and a mixed metal quality control solution of 4 mg/l for each metal, other than mercury at 80 µg/l. All control samples were prepared in an identical manor to the samples.

Calibration of the ICP-AES was validated by the use of quality control standards at 4 mg/l and 0.4 mg/l (water samples) prepared in an identical manner but from different reagent stocks to the instrument calibration standards. For cold vapour generation mercury analysis, the calibration was validated using two quality control standards (10 µg/l and 80 µg/l), prepared internally from different reagent stock.

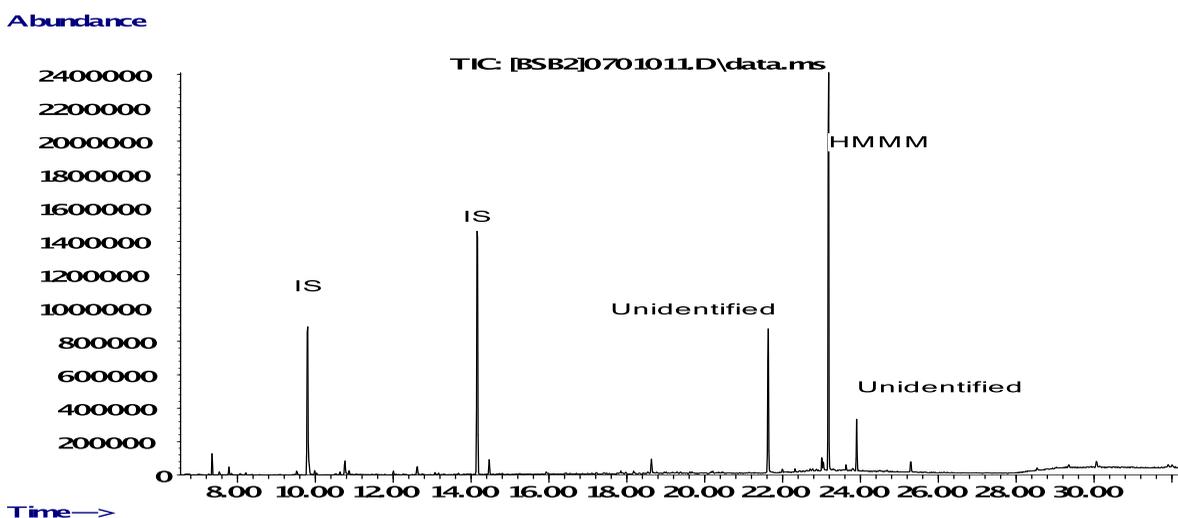
For chromium (VI) determination, two samples were prepared and analysed in duplicate, along with a blank sample, and two quality control solutions of 100 and 400 µg/l prepared in an identical manor to the samples.

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

Appendix 2: Detailed organic analytical screening data for samples MX12004 –MX12008

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

Sample code	MX12004
Location	Kaltex facility, San Juan del Río, Queretaro, Mexico
Sample type	Wastewater
Date & time	02/05/2012
Description	Collected from wastewater discharge channel of Kaltex facility



Number of compounds isolated: 22

Compounds identified to better than 90%:

