

Heavy metal and organic chemical contaminants in wastewater discharged from leather tanneries in the Lanús district of Buenos Aires, Argentina, April 2011

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Executive Summary

Five wastewater and three sediment samples associated with five leather tanning facilities located in the Lanús district of Buenos Aires (Argentina) were analysed at the Greenpeace Research Laboratories for the presence of heavy metal and organic chemical contaminants, as well as a single sample of water from the main Millán 'pluvial' rainwater collection system serving the district. All samples were collected between 28th April and 5th May 2011 and stored and transported refrigerated and in the dark prior to analysis. A range of metals and volatile organic chemical contaminants (VOCs) were analysed quantitatively using appropriate standards. Semi-volatile organic chemicals were analysed qualitatively (to determine their presence only) through a process of GC-MS screening in SCAN mode.

Key results can be summarized as follows:

- Concentrations of dissolved chromium in (filtered) wastewaters being discharged by all five tanneries were above what may be expected for uncontaminated surface waters, and furthermore the concentrations in effluents from the Maria Lettieri and Angel Giordano facilities were particularly high (2330 and 3430 ug/l respectively). Such high dissolved chromium concentrations, in the absence of detectable levels of chromium (VI), suggest that the less soluble form chromium (III) is being held in solution in the form of soluble complexes with other chemicals in the wastewater. Despite the apparent absence of chromium (VI) residues in these cases, the toxicity of chromium (III) to the aquatic environment (especially to algae and fish) following release of wastewaters at these levels should not be disregarded, and there is also the potential for oxidative conversion of a proportion of the chromium (III) to chromium (VI) following release.
- Chromium concentrations were even higher in the whole (unfiltered) water samples, as this includes chromium in suspended matter also. Concentrations in the five effluents ranged from 208 ug/l to more than 14 000 ug/l (14 mg/l), the highest being recorded in effluent from the Maria Lettieri facility. Sediments collecting in the effluent discharge pipes which carry wastewater from three of the facilities to the sewer system were found to contain between 3% and 8% chromium by weight, extremely high concentrations possibly resulting in part from the accumulation of insoluble chromium compounds and perhaps small fragments of tanned hide. Such heavily contaminated sediments may be acting as longer term sources of chromium to the sewer and, thereby, the aquatic environment.
- Elevated chromium concentrations were even detectable in a single sample of water collected from the Millán 'pluvial' rainwater collection system, despite the potential for dilution with run-off and discharges from other sources. Unfiltered (whole) water from the collector contained 2380 ug/l chromium (i.e. more than 2 mg/l), suggesting a clear signature of chromium inputs arising from the high density of small and medium leather processing enterprises located in the Lanús district.
- Patterns of contamination of wastewaters and sediments with semi-volatile organic compounds were complex, but showed some characteristics common to many or all of the five facilities sampled. Between 55 and 83 individual organic compounds were resolved in wastewater

samples, and between 94 and 137 in sediment samples, though in both cases the proportion of these which could be reliably identified was relatively low (e.g. only 31-49% total number of compounds in the case of the effluents). Such a result is common to organic screening analysis of complex wastewaters of this nature, but nonetheless inevitably limits the overall assessment of the nature and extent of chemical contamination.

- The biocide/preservative chemical 4-chloro-3-methylphenol (*p*-chlorocresol), known to be used in preventing degradation of hides during processing, was a prominent characteristic in all five tannery effluents and in the water from the 'pluvial' collector. This compound is classified as 'harmful' and as 'very toxic to aquatic life' under the UN Globally Harmonised System for classification and labeling of chemicals.
- Among other organic compounds commonly found were other chemicals reportedly used as biocides and leather auxiliaries, including 2-butoxyethanol phosphate, 2-(2-butoxyethoxy)ethanol, quinoline and isoquinoline, hydroxybiphenyl, benzothiazole and 2-methylthiobenzothiazole. Phthalate esters were also prominent components in some samples, including DEHP, DBP, DiBP and BBP which are all recognised as Substances of Very High Concern under the REACH Regulation within Europe because of their toxicity to reproduction.
- Effluent from two of the five tanneries (La Teresa and Angel Giordano) also contained residues of the surfactant chemicals nonylphenol ethoxylates, or NPEs (monoethoxylates in this case); that from Angel Giordano also contained the related chemical nonylphenol, also as an isomeric mix. Nonylphenol (NP) is widely recognised and regulated as a priority pollutant in water, primarily because of its endocrine- (hormone-) disrupting properties in fish and other organisms. Nonylphenol ethoxylates (NPEs) will also degrade over time to form NP. The use of these chemicals is therefore prohibited or severely restricted in Europe and in several other parts of the world.
- Traces of volatile organic compounds (VOCs), in this case chlorinated solvents and by-products of chlorination, were found in all six wastewater samples, though by far the most significantly contaminated was the effluent from the Maria Lettieri tannery. This sample contained 103 µg/l of *cis*-1,2-dichloroethene (1,2-dichloroethylene) and 216 µg/l of trichloroethene (trichloroethylene), both of which are classified under the UN GHS as harmful to the aquatic environment. In addition, trichloroethene is classified as carcinogenic (category 1B) and as a possible genotoxic substance under the UN system.

Further investigations would be necessary in order to try to identify specific process sources of the chemicals identified in the wastewater discharges and associated sediments. Nonetheless, taken together, the results from this study indicate that the leather tanning and processing industry in Lanús is a significant source of chromium and various organic chemical contaminants to the wastewater receiving system, which ultimately links to, and contaminates, the main 'pluvial' rainwater collection system. Depending on the existence, nature and effectiveness of any subsequent treatment downstream from the point at which the wastewater sample was collected from the Millán 'pluvial', such discharges could well also be a significant contributor to wider contamination of surface waters and sediments of the Riachuelo basin.

Introduction

A total of 9 waste samples, including wastewaters and associated sediments, were received from Greenpeace Argentina for analysis at the Greenpeace Research Laboratories on 19th May 2011. According to documentation supplied, all samples were collected between 28th April and 5th May 2011, from a range of industrial locations within the Lanús district of Buenos Aires, a district characterized by high numbers of small to medium sized enterprises engaged in the tanning and processing of leather and the manufacture of leather goods. Eight of the nine samples were collected from wastewater discharge pipes serving tanneries, and an additional single waste water sample was collected from the main 'pluvial' collector which carries rainwater, surface run-off and industrial discharges from the Lanús district and ultimately discharges to the Riachuelo River.

Details of the samples received are provided in Table 1 below. An additional sample (sediment from the discharge pipe associated with the Americo Gaita tannery) was broken on arrival at the Greenpeace Research Laboratories and was not therefore included in the subsequent analysis.

All nine remaining samples were analysed quantitatively for the presence of a range of metals, including chromium, the salts of which are widely used as components of tanning liquor. In the case of wastewater samples, concentrations of metals in both whole and filtered water were determined in order to distinguish between metals associated with suspended matter and those present in dissolved form in the water. All nine samples were also analysed qualitatively for the presence of semi-volatile (solvent-extractable) organic compounds. In addition, each of the six wastewater samples was analysed for the presence of volatile organic compounds (VOCs), including quantitative analysis for a range of common VOC environmental contaminants.

