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**Laguna Lake, The Philippines:
Industrial Contamination Hotspots**

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Laguna Lake, The Philippines: industrial contamination hotspots

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1. Introduction

Contamination of natural water resources by discharges from the industrial sector in the Philippines continues to be a significant problem. In 2007, Greenpeace launched the Water Patrol to document the impact of water pollution on local communities in the Philippines. Within the framework of this project, several industrial sites located around Laguna Lake were visited in July 2010. During these visits, samples of wastewater discharges into creeks and tributaries of Laguna Lake and corresponding sediment or soil samples were collected. The sites which were chosen for investigation in this study were those accommodating potentially polluting facilities in the area.

The selection of the facilities was based on the following criteria:

- facility operations were thought to involve the use of toxic chemicals;
- the facility discharged wastewater directly into Laguna Lake or one of its tributaries;
- in some cases, the facility had been previously identified by government agencies as a polluting industry and listed in the black or red lists by the Laguna Lake Development Authority or the Department of Environment and Natural Resources.

Four facilities located to the south-east of Laguna Lake were targeted in the current study: Mayer Textile; Philippine Industrial Sealants and Coatings Corporation (PIS); TNC Chemicals; Carmelray 1 Industrial Park. Wastewater is discharged from these facilities into the San Juan River and the San Cristobal River. Two other target facilities were located to the north of Laguna Lake – Unilever-RFM (including Hansson Papers, Banner Plasticard Inc and a number of food manufacturers) and Litton Mills. These facilities discharge into creeks which ultimately drain into the Marikina River and Pasig River respectively.

2. Sampling sites description

16 samples were taken consisting of 8 wastewaters, 6 sediments and 2 soils. These were collected from the six target industries discharging wastewaters into watercourses which ultimately drain into Laguna Lake. A description of the samples, their origin, the type of facility involved and a site description are presented in Table 1. Locations of sampling sites are presented in sketch maps in Fig 1-6.

Industry name	Industry type	Lab Code	Sample type	Sampling site description
Mayer textile	Textile dyeing	PH10001	waste water	Sample collected from a pipe located on the wall of the facility. Wastewater discharges into a concrete channel located alongside the facility.
		PH10002	sediment	Sample collected from the concrete channel about 1m downstream of the sampling point PH10001.
		PH10003	waste water	Sample collected from the pipe located at the end of the concrete channel. At this point wastewater discharges into a creek which ultimately drains into Laguna Lake.
		PH10004	sediment	Sample collected from the creek immediately below the wastewater discharge.
PIS	Sealants and Coatings	PH10005	sediment	Sample collected (about 270m upstream) from the same creek as sample PH10004 below the discharge pipe from the facility. There was no wastewater discharge from the pipe at the sampling time.
TNC Chemicals	Nitrocellulose and industrial pigments	PH10006	waste water	Sample collected from the 1 st wastewater outfall about 35m below the actual discharge pipe which comes from the facility located on the cliff. Wastewater directly discharged into San Juan River, a tributary of Laguna del Bay.
		PH10007	soil	Sample collected from the bank of the San Juan River at the place where the wastewater discharge reaches ground level
		PH10008	waste water	Sample collected from 2 nd wastewater outfall located about 20m downstream of the 1 st discharge. Wastewater directly discharged into San Juan River, a tributary of Laguna del Bay.
Litton Mills	Textile/garments spinning, dyeing, weaving	PH10009	waste water	Sample collected from pipe discharging wastewater into the Pasig River, which flows into Manila Bay.
		PH10010	sediment	Sample collected from the edge of the Pasig River close to the end of the facility's discharge pipe. This river also receives wastewater from the city's sewage treatment facility and characterized by high siltation and vigorous aquatic vegetation growth .
Carmelray 1	Mixed industrial park, predominantly electronics and semiconductors	PH10011	waste water	Sample collected from the pipe discharging wastewater into Cauang Cauang Creek which flows into the San Cristobal River, a tributary of Laguna Lake.
		PH10012	sediment	Sample collected from Cauang Cauang Creek below the wastewater discharge pipe which ends about 5 meters above the level of the creek.
Unilever RFM Compound	Including Hansson Papers (paper mill, paper and paper products, paper recycling); Banner Plasticard Inc. (ATM & ID cards, etc. offset and silkscreen printing for plastic products); various food manufacturing companies	PH10013	waste water	Sample collected from the 1 st pipe discharging wastewater from compound into the Marikina River, a tributary of Laguna Lake.
		PH10014	sediment	Sample collected from inside of the 1 st discharge pipe
		PH10015	waste water	Sample collected from the 2 nd pipe discharging wastewater from compound into the Marikina River, a tributary of Laguna Lake. This discharge is located about 10m downstream of the 1 st pipe from the compound.
		PH10016	soil	Sample collected from the bank of the Marikina River, about 1m from the point of discharge from the 2 nd pipe.