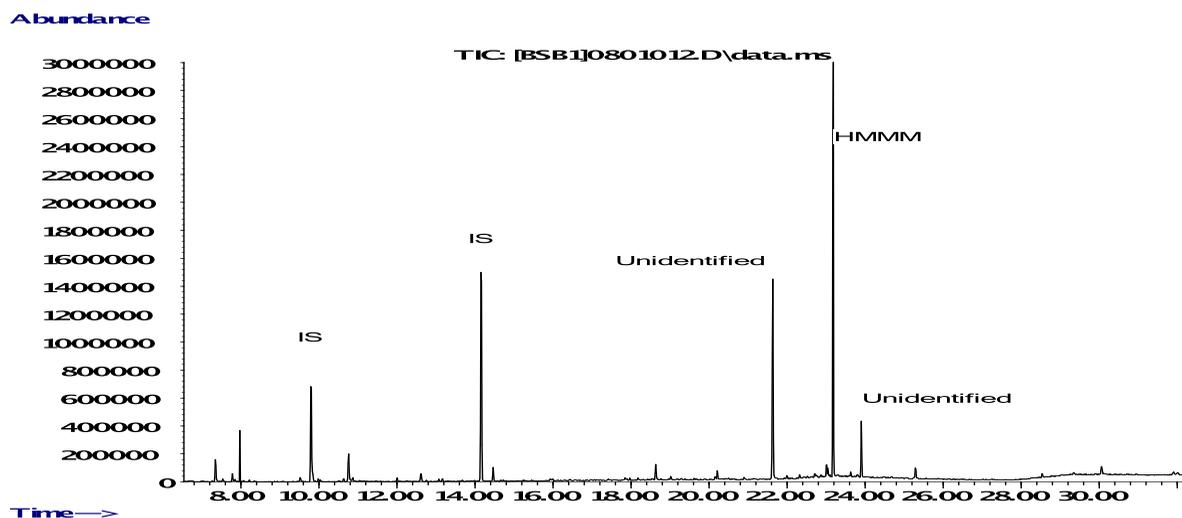
CAS#	Name
000126-86-3	2,4,7,9-Tetramethyl-5-decyne-4,7-diol (synonyms: TMDD, Surfynol)
003398-16-1	4-Bromo-3,5-dimethylpyrazole
000120-82-1	Benzene, 1,2,4-trichloro- (SIM)
000087-61-6	Benzene, 1,2,3-trichloro- (SIM)
000117-81-7	Bis(2-ethylhexyl) phthalate*
000075-25-2	Bromoform (SIM)
000067-66-3	Chloroform (SIM)
000084-69-5	Diisobutyl phthalate*
068002-20-0	Hexa(methoxymethyl)melamine (abbreviation: HMMM)
000075-27-4	Methane, bromodichloro- (SIM)
000124-48-1	Methane, dibromochloro- (SIM)
007683-64-9	Squalene

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

* indicates a minor component of the total ion chromatogram

Note: For the 2 unidentified compounds at 21.635 and 23.909 minutes, MS fragmentation patterns suggest the presence of compounds related to HMMM.

Sample code	MX12005
Location	Kaltex facility, San Juan del Río, Queretaro, Mexico
Sample type	Wastewater
Date & time	03/05/2012
Description	Collected from wastewater discharge channel of Kaltex facility



Number of compounds isolated: 24

Compounds identified to better than 90%:

CAS#	Name
000126-86-3	2,4,7,9-Tetramethyl-5-decyne-4,7-diol (synonyms: TMDD, Surfynol)
003398-16-1	4-Bromo-3,5-dimethylpyrazole
000120-82-1	Benzene, 1,2,4-trichloro- (SIM)
000087-61-6	Benzene, 1,2,3-trichloro- (SIM)
000117-81-7	Bis(2-ethylhexyl) phthalate*
000075-25-2	Bromoform (SIM)
000067-66-3	Chloroform (SIM)
000084-69-5	Diisobutyl phthalate*
000295-65-8	Cyclohexadecane
000000-00-0	Docosa-2,6,10,14,18-pentaen-22-al, 2,6,10,15,18-pentamethyl-
068002-20-0	Hexa(methoxymethyl)melamine (abbreviation: HMMM)
000075-27-4	Methane, bromodichloro- (SIM)
000124-48-1	Methane, dibromochloro- (SIM)

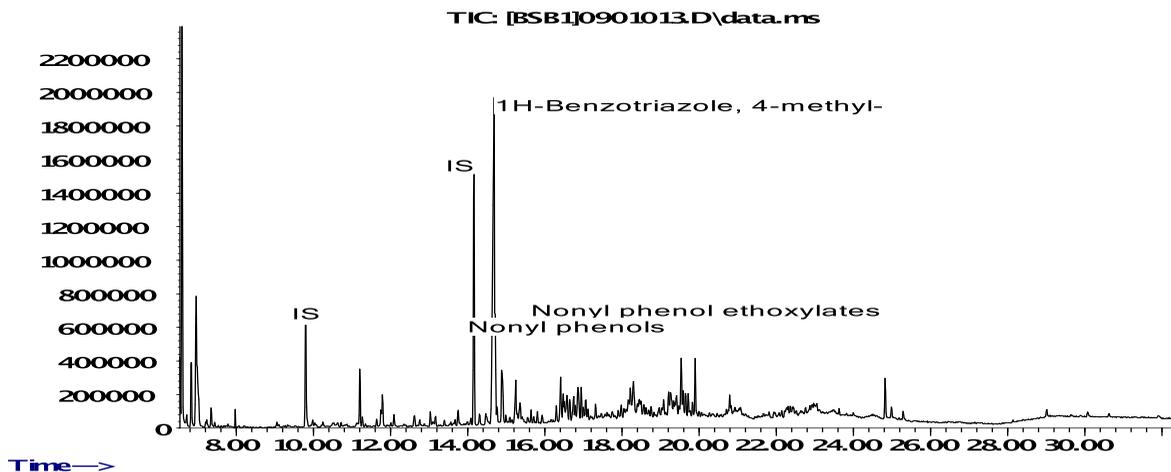
SIM indicates detection at trace levels only using Selected Ion Monitoring mode of analysis.