Sample code	Location/tannery	Sample type	Date & time	Description
AR11001	La Teresa	wastewater	28/04/2011 22:20	Collected from low flow of effluent beneath access cover in sidewalk in front of tannery, discharging to underground chamber linking to 'pluvial' collector system
AR11002		sediment	28/04/2011 22:20	
AR11003	Maria Lettieri	wastewater	28/04/2011 21:40	Collected from very low flow pipe discharging into 'pluvial' collector system
AR11004		sediment	28/04/2011 22:40	
AR11005	Angel Giordano	wastewater	29/04/2011 17:50	Collected from very high flow of effluent beneath access cover in sidewalk in front of tannery, discharging to underground chamber linking to 'pluvial' collector system
AR11006		sediment	29/04/2011 17:50	
AR11007	La Hispano	wastewater	28/04/2011 00:10	Collected from effluent pipe beneath access cover in sidewalk in front of tannery, thought to discharge to sewer
AR11008	Americo Gaita	wastewater	05/05/2011 17:00	Collected from pipe discharging very high flow of effluent
AR11009	Millán 'pluvial'	wastewater	05/05/2011 16:30	Collected from main 'pluvial' rainwater collector system serving the Lanús district

Table 1: details of samples received and analysed at the Greenpeace Research Laboratories

Materials and methods

For those samples analysed at the Greenpeace Research Laboratories, a number of different analyses were carried out on the wastewater and sediment samples. Heavy metal concentrations were determined for all samples by ICP atomic emission spectrometry (AES), following acid digestion and using appropriate certified reference materials in addition to intra-laboratory standards. For all water samples both the total concentrations in the whole (unfiltered) sample and the concentrations of dissolved forms in a filtered sample were determined separately. Hexavalent chromium concentrations were determined colorimetrically using a diphenylcarbazide method.

Semi-volatile organic compounds were isolated from each sample using accelerated solvent extraction (ASE) into a mixture of pentane and acetone for solid samples or solid phase extraction (SPE) with ethyl acetate, pentane and toluene for wastewater samples. Extracted compounds were subsequently identified as far as possible using gas chromatography/mass spectrometry (GC/MS). Volatile organic chemicals (VOCs) were identified and quantified in wastewater samples as received (with no pre-treatment) using GC/MS with HeadSpace sample introduction technique. Quantification of the detected VOCs was carried out using external standards calibration. Detailed descriptions of the sample preparation and analytical procedures are presented in the Appendix 1, including a list of VOCs quantified in the water samples, with limits of quantification (Table 6).

Results and Discussion

4.1 Metals

Concentrations of 15 metals and metalloids in filtered (dissolved metals) and in whole waters (dissolved and suspended metals) are reported in Tables 2a and 2b below. The very high concentrations of dissolved chromium detected in wastewater samples AR11003 (Maria Lettieri, 2330 ug/l) and AR11005 (Angel Giordano, 3430 ug/l) are characteristic of effluents from chrome-based leather tanning operations with only limited or no effluent treatment. The dissolved chromium concentration in effluent AR11001 from the La Teresa tannery was somewhat lower, but at 579 ug/l was nonetheless still very high compared to background concentrations expected for chromium in uncontaminated waters (median values commonly around 10 ug/l, ATSDR 2008). Concentrations were also notably above background values for effluents AR11007 (La Hispano) and AR11008 (Americo Gaita), despite being around 20-70 times lower than in effluents from the Maria Lettieri and Angel Giordano tanneries at the time of sampling.

It must be noted, however, that chromium (IV), generally considered to be the most toxic (and carcinogenic) form of chromium, was not detected in any of the filtered water samples analysed in this study. This does not in any way imply that the very high concentrations of dissolved chromium (III) are of no toxicological significance (see below) but does at least indicate that conditions in the wastewaters are not currently such that the carcinogenic form of chromium is prevalent.

Chromium is a naturally occurring element that is an essential trace nutrient at very low concentrations but which, in common with many other metals, can be toxic to plants and animals at high concentrations. Although chromium (VI) is generally considered to be more toxic than chromium (III), this is by no means exclusively the case, especially in the aquatic environment. For example, chromium (III) has been found to exert greater toxicity than chromium (VI) to algae and cyanobacteria at the base of the food web (Thompson *et al.* 2002, Jasso-Chavez *et al.* 2010, Vignati

et al. 2010), and to induce greater oxidative stress in the liver and kidneys of goldfish (Lushchak *et al.* 2009).

Chromium (III) toxicity can be limited by its lower solubility, though this can be greatly influenced through the formation of soluble complexes with other chemicals present in water or wastewater, including organic chemicals (Walsh & O'Halloran 1996, Belay 2010). Given the very high dissolved concentrations of chromium in the effluent samples analysed in this study, and the apparent absence of chromium (VI), it seems likely that the formation of such complexes is prevalent under the conditions present in the discharged wastewaters from the tannery sector. Furthermore, although conversion may be expected to be slow and partial in extent, chromium (III) can be oxidised to chromium (VI) in freshwater environments under certain conditions, especially in the presence of chemical oxidising agents (ATSDR 2008). While this may be of limited significance in relation to most waters and wastewaters, given the extremely high concentrations of dissolved chromium (III) measured in the tannery effluents in this study, the potential for such conversion to generate toxicologically significant concentrations of chromium (VI) in waters downstream from the plants cannot be excluded.

Concentrations of the other 14 dissolved metals included in the analysis showed little sign of elevation above typical background concentrations for uncontaminated surface waters (see e.g. Salomons & Forstner 1984, Alloway 1990, ATSDR 2004, 2005, Comber *et al.* 2008), with the possible exception of copper in sample AR11001 (La Teresa) and zinc in sample AR11005 (Angel Giordano). In many cases, concentrations were below limits of detection for the analytical methods employed in this study. Clearly, therefore, the over-riding concern regarding metal contamination of tannery wastewaters is that arising from the high concentrations of residual chromium salts dissolved in the water.

Despite the fact that the main 'pluvial' collector system sampled in this study receives rainwater run-off from much of the Lanús region, an elevated concentration of dissolved chromium in this water sample (136 ug/l, around 10 times typical background concentrations) also almost certainly relates to the high numbers of chrome-based tanning enterprises located in the area and discharging effluent (whether treated or untreated) to the sewer system. This sample also contained what appear to be elevated concentrations of zinc, nickel and iron (compared to background levels typical for surface waters), though these may well arise from a range of other point and diffuse sources in the area.

The predominance of chromium as the key metal contaminant of concern in the wastewaters and in the water in the 'pluvial' collector system is highlighted even further through analysis of whole (unfiltered) water samples (Table 2b above). These results therefore include both the dissolved metals and metals associated with suspended particulate matter carried along with the water and contributing to overall levels of pollution. Total chromium concentrations in the tannery effluent samples ranged from 208 ug/l (La Hispano, AR11007) to as high as 14200 ug/l (Maria Lettieri, AR11003), the latter being well over 1000 times higher than may typically be expected in uncontaminated surface waters. Even the water sampled from the main 'pluvial' collector contained more than 2000 ug/l total chromium, again illustrating the scale of the pollution problem arising from the widespread and poorly controlled use of chromium tanning liquor in the Lanús district. It

was not possible to carry out specific quantification of chromium (VI) in unfiltered samples because of interference from suspended particulates in the colourimetric assay.