Table 1. Description of sampling sites and samples collected around the Laguna Lake, Philippines, 2010.



Fig. 1. Location of sampling sites around the Laguna Lake, Philippines, 2010.

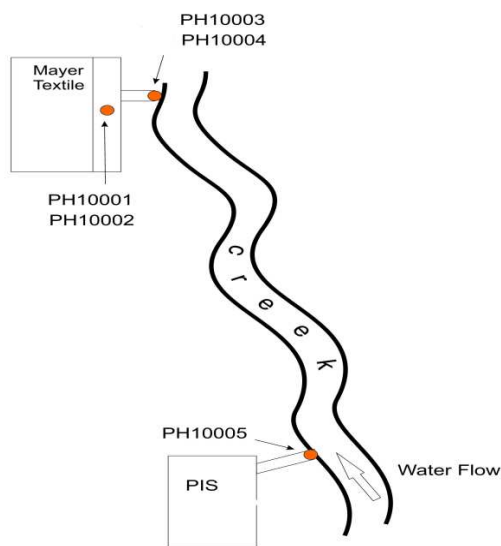


Figure 2. Sampling points for Mayer Textile and Philippine Industrial Sealants and Coatings Corporation (PIS) discharging into an unnamed creek which flows into Laguna Lake, Calamba, Laguna, Philippines, 2010.

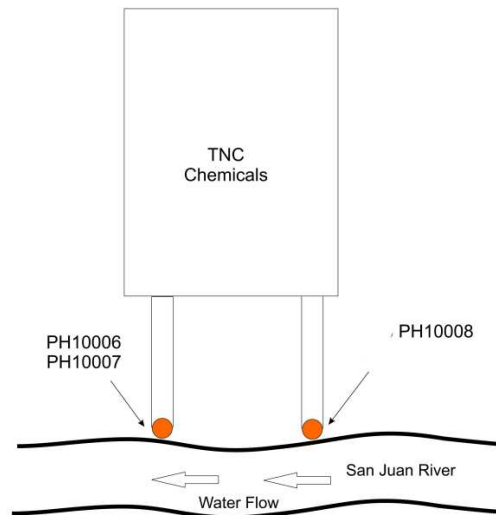


Figure 3. Sampling points for TNC Chemicals at a place of discharge to the San Juan River, a tributary of Laguna Lake, Calamba, Laguna, Philippines, 2010.

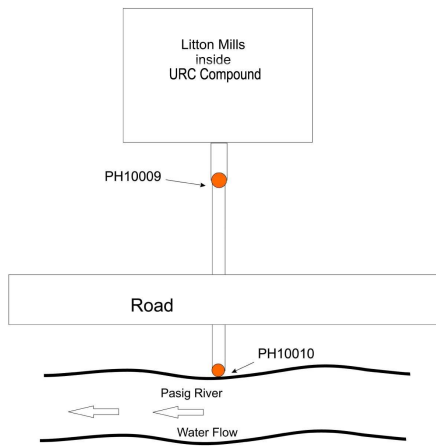


Figure 4. Sampling point for Litton Mills in Pasig City, Metro Manila, Philippines, 2010.