* indicates a minor component of the total ion chromatogram

Note: For the 2 unidentified compounds at 21.635 and 23.909 minutes, MS fragmentation patterns suggest the presence of compounds related to HMMM.

Sample code	MX12006
Location	Lavamex facility, Aguascalientes, Aguascalientes, México
Sample type	Wastewater
Date & time	02/05/2012
Description	Collected from wastewater discharge pipe of Lavamex facility

Abundance



Number of compounds isolated: 87

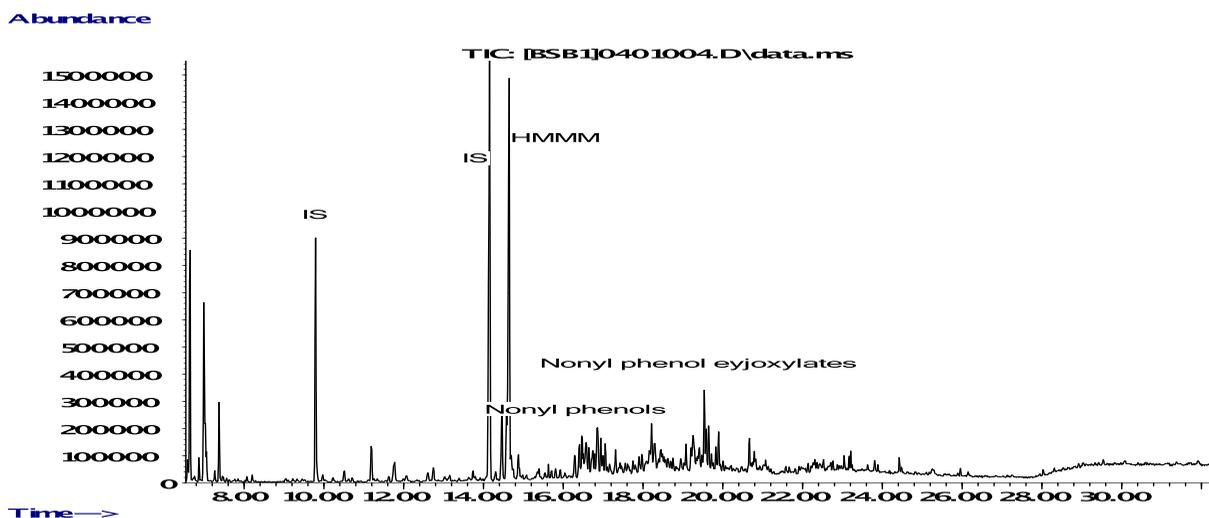
Compounds identified to better than 90%:

CAS#	Name
000095-14-7	1H-Benzotriazole*
000126-86-3	2,4,7,9-Tetramethyl-5-decyne-4,7-diol (synonyms: TMDD, Surfynol)*
000634-93-5	Benzenamine, 2,4,6-trichloro-*
000067-66-3	Chloroform (SIM)
000551-93-9	Ethanone, 1-(2-aminophenyl)-*
000126-73-8	Phosphoric acid, tributyl ester*
000000-00-0	1H-Benzotriazole, 4-methyl-
000091-56-5	1H-Indole-2,3-dione
002075-46-9	1H-Pyrazole, 4-nitro-
000087-61-6	Benzene, 1,2,3-trichloro- (SIM)
000120-82-1	Benzene, 1,2,4-trichloro- (SIM)
000108-70-3	Benzene, 1,3,5-trichloro- (SIM)
004986-50-9	Hydrazine, 1,1-dipropyl-
000000-00-0	Indolo[2,1-b]quinazoline-6,12-dione
000075-27-4	Methane, bromodichloro- (SIM)
000000-00-0	Nonylphenol ethoxylate (mixture of 10 isomers)
084852-15-3	Nonylphenol (mixture of 13 isomers)
013481-70-4	Phenol, 2,6-dichloro-3-methyl-*
000120-83-2	Phenol, 2,4-dichloro- (SIM)
007683-64-9	Squalene

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

* indicates a minor component of the total ion chromatogram

Sample code	MX12007
Location	Lavamex facility, Aguascalientes, Aguascalientes, México
Sample type	Wastewater
Date & time	03/05/2012
Description	Collected from wastewater discharge pipe of Lavamex facility