Sample code	AR11001	AR11003	AR11005	AR11007	AR11008	AR11009
Location	La Teresa	Maria Lettieri	Angel Giordano	La Hispano	Americo Gaita	Millán 'pluvial'
Antimony	<50	<50	<50	<50	<50	<50
Arsenic	<50	<50	<50	<50	<50	<50
Barium	24	30	39	44	31	38
Cadmium	<5	<5	<5	<5	<5	<5
Chromium	579	2330	3430	100	47	136
Chromium (VI)	<50	<50	<50	<50	<50	<50
Cobalt	<20	<20	26	<20	<20	<20
Copper	62	<20	<20	<20	<20	<20
Iron	190	323	413	63	56	3860
Lead	<50	<50	<50	<50	<50	<50
Manganese	125	191	115	13	13	338
Mercury	<2	<2	<2	<2	<2	<2
Nickel	<20	<20	<20	<20	<20	67
Selenium	<200	<200	<200	<200	<200	<200
Vanadium	24	<20	40	36	<20	<20
Zinc	65	<10	179	11	52	306

Table 2a: concentrations of metals and metalloids (ug/l) in filtered wastewater samples

Sample code	AR11001	AR11003	AR11005	AR11007	AR11008	AR11009
Location	La Teresa	Maria Lettieri	Angel Giordano	La Hispano	Americo Gaita	Millán 'pluvial'
Antimony	<50	<50	<50	<50	<50	<50
Arsenic	<50	<50	<50	<50	<50	<50
Barium	27	35	58	54	31	80
Cadmium	<5	<5	<5	<5	<5	<5
Chromium	817	14200	9320	208	1450	2380
Chromium (VI)	n/a	n/a	n/a	n/a	n/a	n/a
Cobalt	<20	<20	46	<20	<20	<20
Copper	78	<20	<20	<20	<20	24
Iron	263	2700	2010	111	516	25300
Lead	<50	<50	<50	<50	<50	<50
Manganese	123	192	141	15	124	392
Mercury	<2	<2	<2	<2	<2	<5
Nickel	<20	<20	<20	<20	<20	98
Selenium	<200	<200	<200	<200	<200	<200
Vanadium	25	<20	60	37	<20	73
Zinc	91	65	233	11	179	2480

Table 2b: concentrations of metals and metalloids (ug/l) in whole (unfiltered) wastewater samples. n/a – not analysed

As may be expected, chromium was also by far the most significant metal contaminant identified in the sediment samples collected from the bottom and sides of the pipelines from which effluent

samples AR11001 (La Teresa), AR11003 (Maria Lettieri) and AR11005 (Angel Giordano) were collected (Table 3). Concentrations ranged from 35800 mg/kg (35.8 g/kg or just over 3% chromium by weight) in sediment from the La Teresa discharge pipe (AR 11002) to more than 80000 mg/kg (more than 80 g/kg or 8% chromium by weight) in sediments from both the Maria Lettieri and Angel Giordano discharge pipes (AR11004 and AR11006 respectively). Although these sediments had, at the time of sampling, been deposited in the discharge channel, any periodic increase in discharge flow rate could resuspend at least a portion of this material, contributing further to chromium pollution of the sewer system and ultimately water ways downstream.

Although of far less significance in terms of contaminant loading and toxicity, all three sediment samples also contained notably high concentrations of zinc (between 515 and 1000 mg/kg). Sample AR11002 (La Teresa) contained 4.5 mg/kg of mercury, while sample AR11004 (Maria Lettieri) contained 236 mg/kg of lead, though in both cases the likely specific process sources of these contaminants within the tanneries are not known.

Sample code	AR11002	AR11004	AR11006
Location	La Teresa	Maria Lettieri	Angel Giordano
Antimony	<20	<20	<20
Arsenic	46	73	71
Barium	95	252	85
Cadmium	<1	<1	<1
Chromium	35800	88500	82900
Chromium (VI)	n/a	n/a	n/a
Cobalt	24	33	24
Copper	105	78	42
Lead	102	236	23
Manganese	103	204	58
Mercury	4.5	<0.2	0.7
Nickel	31	56	27
Selenium	<30	<30	<30
Vanadium	104	127	89
Zinc	668	515	1000

Table 3: concentrations of metals and metalloids (mg/kg) in sediment samples. n/a – not analysed

4.2 Organic contaminants

All five tannery effluents and the wastewater sample from the 'pluvial' collector serving the Lanús district were found to contain a range of organic chemical contaminants (Table 4 and Appendix 2), some of which may be of natural origin (e.g. arising from the animal hides themselves), though a high proportion of those which could be identified appear to be man-made chemicals. Of the 55-83 individual compounds isolated from these effluents, only between 19 and 30 could be identified using GC-MS spectral library matching to any degree of reliability. Typically, therefore, between 50 and 70% of the organic compounds isolated from the effluent samples remain unidentified and

therefore cannot be assessed in relation to their significance as environmental pollutants. A slightly higher proportion of organic chemical contaminants (24 of 37, 65%) could be identified in the wastewater from the 'pluvial' collector, and included a number of man-made chemicals which were commonly found in the tannery effluents themselves. In effluents containing complex mixtures of organic contaminants, it is not unusual to be able to identify only a fraction of those present to a high degree of reliability even using state-of-the-art techniques, though this inevitably limits the overall assessment of the likely impacts of the wastes.

A number of organic chemicals and chemical groups were common to most of the tannery effluents sampled, including the preservative 4-chloro-3-methylphenol (found in all wastewaters and one sediment sample), 2-butoxyethanol phosphate (also used as a leather preservative), 2-(2-butoxyethoxy)ethanol, quinoline and isoquinoline, hydroxybiphenyl, benzothiazole and 2-methylthiobenzothiazole (the latter two substances also used as dye-stuffs or preservatives in leather goods). Phthalate esters were also identified in some of the samples, DEHP in sample AR11001 (La Teresa), BBP in AR11005 (Angel Giordano), DiBP in AR11007 (La Hispano) and a combination of BBP, DBP and DEP in the main 'pluvial' collector (AR 11009). Phthalate esters are used as solvents and additives in a very wide range of industrial chemical formulations, including in leather finishing products, though their likely process origin in effluents in the current study cannot be determined without further investigation. DEHP, BBP, DBP and DiBP have recently been listed as Substances of Very High Concern under the European REACH Regulation (ECHA 2011).

4-chloro-3-methylphenol (*p*-chlorocresol) is used as a general biocide to prevent micro-organisms degrading organic material, including in metal working fluids, pharmaceuticals & cosmetics, glues, paints & inks and textile & leather goods (EC 2002), as well as being an intermediate in the manufacture of chlorophenoxy herbicides (Irmak *et al.* 2004). 4-chloro-3-methylphenol is classified under the United Nations Globally Harmonised System of Classification and Labelling of Chemicals (GHS) as harmful in contact with skin and if swallowed (H302 & H317) and as very toxic to aquatic life (H400).

Perhaps of even greater significance, however, was the prominent presence of 10 isomers of the detergent-related chemical nonylphenol monoethoxylate in effluent sample AR11001 (La Teresa), and the similar presence of 11 isomers of this compound and 8 isomers of the closely related parent chemical nonylphenol in effluent sample AR11005 (Angel Giordano). Nonylphenol is widely recognised as a priority pollutant in water systems primarily because of its long environmental persistence and well described hormone (endocrine) disrupting properties, and nonylphenol ethoxylates undergo degradation in the environment to form nonylphenol.

Nonylphenol (NP) is a group of related (isomeric) chemicals that are manufactured for a range of specialised industrial uses as well as to produce nonylphenol ethoxylates (NPEs), a group of non-ionic surfactants. NPEs have long been used as surfactants (e.g. in detergents), emulsifiers, dispersants and/or wetting agents in, for example, the manufacture and finishing of textiles and leather goods, as well as in pesticide formulations and other agricultural products and in some water-based paints (OSPAR 2004, Guenther *et al.* 2002). Once released to the environment, NPEs can degrade back to NP isomers, which are persistent, bioaccumulative and toxic to aquatic life. 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, Brigden *et al.* 2010b). NP has also been detected as a contaminant in human tissues (Lopez-Espinosa *et al.* 2009).

The most widely recognised hazard associated with NP is its estrogenic activity, i.e. its 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 which 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 the significance of these findings has been challenged by some. Impacts on immune system cells *in vitro* have also been described (Iwata *et al.* 2004).

For more than a decade, NP/NPEs have been recognised as priority pollutants in the freshwater and marine environment on a regional basis, being included on the first list of chemicals for priority action under the (North-East Atlantic) OSPAR Convention (with the target therefore of cessation of discharges, emissions and losses to the marine environment by 2020) and subsequently listed as a 'priority hazardous substance' under the European Union (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). Furthermore, within the EU, products 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 2003).