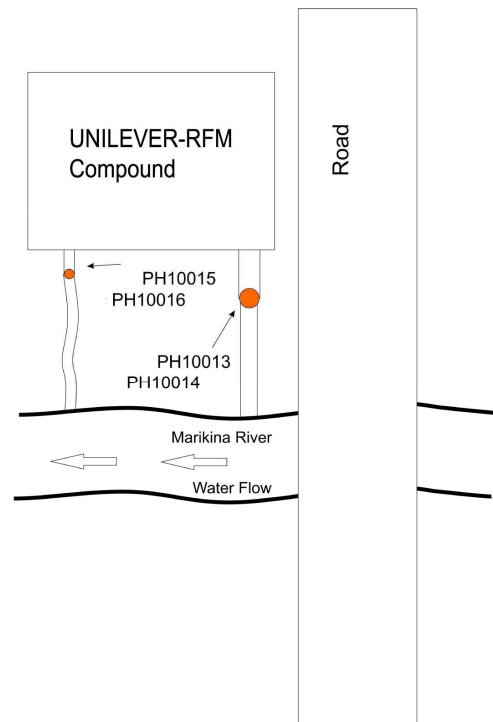


Figure 5: Sampling points for Unilever-RFM Compound, Pasig City, Metro Manila, Philippines, 2010.

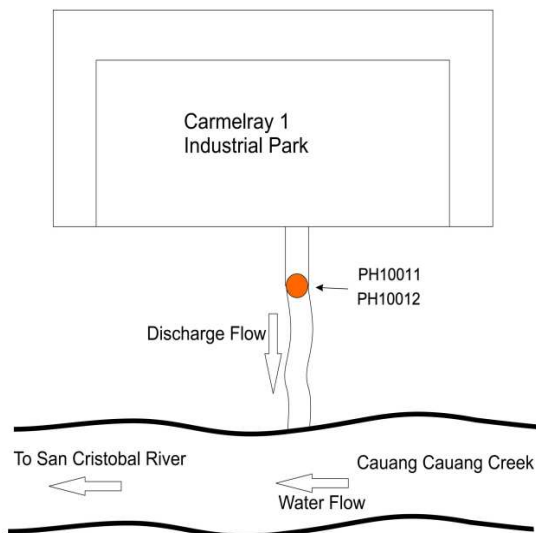


Figure 6. Sampling points for Carmelray 1 Industrial Park, Calamba, Laguna, Philippines, 2010.

3. Results and discussion

Wastewater, sediment and soil samples collected around industrial sites located in the Laguna Lake area, Philippines, were subjected to quantitative analysis for heavy metals and a qualitative organic screening analysis. In addition, wastewater samples were analysed for the presence of volatile organic compounds (VOCs) and additional quantitative analyses were performed for 16 chlorinated VOCs. None of the wastewater samples analysed in this study exhibited concentrations of chlorinated VOCs above the limit of quantification (LOQ). Accordingly these results are not included in the discussion below. Detailed methodology for the analyses performed in this study together with LOQs for VOCs are presented in the Appendix. Results for heavy metals and organic screening analyses are presented in Tables 2-3. The results for each industrial site considered in this study are discussed below.

3.1 Mayer Textile

Four samples were collected in the vicinity of the Mayer Textile industry located in Calamba, Laguna, comprised of two wastewater samples PH10001 and PH10003 and two sediment samples PH10002 and PH10004.

The wastewater PH10001 contained chromium at a concentration of 196 µg/l (in soluble form), somewhat higher than would be expected for an uncontaminated surface water. The most toxic form of chromium, hexavalent chromium, was not present in this sample above the method detection limit of 50 µg/l. Copper, nickel and zinc were detected at concentrations of 102 µg/l (dissolved concentration 56 µg/l), 59 µg/l, and 117 µg/l respectively, which is slightly higher than is generally found for uncontaminated surface waters. Concentrations detected in uncontaminated surface waters are typically below 10 µg/l for chromium, 20 µg/l for nickel, and 50 µg/l for zinc. Background concentrations of soluble copper in uncontaminated surface waters are typically below 10 µg/l. By contrast, vanadium was present in sample PH10001 at a relatively high concentration of 314 µg/l (in soluble form). Concentrations of this metal in surface waters can vary considerably depending on geography and underlying geology but are generally below 100 µg/l, and often far less than this. For comparison, all other wastewater samples analysed in this study contained levels of vanadium in the range of <20 to 76 µg/l.