Number of compounds isolated: 51

Compounds identified to better than 90%:

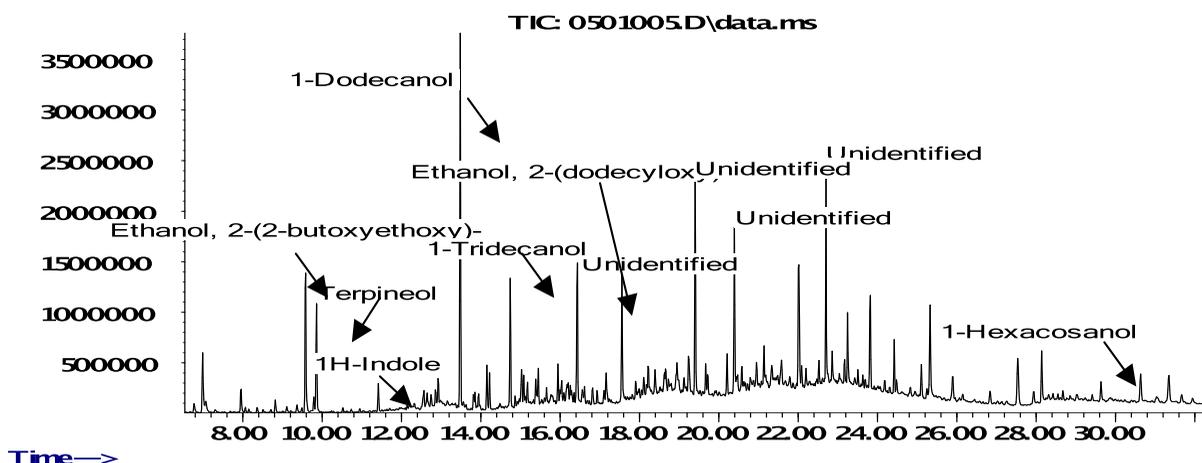
CAS#	Name
000000-00-0	1H-Benzotriazole, 4-methyl-
000126-86-3	2,4,7,9-Tetramethyl-5-decyne-4,7- (synonyms: TMDD, Surfynol)*
000634-93-5	Benzenamine, 2,4,6-trichloro-*
000087-61-6	Benzene, 1,2,3-trichloro- (SIM)
000120-82-1	Benzene, 1,2,4-trichloro- (SIM)
000108-70-3	Benzene, 1,3,5-trichloro- (SIM)
000000-00-0	Nonylphenol ethoxylate (mixture of 7 isomers)
084852-15-3	Nonylphenol (mixture of 8 isomers)
013481-70-4	Phenol, 2,6-dichloro-3-methyl-*
000120-83-2	Phenol, 2,4-dichloro- (SIM)
000126-73-8	Tributyl phosphate*

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

* indicates a minor component of the total ion chromatogram

Sample code	MX12008
Location	Lavaexport S.A DE C.V facility, Tehuacan, Puebla, Mexico
Sample type	Wastewater
Date & time	16/05/2012
Description	Collected from wastewater discharge pipe of Lavaexport S.A DE C.V facility

Abundance



Number of compounds isolated: 93

Compounds identified to better than 90%:

CAS#	Name
003913-02-8	1-Octanol, 2-butyl- *
000091-56-5	1H-Indole-2,3-dione *
000000-00-0	Indolo[2,1-b]quinazoline-6,12-dione *
000112-53-8	1-Dodecanol
000506-52-5	1-Hexacosanol
000112-70-9	1-Tridecanol
000120-72-9	1H-Indole
000112-34-5	Ethanol, 2-(2-butoxyethoxy)-
004536-30-5	Ethanol, 2-(dodecyloxy)-
000083-46-5	.beta.-Sitosterol
002425-77-6	1-Decanol, 2-hexyl-
057289-26-6	1-Dodecanol, 2-methyl-
036653-82-4	1-Hexadecanol
002490-48-4	1-Hexadecanol, 2-methyl-
000104-76-7	1-Hexanol, 2-ethyl-
010522-26-6	1-Undecanol, 2-methyl-
019780-79-1	2-Hexyl-1-octanol
007429-44-9	2-Methoxycyclohexanone
000301-02-0	9-Octadecenamide, (z)-
000067-66-3	Chloroform (SIM)
000470-82-6	Eucalyptol
000470-67-7	Isocineole
000075-27-4	Methane, bromodichloro- (SIM)
000112-61-8	Octadecanoic acid, methyl ester
000586-82-3	Terpinen-1-ol
000098-55-5	Terpineol