Although it was not possible to quantify concentrations of NP and NPEs in these samples as part of the current study, the high relative peak areas attributable to these compounds in the sample extracts (see Figure 1), combined with the high concerns relating to the environmental impacts of this chemical group, clearly justify urgent further investigation in order to identify possible sources within the tanning process. It is also worth noting that, in addition to the NP/NPEs identified, traces of another hormone disrupting chemical, bisphenol F (Cabaton *et al.* 2009), could also be identified in three of the wastewater samples (AR11005, AR11007 and AR11009).

In contrast to the wastewater samples, the three sediment samples collected from the tannery effluent discharge pipes contained quite different patterns of organic contaminants, as may be expected from the process of partitioning of the relatively more water-soluble organics (such as phenols, thiazoles, alcohols and quinolines) to the water phase and of the more lipophilic compounds (hydrocarbons) to the more organic-rich sediment fraction. Although total numbers of compounds isolated from the sediments were higher than from the related effluents (between 94 and 137 chemicals in total), a similarly high proportion (64-70%) remain unidentifiable using GC-MS screening techniques. Of those which could be identified, medium to long-chain linear hydrocarbons and a mixture of linear and branched alkylbenzenes predominated. Although at least some of the aliphatic (long-chain) hydrocarbons present may have arisen as components of the natural fatty compounds washed out from the hides being processed in the tannery facilities, the linear and branched alkylbenzenes (LABs and BABs) are perhaps more likely to have arisen from the use of man-made linear alkylbenzene sulphonates (LAS) and branched alkylbenzene sulphonates (BAS) in detergent preparations for such cleaning operations (OECD 2005). LABs and BABs are relatively common contaminants in urban and industrial wastewater for this reason and, while their origin

cannot be determined with certainty in these cases, the use of LAS and BAS detergents is perhaps a likely source.

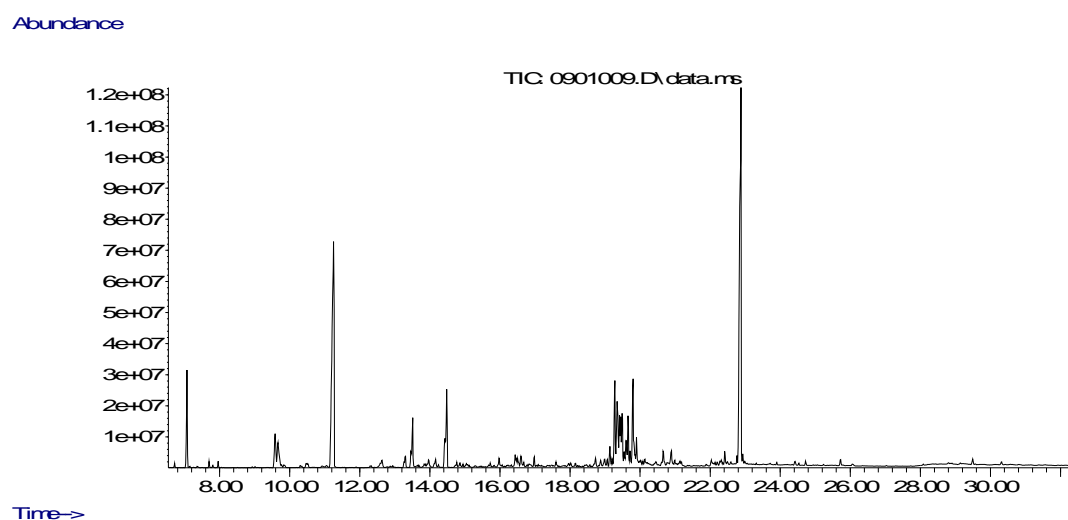
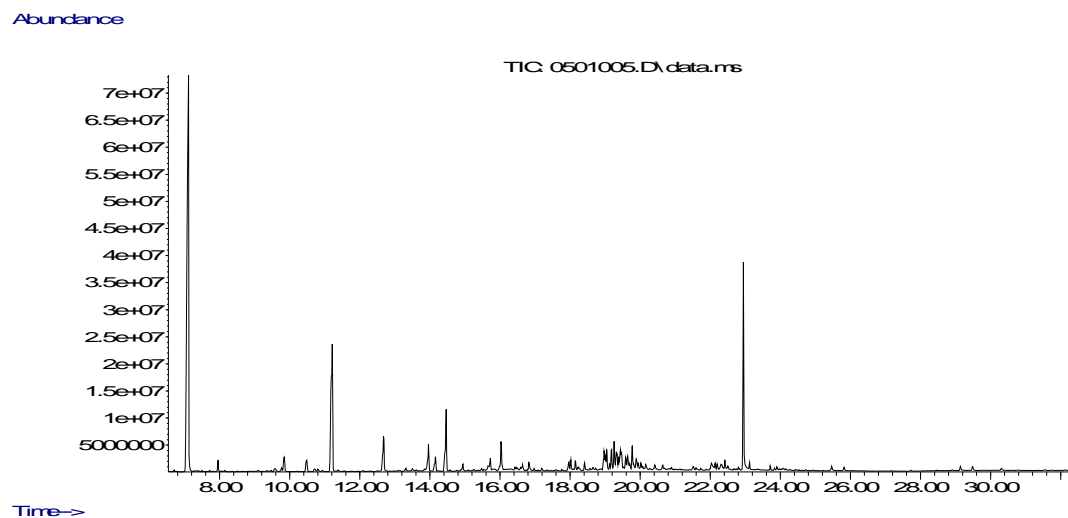


Figure 1: total ion chromatograms for solvent extracts of wastewater samples a) AR11001 and b) AR11005, showing a range of peaks corresponding to individual and/or groups of semi-volatile substances. Nonylphenol ethoxylates appear in both chromatograms as a series of closely packed peaks eluting between 19 and 20 minutes. Nonylphenol itself appears as a smaller set of peaks in the region of 16.5 minutes. Discrete peaks eluting at 11 minutes and approximately 23 minutes were identified as 4-chloro-3-methylphenol and phthalate esters respectively.

Sample code	AR11001	AR11002	AR11003	AR11004	AR11005	AR11006	AR11007	AR11008	AR11009
Location	La Teresa		Maria Lettieri		Angel Giordano		La Hispano	Americo Gaita	Millán 'pluvial'
Sample type	w/w	sed	w/w	sed	w/w	sed	w/w	w/w	w/w
Number of compounds isolated	59	137	62	94	83	114	59	55	37
Number of compounds identified to >90%	20	44	19	25	30	42	20	27	24
Percentage identified to >90%	34%	32%	31%	27%	36%	37%	34%	49%	65%
Nonylphenol isomers					8 isomers				
Nonylphenol monoethoxylate isomers	10 isomers				11 isomers				
4-chloro-3-methylphenol	✓		✓		✓	✓	✓	✓	✓
4-chloro-3,5-dimethylphenol								✓	✓
4-methylphenol					✓		✓	✓	
Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-	✓	✓		✓	✓	✓			
Phenol, 4,4'-methylenebis-(Bisphenol F)					✓		✓		✓
4,4'-sulfonylbisphenol	✓						✓		
2-butoxyethanol phosphate	✓		✓		✓			✓	
2-(2-butoxyethoxy)ethanol	✓		✓		✓		✓	✓	
Quinoline			✓		✓				✓
Isoquinoline	✓		✓		✓		✓	✓	
Phthalate esters	DEHP				BBP DPhMP		DiBP		DEP DBP BBP
o-hydroxybiphenyl	✓		✓		✓			✓	✓
Benzothiazole	✓		✓		✓		✓	✓	✓
2-(methylthio)benzothiazole	✓		✓		✓			✓	✓
1,2,4-trimethylbenzene	✓	✓		✓		✓			
2-ethyl-1-hexanol			✓		✓			✓	
1,1'-[oxybis(2,1-ethanedioxy)]bis butane			✓					✓	
Alkylbenzenes (linear & branched)		12 congeners		1 congener		9 congeners			
Linear hydrocarbons		C13-C24 C26 C28-C29 C31-C32		C16-C26 C28-C32		C13 C15-17 C19-C20 C33-C26 C30-C32		C17 C19-20	C17 C20 C24

Table 4: summary of results of qualitative organic screening of all wastewater and sediment samples for semi-volatile (solvent extractable) organic compounds, including numbers of individual compounds isolated and identified to >90% reliability, and an indication of presence for the compounds most commonly identified in these samples including, in the case of alkylphenols and their ethoxylates and branched alkylbenzenes, a record of the numbers of individual isomers or congeners resolved. w/w – wastewater; sed – sediment; BBP – butylbenzylphthalate, DPhMP – diphenylmethylphthalate, DiBP – di-iso-butylphthalate, DEP – diethylphthalate, DBP – di-n-butylphthalate.