Sample PH10001 contained a large number of organic compounds of which only a small proportion (26%) could be reliably identified. Identified chemicals included:

- two phthalate esters, dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP), toxic and persistent chemicals used primarily as plasticizers, but which also have known uses in textile manufacture;
- three isomers of nonylphenol, widely known toxic and persistent organic chemicals with estrogenic properties. These are mainly used to produce nonylphenol ethoxylates used as detergents and may degrade back to nonylphenol;
- nitroaniline, which is used in the manufacture of textile dyes, and is very harmful to aquatic organisms if released as a pollutant;
- quinoline and two its methylated derivatives, methyl- and dimethylquinoline;
- alcohols and related compounds: 2-(dodecyloxy)- and 2-(hexadecyloxy)ethanol, non-ionic surfactants;
- four carboxylic acids: octanoic, nonanoic, hexadecanoic, and dodecanoic acid;
- phthalic anhydride; used as a dyestuff precursor chemical;
- alkylated benzenes: possible components of linear alkyl benzene sulfonate detergents;
- derivative and metabolite of the antioxidant butylated hydroxytoluene (BHT): 2,6-Di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one;
- nonylcyclopropane,
- benzylacetaldehyde; and
- several aliphatic hydrocarbons.

Sediment sample PH10002 was collected from the channel into which wastewaters are directly discharged from the facility. It contained high concentrations of copper and zinc (both approximately 6-7 times higher than levels typically found in uncontaminated freshwater sediment), together with lesser concentrations of vanadium. Despite their slightly elevated concentrations in wastewater sample PH10001, the levels of chromium and nickel in the sediment (PH10002) were not substantially higher than typical background levels for freshwater sediments. Organic compounds detected in this sediment sample were mainly

presented by a range of aliphatic hydrocarbons together with alkylated benzenes and polycyclic aromatic hydrocarbons (PAHs). This pattern of organic pollutants may indicate contamination by oil and/or petroleum products.

Sample PH10003 collected at the point discharge from the canal into the creek *via* a pipe was not significantly contaminated with any of the quantified metals. Their concentrations were either below limits of detection for the methods used or within the ranges expected for uncontaminated surface waters. This may be as a result of the wastewater being diluted by the receiving waters in the channel or through adsorption to sediments. At the same time, several organic compounds detected in the original discharge (sample PH10001) were also present in the water sample PH10003 taken from the channel. These included DBP; six isomers of nonylphenol; BHT derivative/metabolite; and aliphatic hydrocarbons. This strongly suggests that contaminants discharged from the Mayer Textile facility can be transported from the channel to the creek and ultimately enter Laguna Lake where creek ends. In addition to these chemicals, sample PH10003 also contained organic compounds such as chlorinated anilines and 2,4-di-*tert*-butylphenol, which were not detected in the wastewater sample PH10001. The source of these pollutants to the channel waters is unclear and needs to be further investigated. However, possible variation in the wastewater composition discharged at different times cannot be ruled out as a possible explanation.

Sediment/soil sample PH10004 was collected from the ground beneath the flow of water from the channel through the pipe where it enters the creek. The concentrations of copper and zinc in this sample were slightly higher (approx 2-4 times) than levels typically found in uncontaminated soils or freshwater sediments. The presence of almost identical levels in soil/sediment sample (PH10005) collected from the nearby pipe of PIS (together with the absence of copper and zinc at elevated levels in the wastewater) suggests the copper and zinc levels are not necessarily due to discharges but may, in fact, be due to locally elevated levels of these metals in soils in this area. Organic compounds detected in sample PH10004 were similar to those found in the sediment sample PH10002 (alkylated benzenes, aliphatic and polycyclic aromatic hydrocarbons) but were less numerous.