Sample code	AR 10001	AR 10003	AR 10005	AR 10007	AR 10008	AR 10009
Location	La Teresa	Maria Lettieri	Angel Giordano	La Hispano	Americo Gaita	Millán 'pluvial'
Methane, dichloro-	2	n/d	n/d	n/d	n/d	22
Ethene, 1,2-dichloro-, trans-	n/d	n/d	n/d	n/d	n/d	n/d
Ethene, 1,2-dichloro-, cis-	n/d	103	n/d	n/d	n/d	<1
Chloroform	5	3	11	<2	n/d	20
Ethane, 1,2-dichloro-	n/d	n/d	n/d	n/d	n/d	n/d
Ethene, trichloro-	n/d	216	n/d	n/d	n/d	n/d
Ethene, tetrachloro-	n/d	10	<1	n/d	n/d	n/d
Benzene, 1,2-dichloro-	n/d	n/d	n/d	n/d	24	3
Benzene, 1,3-dichloro-	n/d	n/d	n/d	n/d	n/d	n/d
Benzene, 1,4-dichloro-	n/d	n/d	n/d	n/d	n/d	n/d
Benzene, 1,2,3-trichloro-	n/d	n/d	n/d	n/d	n/d	n/d
Benzene, 1,2,4-trichloro-	n/d	n/d	n/d	n/d	n/d	n/d

Table 5: concentrations of selected volatile organic compounds (VOCs) in wastewater samples (ug/l). Limits of quantification 2 ug/l for chloroform, 1 ug/l for all others. n/d - not detected.

In addition to the semi-volatile (solvent extractable) organic chemical contaminants identified above, a number of common volatile organic compounds were also identified (and quantified down to limits of 1-2 ug/l) in several of the effluent samples (Table 5). While chloroform (trichloromethane) was detected at relatively trace levels in samples AR11001, AR11003, AR11005 and AR11009, substantially higher levels of the industrial solvents 1,2-dichloroethene (103 ug/l) and trichloroethene (216 ug/l) were found in sample AR11003 arising from the Maria Lettieri tannery, as well as lower levels of tetrachloroethene. Both 1,2-dichloroethene (1,2-dichloroethylene or 1,2-DCE) and trichloroethene (trichloroethylene or TCE) are harmful to humans and the environment, being listed under the United Nations Globally Harmonised System of Classification and Labelling of Chemicals (GHS) as harmful to aquatic life with the potential for long-lasting effects (H412). In addition, trichloroethene is also identified as a carcinogen (Cat. 1B, H350) and as having potential genotoxic effects (H341), and as a result has been identified as a Substance of Very High Concern under REACH Regulations in Europe (ECHA 2011). Although precise origins of such chemicals cannot be determined from these results, it seems likely that such contaminants appear in the wastewater as a result of specific industrial uses in the tannery. Among other VOCs detected were 24 ug/l of 1,2-dichlorobenzene in sample AR11008 and 22 ug/l of dichloromethane in the wastewater flowing through the main 'pluvial' collector at the time of sampling.

Conclusions

The results of this investigative study, though limited in scope to a small number of tanning operations in the Lanús area, nonetheless demonstrate the complexity of industrial discharges from the sector to the underground sewer/collector system, discharges which are acting as significant point sources of chemicals of clear concern for the environment and human health.

In terms of metals, chromium is the key concern in both dissolved and suspended/particulate fractions of these wastewaters, reaching concentrations which in many cases were thousands of times higher than may typically be expected for uncontaminated surface waters. Although the

carcinogenic form of chromium, chromium (VI), was not in evidence in these wastewater samples, the extremely high levels of chromium (III) which were present are of toxicological concern nonetheless. Furthermore, despite the relatively high volumes of water commonly flowing through the main Millán 'pluvial' collector system, which inevitably includes rainfall run-off from a wide area, a signal of elevated chromium concentrations was still detectable in the sample collected, suggesting that the Lanús region as a whole is acting as a substantial source of chromium to the downstream water system and, ultimately, the wider environment. Sediments collected from the points of discharge from the tanneries were found to be extremely heavily contaminated with chromium, and may act as a long-term reservoir of the metal to the water collection system.

The complexity of the wastewaters was best illustrated by the presence of a wide array of organic contaminants, some of which may well have been of natural origin (arising, perhaps, from the natural fats and oils washed from the hides during preparation) but including many more that were clearly man-made in nature. Phenols, alcohols, thiazoles and quinolines were particularly evident in the wastewater samples, including 4-chloro-3-methylphenol (known to be used as a preservative in the leather industry, as well as in many other sectors) which was present in all five tannery effluents and in the wastewater in the Millán 'pluvial'. Of even greater concern, however, was the confirmed presence of 10 isomers of nonylphenol monoethoxylate in sample AR11001 (from the La Teresa facility) and 8 isomers of nonylphenol and 11 of nonylphenol monoethoxylate in sample AR11005 (from the Angel Giordano facility), compounds which are widely recognised as priority pollutants in relation to freshwater systems because of their known endocrine (hormone) disrupting properties.

Traces of certain volatile organic compounds (VOCs) were also identified in the wastewater samples, including some known to be used as industrial solvents. Of particular concern were the substantially higher concentrations of the industrial solvents 1,2-dichloroethene (103 ug/l) and trichloroethene (216 ug/l) found in sample AR11003 arising from the Maria Lettieri tannery.

Overall, a higher number of individual organic compounds could be isolated from the three sediment samples collected than from the associated effluents, but with differing patterns of contamination reflecting the differential partitioning of substances to the water and sediment phase. Medium to long-chain hydrocarbons (C13-C32) were particularly prominent in the sediments, for example, as were a range of branched alkylbenzenes in sediments AR11002 (La Teresa) and ART11006 (Angel Giordano), which may arise from the use of branched alkylbenzene sulphonates (BAS) in detergent formulations at these facilities.

Further investigations would be necessary in order to try to identify specific process sources of the chemicals identified in the wastewater discharges and associated sediments. Nonetheless, taken together, the results from this study indicate that the leather tanning and processing industry in Lanús is a significant source of chromium and various organic chemical contaminants to the wastewater receiving system, which ultimately links to, and contaminates, the main 'pluvial' rainwater collection system. Depending on the existence, nature and effectiveness of any subsequent treatment downstream from the point at which the wastewater sample was collected from the Millán 'pluvial', such discharges could well also be a significant contributor to wider contamination of surface waters and sediments of the Riachuelo basin.