3.2 P I S

A single sample of sediment PH10005 was collected from area below the outfall pipe from the PIS facility which is located about 270m upstream of the Mayer Textile plant. There was no discharge from the pipe at the time of sampling. No wastewater sample was therefore collected from the PIS facility. The concentrations of copper and zinc in sample PH10005 were slightly higher (approx 2-4 times) than levels typically found in uncontaminated soils or freshwater sediments. It is important to note that the levels of these metals were almost identical to those detected in sample PH10004 collected nearby the discharge pipe from the Mayer Textile facility downstream. It is possible, therefore, that concentrations of these metals (as noted above) are generally elevated in this area and may not reflect input from the wastewater discharges. No organic compounds were detected which could be reliably identified in this sample.

Industry name Sample Type	Mayer textile					PIS	TNC Chemicals					
	PH10001		PH 10002	PH 10003		PH 10004	PH 10005	PH 10006		PH 10007	PH 10008	
	wastewater		sediment	wastewater		sediment	sediment	wastewater		soil	wastewater	
	total	dissolved		total	dissolved			total	dissolved		total	dissolved
METAL	µg/l	µg/l	mg/kg	µg/l	µg/l	mg/kg	mg/kg	µg/l	µg/l	mg/kg	µg/l	µg/l
Antimony	<50	<50	48	<50	<50	<20	<20	<50	<50	<20	<50	<50
Arsenic	<50	<50	<20	<50	<50	<20	<20	<50	<50	<20	<50	<50
Barium	320	313	86	20	16	283	292	17	14	78	59	33
Cadmium	<5	<5	<1	<5	<5	<1	<1	<5	<5	<1	<5	<5
Chromium	224	196	77	<20	<20	14	14	<20	<20	44	210	206
Chromium (VI)	-	<50	-	-	<50	-	-	-	<50	-	-	<50
Cobalt	34	25	6	<20	<20	39	38	<20	<20	3	<20	<20
Copper	102	56	298	<20	<20	119	120	<20	<20	7	29	27
Lead	<50	<50	44	<50	<50	9	10	<50	<50	13	<50	<50
Manganese	700	683	429	14	<10	1340	1340	41	<10	24	162	162
Mercury	<2	<2	<0.5	<2	<2	<0.5	<0.5	<2	<2	<0.5	<2	<2
Nickel	59	57	25	<20	<20	12	12	<20	<20	50	124	125
Selenium	<200	<200	<30	<200	<200	<30	<30	<200	<200	<30	<200	<200
Vanadium	331	314	246	57	32	150	144	21	22	20	76	76
Zinc	117	115	715	17	<10	146	144	<10	<10	49	29	25
№ of isolated organic compounds	124		50	56		36	1	27		none	96	
№ of reliably identified (% total)	32(26%)		41(82%)	22(39%)		15(42%)	none	11(31%)		none	19(20%)	
Phthalate esters	2		n/d	1		n/d	n/d	1		n/d	n/d	
Nonylphenol, mix of isomers	3		n/d	6		n/d	n/d	n/d		n/d	n/d	
2,4-Di- <i>tert</i> -butylphenol	n/d		n/d	1		n/d	n/d	1		n/d	n/d	
Nitrophenols & nitrocresols	n/d		n/d	n/d		n/d	n/d	n/d		n/d	2	
Chlorinated anilines	n/d		n/d	2		n/d	n/d	n/d		n/d	n/d	
Nitroaniline	1		n/d	n/d		n/d	n/d	n/d		n/d	n/d	
Chlorinated toluenes	n/d		n/d	4		n/d	n/d	n/d		n/d	n/d	
Nitrotoluenes	n/d		n/d	n/d		n/d	n/d	n/d		n/d	3	
Quinoline & derivatives	3		n/d	n/d		n/d	n/d	n/d		n/d	n/d	
Phthalic anhydride	1		n/d	n/d		n/d	n/d	n/d		n/d	1	
Alcohols & derivatives	5		n/d	n/d		n/d	n/d	n/d		n/d	n/d	
Carboxylic acids and/or their esters	4		n/d	n/d		n/d	n/d	n/d		n/d	9	
Alkylated benzenes	3		11	n/d		4	n/d	n/d		n/d	n/d	
PAHs	n/d		3	n/d		1	n/d	n/d		n/d	n/d	
Aliphatic hydrocarbons	9		27	6		10	n/d	9		n/d	1	
Other compounds	2		n/d	2		n/d	n/d	n/d		n/d	3	