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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 35°C (held for 4min), rising to 55°C at 5°C/min, and then to 210°C at 15°C/min. The carrier gas was helium, supplied at 1ml/min. From each sample, three 10ml portions were sub-sampled into 20ml headspace vials. One sub-sample was analysed with the GC-MS in total ion monitoring (SCAN) mode to identify as many of the volatile organic compounds present as possible. Identification of compounds was carried out by matching spectra against the Wiley7N Library, employing expert judgment in order to avoid misidentifications. The two remaining sub-samples were then used for duplicate quantitative analysis for those halogenated (chlorinated, brominated and mixed) VOCs which had been detected in the samples through screening. Quantification was performed in Selective Ion Monitoring (SIM) mode using a 5 point external calibration method. Chlorinated VOCs quantified in the water samples with limits of quantification are presented in Table 6 below.

Quality control

Limits of quantification (LOQ) were determined as the lowest concentration in the linear regression used for quantification. A number of blanks of laboratory air capped at the time that sub-sampling had taken place were also analysed, alongside samples of the ultra pure reagent water which was used for the preparation of standard calibration solutions. The initial calibration curve for each compound of interest was verified immediately prior to sample analysis by analyzing a calibration standard at a concentration near the midpoint concentration for the calibration range of the GC-MS.

Compound	LOQ, µg/l	r ²
Benzene, 1,2,3-trichloro-	1	1.000
Benzene, 1,2,4-trichloro-	1	0.999
Benzene, 1,2-dichloro-	1	1.000
Benzene, 1,3-dichloro-	1	1.000
Benzene, 1,4-dichloro-	1	1.000
Benzene, chloro-	2	0.996
Chloroform	1	0.998
Ethane, 1,1,1-trichloro-	1	1.000
Ethane, 1,2-dichloro-	1	0.998
Ethene, 1,2-dichloro-, cis-	1	0.999
Ethene, 1,2-dichloro-, trans-	2	0.999
Ethene, tetrachloro-	1	0.996
Ethene, trichloro-	1	0.998
Methane, dichloro-	1	0.992
Toluene, 2-chloro-	2	0.999
Vinyl chloride	1	0.999

Table 6. Limit of quantification (LOQ) is the lowest concentration in the linear regression (r² – corresponding correlation coefficient) used for quantification.

Analysis for extractable organic compounds

Preparation

20 µg of deuterated naphthalene was added as an Internal Standard (IS) to each portion of sample that was subject to extraction. For sediment samples, approximately 10 g of each sample (wet weight) was extracted employing Accelerated Solvent Extraction (ASE) technique using Dionex ASE-350 with a mixture of pentane and acetone 3:1, at a temperature of 100°C. Water samples (500ml) were prepared using solid phase extraction technique with Dionex AutoTrace workstation, eluting with ethyl acetate followed by a mixture of pentane and toluene (95:5). Obtained extracts were concentrated to a volume of 3ml with a stream of clean nitrogen and cleaned up prior to analysis.

Clean-up procedures were the same for the crude extracts from both aqueous and sediment samples. Each extract was shaken with 3ml isopropyl alcohol and 3ml TBA-reagent (mixture of 3% tetrabutylammonium hydrogen sulphate and 20% sodium sulphite in deionised water) and left to stand until the aqueous and organic phases had separated. The pentane phase was collected and eluted through a Florisil column, using a 95:5 pentane:toluene mixed eluent, and the cleaned extract concentrated to a final volume of 1ml as before. 20 µg of bromonaphthalene was added to each extract as a second IS prior to GC-MS analysis.

Analysis

For the total organic compounds screening, samples were analysed using an Agilent 6890 Series II GC with Restek Rtx-XLB column (30m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5973 Inert MSD operated in EI mode and interfaced with an Agilent Enhanced Chem Station data system. The GC oven temperature program employed was as follows: an initial temperature of 35°C, held for 2 minutes, raised to 260°C at 10°C/min, then to 320°C at 6°C/min (held for 8min). The carrier gas was helium, supplied at 1ml/min. Identification of compounds was carried out by matching spectra against both the Wiley 7N and Pesticides Libraries, using expert judgment as necessary in order to avoid misidentifications. Additionally, both the spectra and retention times of compounds isolated from the samples were matched against those obtained during GC-MS analysis of standard mixtures containing a range of chlorinated benzenes, phenols and pesticides, polychlorinated biphenyls (PCBs), phthalates, polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons.

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

A representative portion of each sediment sample was air dried to constant weight, homogenised, sieved through a 2mm mesh and then ground to a powder using a pestle and mortar. Approximately 0.5g of each sample was digested with 2 ml concentrated hydrochloric acid and 8 ml concentrated nitric acid, firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 180°C over 15 minutes followed by holding

at 180°C for a further 15 minutes. Following cooling, digests were filtered and made up to 50ml with deionised water.

For water samples, to obtain total metal concentrations, a representative portion of each whole sample was acidified by the addition of concentrated nitric acid to give a final concentration of 10% v/v. Separately, a portion of each whole sample was filtered 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 10 mg/l respectively, and matrix matched to the samples, were used for instrument calibration. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed. Analysis of the mercury content in the samples was carried out separately. Mercury (Hg) was determined using cold vapour generation ICP-AES. Ionic mercury, Hg (II), was reduced to elemental mercury, Hg (0), through reaction of the sample with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The elemental mercury vapour was carried in a stream of argon into the spectrometer. Two calibration standards were prepared, at 10 µg/l and 100 µg/l, matrix matched to the samples.

Concentrations of chromium (VI) were determined colorimetric for each water sample following filtration. 0.5 ml of a 1,5-diphenylcarbazide testing solution (freshly prepared from 0.4 g of 1,5-diphenylcarbazide, 20 ml acetone, 20 ml ethanol, 20 ml orthophosphoric acid solution and 20 ml of demineralised water) was added to 9.5 ml of each filtered sample. The solution was mixed and let to stand for 10 minutes to allow full colour development. Concentrations were determined using a spectrophotometer at 540 nm, correcting with a blank prepared from deionised water, using standards freshly prepared from potassium dichromate at concentrations of 0, 50, 100, 200 and 500 µg/l respectively. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Quality control

For sediment samples, one sample was prepared in duplicate and analysed to verify method reproducibility, along with an identically prepared blank. To check the method efficiency, certified reference material (CRM) samples were prepared in an identical manner; GBW07311, stream sediment certified by the China National Analysis Centre for Iron and Steel, Beijing, China, and LGC6187, leachable metals in river sediment certified by the Laboratory of the Government Chemist, UK.

For water samples, 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, 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 8 mg/l and 0.8 mg/l (sediment samples) or 4 mg/l and 0.4 mg/l (water samples) prepared in an identical manner but from different reagent stocks to the instrument calibration standards. For cold vapour

generation mercury analysis, the calibration was validated using two quality control standards (10 µg/l and 80 µg/l), prepared internally from different reagent stock.

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

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

Appendix 2: detailed semi-volatile organic analytical screening data for samples AR1100—AR11009

Detailed screening data arising from GC-MS analysis of solvent extracts of each of the samples are presented below. These data list only those semi-volatile organic compounds identified following solvent extraction and do not include any volatile organic compounds (VOCs) identified through separate headspace GC-MS analysis of sub-samples; the VOCs identified in each sample are listed in Table 5 in the main body of the report. Only those semi-volatile substances identified to greater than 90% quality match (following verification by expert interpretation) are listed here.