Table 2. Organic compounds identified, and concentrations of metals, in samples of wastewater, sediment and soil collected in association with Mayer Textile, Philippine Industrial Sealants and Coatings Corporation (PIS) and TVC Chemicals, Calamba, Laguna, Philippines, 2010. Concentrations of metals in wastewater samples are reported in µg/l, both as total concentrations in the whole (unfiltered) sample and separately as (dissolved) concentrations in filtered samples. Concentrations of metals in sediments are reported as mg/kg dry weight. nd – not detected

3.3 TNC Chemicals

Three samples were collected from around the site where the TNC Chemicals plant is located in Calamba, Laguna, comprising two wastewater samples PH10006 and PH10008 and one sediment sample PH10007.

Wastewater sample PH10006 collected from the discharge pipe was not contaminated with any of the metals considered in this study. Concentrations were either below limits of detection for the methods used or within the ranges expected for uncontaminated surface waters. The loading of organic compounds in the sample was also not very high with only eleven compounds detected. These were mainly aliphatic hydrocarbons, with, additionally, 2,4-di-*tert*-butylphenol and DEHP.

Soil sample PH10007, which was collected on the bank of the San Juan River over which wastewater from the pipe flows, was also not found to be contaminated with metals or any organic compounds using the methods employed in this study.

By contrast, wastewater sample PH10008, collected from a second discharge point at the facility, contained concentrations of chromium (210 µg/l) and nickel (125 µg/l) somewhat higher than would be expected to be present in uncontaminated water; this is also true of copper concentrations at (29 µg/l) but to a lesser extent. The most toxic form of chromium, hexavalent chromium, was not present in the wastewater above the method detection limit (<50 µg/l). For comparison, levels found in uncontaminated surface waters are typically below 10 µg/l (chromium) and 20 µg/l (nickel). Background concentrations of soluble copper in uncontaminated surface waters are typically below 10 µg/l, but are often far lower than this.

Sample PH 10008 also had a much higher loading of detected organic compounds than wastewater sample PH10006 that was collected from another discharge point at the facility. Organic compounds detected in the sample included a range of industrial chemicals such as nitrophenols, nitrocresols, nitrotoluenes, phthalic anhydride, 4-methyl-2-phenyl-1,3-dioxolane, 5-acetoxymethyl-2-furaldehyde, and 4,4'-dimethylbiphenyl (also known as *p,p'*-bitoluene). This sample also contained several representatives of carboxylic acid esters including ethyl and diethyl esters of the following acids: acetic, pimelic, sebacic, stearic, suberic, tartaric and nonanoic. Thus, this wastewater discharge acts as a point source of a diverse range of organic chemicals some of which are toxic both to humans and to organisms in the wider environment. These are likely to contribute in turn to contamination of the San Juan River and, ultimately to contamination of Laguna Lake.

3.4 Litton Mills

Wastewater sample PH10009 was collected from the Litton Mill facility's discharge pipe while sediment sample PH10010 was collected from the edge of the Pasig River close to the end of the pipe. The wastewater sample did not appear to be contaminated with most of the metals investigated.