Sample code	AR11001
Location	La Teresa
Sample type	Wastewater
Date & time	28/04/2011 @ 22:40
Description	Collected from low flow of effluent beneath access cover in sidewalk in front of tannery, discharging to underground chamber linking to 'pluvial' collector system

Number of compounds isolated: 59

Compounds identified to better than 90%:

CAS#	Name
000117-81-7	1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester
000777-95-7	1,6-Dioxacyclododecane-7,12-dione
000000-00-0	2,6-Di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one
000098-55-5	3-Cyclohexene-1-methanol, .alpha., .alpha.4-trimethyl-
000301-02-0	9-Octadecenamide, (z)-
000095-63-6	Benzene, 1,2,4-trimethyl-
000095-16-9	Benothiazole
000615-22-5	Benothiazole, 2-(methylthio)-
032390-26-4	Binaphthyl sulfone
000057-88-5	Cholest-5-en-3-ol (3.beta.)-
013151-43-4	Cyclodecane, methyl-
000112-34-5	Ethanol, 2-(2-butoxyethoxy)-
000078-51-3	Ethanol, 2-butoxy-, phosphate (3:1)
000119-65-3	Isoquinoline
000000-00-0	Nonylphenol monoethoxylate, mix of 10 isomers
000090-43-7	o-Hydroxybiphenyl
000119-47-1	Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-
000128-37-0	Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-
000080-09-1	Phenol, 4,4'-sulfonylbis-
000059-50-7	Phenol, 4-chloro-3-methyl-

Sample code	AR11002
Location	La Teresa
Sample type	Sediment
Date & time	28/04/2011 @ 22:40
Description	Collected from low flow of effluent beneath access cover in sidewalk in front of tannery, discharging to underground chamber linking to 'pluvial' collector system

Number of compounds isolated: 137

Compounds identified to better than 90%:

CAS#	Name
013466-78-9	.delta.3-Carene
018835-33-1	1-Hexacosene
000000-00-0	14-.beta.-H-Pregna
004537-15-9	Benzene, (1-butylheptyl)-
004537-11-5	Benzene, (1-butylhexyl)-
004534-50-3	Benzene, (1-butylnonyl)-
002719-63-3	Benzene, (1-butylloctyl)-
002400-00-2	Benzene, (1-ethyldecyl)-
004536-87-2	Benzene, (1-ethylnonyl)-
004534-52-5	Benzene, (1-ethylundecyl)-
004536-88-3	Benzene, (1-methyldecyl)-
002719-61-1	Benzene, (1-methylundecyl)-
002719-62-2	Benzene, (1-pentylheptyl)-
004534-49-0	Benzene, (1-pentylloctyl)-
002719-64-4	Benzene, (1-propylnonyl)-
000095-63-6	Benzene, 1,2,4-trimethyl-
000824-90-8	Benzene, 1-butenyl-
054676-39-0	Cyclohexane, 2-butyl-1,1,3-trimethyl-
006975-98-0	Decane, 2-methyl-
013151-34-3	Decane, 3-methyl-
000138-86-3	dl-Limonene
000629-97-0	Docosane
000544-85-4	Dotriacontane
000112-95-8	Eicosane
000629-94-7	Heneicosane
000630-04-6	Hentriacontane
000629-78-7	Heptadecane
000630-01-3	Hexacosane
000544-76-3	Hexadecane
000090-12-0	Naphthalene, 1-methyl-
000091-57-6	Naphthalene, 2-methyl-
000571-61-9	Naphthalene, 1,5-dimethyl-
000582-16-1	Naphthalene, 2,7-dimethyl-
000630-03-5	Nonacosane
000629-92-5	Nonadecane
000630-02-4	Octacosane
000593-45-3	Octadecane
000629-62-9	Pentadecane
000128-37-0	Phenol, 2,6-bis(1,1-dimethylethyl)-4-methyl-

000646-31-1	Tetracosane
000629-59-4	Tetradecane
000638-67-5	Tricosane
000629-50-5	Tridecane
017301-23-4	Undecane, 2,6-dimethyl-

Sample code	AR11003
Location	Maria Lettieri
Sample type	Wastewater
Date & time	28/04/2011 @ 21:40
Description	Collected from very low flow pipe discharging into 'pluvial' collector system

Number of compounds isolated: 62

Compounds identified to better than 90%:

CAS#	Name
010482-56-1	.alpha.-Terpineol
000586-62-9	.alpha.-Terpinolene
000104-76-7	1-Hexanol, 2-ethyl-
000934-34-9	2(3H)-Benzothiazolone
001677-27-6	3H-1,2-Benzodithiol-3-one
000108-67-8	Benzene, 1,3,5-trimethyl-
000095-16-9	Benzothiazole
000615-22-5	Benzothiazole, 2-(methylthio)-
000112-73-2	Butane, 1,1'-[oxybis(2,1-ethanedioxy)]bis-
013151-34-3	Decane, 3-methyl-
000112-34-5	Ethanol, 2-(2-butoxyethoxy)-
000112-07-2	Ethanol, 2-butoxy-, acetate
000078-51-3	Ethanol, 2-butoxy-, phosphate (3:1)
055320-06-4	Heneicosane, 11-decyl-
000119-65-3	Isoquinoline
000090-43-7	o-Hydroxybiphenyl
001119-40-0	Pentanedioic acid, dimethyl ester
000059-50-7	Phenol, 4-chloro-3-methyl-
000091-22-5	Quinoline

Sample code	AR11004
Location	Maria Lettieri
Sample type	Sediment
Date & time	28/04/2011 @ 22:40
Description	Collected from very low flow pipe discharging into 'pluvial' collector system

Number of compounds isolated: 94

Compounds identified to better than 90%:

CAS#	Name
000112-41-4	1-Dodecene
040710-42-7	1-Hentetracontanol
001120-36-1	1-Tetradecene
074630-69-6	4-Undecene, 5-methyl-, (z)-
004534-53-6	Benzene, (1-methyldodecyl)-
000095-63-6	Benzene, 1,2,4-trimethyl-
000629-97-0	Docosane
000544-85-4	Dotriacontane
000112-95-8	Eicosane
000630-04-6	Hentriacontane
000593-49-7	Heptacosane
000629-78-7	Heptadecane
000630-01-3	Hexacosane
000544-76-3	Hexadecane
000630-03-5	Nonacosane
000629-92-5	Nonadecane
000630-02-4	Octacosane
000593-45-3	Octadecane
000629-99-2	Pentacosane
000128-37-0	Phenol, 2,6-di- <i>tert</i> -butyl-4-methyl- (BHT)
000646-31-1	Tetracosane
000638-68-6	Triaccontane
000638-67-5	Tricosane
000000-00-0	Tritriacontane
000000-00-0	Tritriacontane,13,17,21-trimethyl-

Sample code	AR11005
Location	Angel Giordano
Sample type	Wastewater
Date & time	29/04/2011 @ 17:50
Description	Collected from very high flow of effluent beneath access cover in sidewalk in front of tannery, discharging to underground chamber linking to 'pluvial' collector system

Number of compounds isolated: 83

Compounds identified to better than 90%:

CAS#	Name
010482-56-1	(-)-.alpha.-Terpineol
000085-68-7	1,2-Benzenedicarboxylic acid, butyl benzyl ester
000523-31-9	1,2-Benzenedicarboxylic acid, bis(phenylmethyl) ester
000112-41-4	1-Dodecene
000104-76-7	1-Hexanol, 2-ethyl-
000111-87-5	1-Octanol
001120-36-1	1-Tetradecene
002437-56-1	1-Tridecene
000126-86-3	2,4,7,9-Tetramethyl-5-decyne-4,7-diol
000078-59-1	2-Cyclohexen-1-one, 3,5,5-trimethyl-
000526-73-8	Benzene, 1,2,3-trimethyl-
000108-67-8	Benzene, 1,3,5-trimethyl-
000095-16-9	Benzothiazole
000615-22-5	Benzothiazole, 2-(methylthio)-
032390-26-4	Binaphthyl sulphone
074663-85-7	Cyclopropane, nonyl-
000112-34-5	Ethanol, 2-(2-butoxyethoxy)-
004536-30-5	Ethanol, 2-(dodecyloxy)-
000078-51-3	Ethanol, 2-butoxy-, phosphate (3:1)
000119-65-3	Isoquinoline
000000-00-0	Nonyl-phenol mix of 8 isomers
000000-00-0	Nonylphenol monoethoxylate, mix of 11 isomers
000090-43-7	o-Hydroxybiphenyl
000123-95-5	Octadecanoic acid, butyl ester
000128-37-0	Phenol, 2,6-di-tert-butyl-4-methyl- (BHT)
000620-92-8	Phenol, 4,4'-methylenebis-
000059-50-7	Phenol, 4-chloro-3-methyl-
000106-44-5	Phenol, 4-methyl-
000091-22-5	Quinoline
000602-09-5	[1,1'-Binaphthalene]-2,2'-diol

Sample code	AR11006
Location	Angel Giordano
Sample type	Sediment
Date & time	29/04/2011 @ 17:50
Description	Collected from very high flow of effluent beneath access cover in sidewalk in front of tannery, discharging to underground chamber linking to 'pluvial' collector system

Number of compounds isolated: 114

Compounds identified to better than 90%:

CAS#	Name
000112-41-4	1-Dodecene
006765-39-5	1-Heptadecene
000629-73-2	1-Hexadecene
013360-61-7	1-Pentadecene
001120-36-1	1-Tetradecene
095008-11-0	10-Heneicosene
000000-00-0	14-.Beta.-h-pregna
000000-00-0	14-Methyldotriacontane
074630-69-6	4-Undecene, 5-methyl-, (z)-
041446-66-6	5-Tetradecene, (e)-
004537-15-9	Benzene, (1-butylheptyl)-
004534-50-3	Benzene, (1-butylonyl)-
002719-63-3	Benzene, (1-butylloctyl)-
002400-00-2	Benzene, (1-ethyldecyl)-
002400-02-4	Benzene, (1-ethyloctadecyl)-
004534-52-5	Benzene, (1-ethylundecyl)-
004534-53-6	Benzene, (1-methyldodecyl)-
004534-49-0	Benzene, (1-pentyloctyl)-
002400-03-5	Benzene, (1-propylheptadecyl)-
002719-64-4	Benzene, (1-propylonyl)-
000095-63-6	Benzene, 1,2,4-trimethyl-
000620-14-4	Benzene, 1-ethyl-3-methyl-
000544-85-4	Dotriacontane
000112-95-8	Eicosane
000629-94-7	Heneicosane
000630-04-6	Hentriacontane
000629-78-7	Heptadecane
000630-01-3	Hexacosane
000544-76-3	Hexadecane
000638-36-8	Hexadecane, 2,6,10,14-tetramethyl-
000582-16-1	Naphthalene, 2,7-dimethyl-
000629-92-5	Nonadecane
000629-99-2	Pentacosane
000629-62-9	Pentadecane
000128-37-0	Phenol, 2,6-di-tert-butyl-4-methyl- (BHT)
000059-50-7	Phenol, 4-chloro-3-methyl-
003386-33-2	Octadecane, 1-chloro-
002425-54-9	Tetradecane, 1-chloro-
000646-31-1	Tetracosane

000638-68-6	Triacontane
000638-67-5	Tricosane
000629-50-5	Tridecane

Sample code	AR11007
Location	La Hispano
Sample type	Wastewater
Date & time	28/04/2011 @ 00:10
Description	Collected from effluent pipe beneath access cover in sidewalk in front of tannery , thought to discharge to sewer

Number of compounds isolated: 59

Compounds identified to better than 90%:

CAS#	Name
000084-69-5	1,2-Benzenedicarboxylic acid, di- <i>iso</i> -butyl ester
010482-56-1	.alpha-Terpineol
000112-70-9	1-Tridecanol
000934-34-9	2(3H)-Benzothiazolone
000126-86-3	2,4,7,9-Tetramethyl-5-decyne-4,7-dione
000135-19-3	2-Naphthalenol
000100-01-6	Benzenamine, 4-nitro-
000095-16-9	Benzothiazole
000076-22-2	Camphor
001839-88-9	Cyclohexane, 1,2,3-trimethyl-
054446-78-5	Ethanol, 1-(2-butoxyethoxy)-
000112-34-5	Ethanol, 2-(2-butoxyethoxy)-
000098-86-2	Ethanone, 1-phenyl-
000119-65-3	Isoquinoline
002467-02-9	Phenol, 2,2'-methylenebis-
000620-92-8	Phenol, 4,4'-methylenebis-
000080-09-1	Phenol, 4,4'-sulfonylbis-
000120-83-2	Phenol, 2,4-dichloro-
000059-50-7	Phenol, 4-chloro-3-methyl-
000106-44-5	Phenol, 4-methyl-

Sample code	AR11008
Location	Americo Gaita
Sample type	Wastewater
Date & time	05/05/2011 @ 17:00
Description	Collected from pipe discharging very high flow of effluent

Number of compounds isolated: 55

Compounds identified to better than 90%:

CAS#	Name
000112-48-1	1,2-Dibutoxy-ethane
001599-67-3	1-Docosene
000104-76-7	1-Hexanol, 2-ethyl-
000112-88-9	1-Octadecene
001120-36-1	1-Tetradecene
000120-72-9	1H-Indole
000933-67-5	7-Methylindole
000095-50-1	Benzene, 1,2-dichloro-
003622-84-2	Benzenesulfonamide, N-butyl-
000095-16-9	Benzothiazole
000615-22-5	Benzothiazole, 2-(methylthio)-
000112-73-2	Butane, 1,1'-[oxybis(2,1-ethanediyloxy)]bis-
000057-88-5	Cholest-5-en-3-ol (3.beta.)-
074663-85-7	Cyclopropane, nonyl-
000112-95-8	Eicosane
000112-34-5	Ethanol, 2-(2-butoxyethoxy)-
002136-71-2	Ethanol, 2-(hexadecyloxy)-
000078-51-3	Ethanol, 2-butoxy-, phosphate (3:1)
000629-78-7	Heptadecane
000119-65-3	Isoquinoline
000629-92-5	Nonadecane
000090-43-7	o-Hydroxybiphenyl
000085-01-8	Phenanthrene
000128-39-2	Phenol, 2,6-bis(1,1-dimethylethyl)-
000088-04-0	Phenol, 4-chloro-3,5-dimethyl-
000059-50-7	Phenol, 4-chloro-3-methyl-
000106-44-5	Phenol, 4-methyl-

Sample code	AR11009
Location	Millán 'pluvial'
Sample type	Wastewater
Date & time	05/05/2011 @ 16:30
Description	Collected from main 'pluvial' rainwater collector system serving the Lanús district

Number of compounds isolated: 37

Compounds identified to better than 90%:

CAS#	Name
000085-68-7	1,2-Benzenedicarboxylic acid, butyl benzyl ester
000084-74-2	1,2-Benzenedicarboxylic acid, dibutyl ester
000084-66-2	1,2-Benzenedicarboxylic acid, diethyl ester
000078-59-1	2-Cyclohexen-1-one, 3,5,5-trimethyl-
004707-33-9	2H-Naphtho[2,3-b]pyran-5,10-dione, 3,4-dihydro-2,2-dimethyl-
000526-73-8	Benzene, 1,2,3-trimethyl-
000095-50-1	Benzene, 1,2-dichloro-
000095-16-9	Benzothiazole
000615-22-5	Benzothiazole, 2-(methylthio)-
000076-22-2	Camphor
024851-98-7	Dihydro methyl jasmonate
000112-95-8	Eicosane
000629-94-7	Heneicosane
000629-78-7	Heptadecane
002216-51-5	L-(-)-Menthol
000119-64-2	Naphthalene, 1,2,3,4-tetrahydro-
000090-43-7	o-Hydroxybiphenyl
000593-45-3	Octadecane
000620-92-8	Phenol, 4,4'-methylenebis-
000088-04-0	Phenol, 4-chloro-3,5-dimethyl-
000059-50-7	Phenol, 4-chloro-3-methyl-
000091-22-5	Quinoline
000646-31-1	Tetracosane
000000-00-0	Z-5-nonadecene