Industry name Sample Type	Litton Mills			Carmelray 1			Unilever-RFM Compound					
	PH10009		PH 10010	PH 10011		PH 10012	PH 10013		PH 10014	PH 10015		PH 10016
	wastewater		sediment	wastewater		sediment	wastewater		sediment	wastewater		sediment
	total	dissolved		total	dissolved		total	dissolved		total	dissolved	
	µg/l	µg/l	mg/kg	µg/l	µg/l	mg/kg	µg/l	µg/l	mg/kg	µg/l	µg/l	mg/kg
METAL												
Antimony	<50	<50	<20	<50	<50	<20	<50	<50	<20	<50	<50	<20
Arsenic	<50	<50	<20	<50	<50	<20	<50	<50	<20	<50	<50	<20
Barium	248	235	76	19	14	368	101	64	59	81	76	80
Cadmium	<5	<5	<1	<5	<5	<1	<5	<5	<1	<5	<5	<1
Chromium	<20	<20	45	<20	<20	13	<20	<20	33	<20	<20	46
Chromium (VI)	-	<50	-	-	<50	-	-	<50	-	-	<50	-
Cobalt	<20	<20	28	<20	<20	26	<20	<20	4	<20	<20	26
Copper	<20	<20	60	131	<20	104	24	<20	56	<20	<20	80
Lead	<50	<50	7	85	59	25	<50	<50	30	<50	<50	15
Manganese	264	258	677	42	38	1015	111	74	167	114	103	747
Mercury	<2	<2	<0.5	<2	<2	<0.5	<2	<2	<0.5	<2	<2	<0.5
Nickel	<20	<20	24	<20	<20	9	<20	<20	16	<20	<20	24
Selenium	<200	<200	<30	<200	<200	<30	<200	<200	<30	<200	<200	<30
Vanadium	<20	<20	161	56	51	98	<20	<20	23	<20	<20	142
Zinc	99	16	119	74	53	199	99	<10	285	25	<10	180
№ of isolated organic compounds	68		1	68		8	92		61	108		58
№ of reliably identified (% total)	28(41%)		none	37(54%)		7(86%)	28(30%)		40(66%)	31(29%)		39(67%)
Phthalate esters	3		n/d	1		n/d	3		n/d	3		n/d
Nonylphenol, mix of isomers	n/d		n/d	15		n/d	n/d		n/d	n/d		n/d
Phenol, methyl- & ethyl-	3		n/d	n/d		n/d	1		n/d	1		n/d
Chlorinated phenols	n/d		n/d	(2)		n/d	n/d		n/d	n/d		n/d
Bisphenol A & bisphenol S	n/d		n/d	n/d		n/d	2		n/d	2		n/d
4-tert-octylphenol	n/d		n/d	n/d		n/d	1		n/d	1		n/d
Biphenyl derivatives	n/d		n/d	n/d		n/d	2		3	2		1
Benzophenone & derivativers	n/d		n/d	n/d		n/d	2		n/d	2		n/d
Diphenyl- & ditolyl-alkanes	n/d		n/d	n/d		n/d	n/d		10	n/d		8
Butachlor & related compounds	n/d		n/d	2		n/d	n/d		n/d	n/d		n/d
Furan derivatives	3		n/d	n/d		n/d	n/d		n/d	n/d		n/d
Alcohols & derivatives	n/d		n/d	n/d		n/d	2		n/d	2		n/d
Glycol ethers	n/d		n/d	n/d		n/d	3		n/d	3		n/d
Carboxylic acids and/or their esters	4		n/d	4		n/d	5		n/d	5		n/d
Phosphoric acid esters	n/d		n/d	2		n/d	1		n/d	1		n/d
Terpenoids	n/d		n/d	4		n/d	1		n/d	1		n/d
PAHs & derivatives	2		n/d	n/d		n/d	n/d		14	n/d		6
Aliphatic hydrocarbons	10		n/d	3		7	1		12	2		23
Other compounds	3		n/d	4		n/d	4		1	6		1

Table 3. Organic compounds identified, and concentrations of metals, in samples of wastewater, sediment and soil collected in association with Litton Mills and various companies located in the Unilever-RFM Compound, Pasig City, Metro Manila; and Carmelray 1 Industrial Park, Calamba, Laguna, Philippines, 2010. For organic compounds, (..) signifies those identified at trace levels using a selective SIM method. Concentrations of metals in wastewater samples are reported in µg/l, both as total concentrations in the whole (unfiltered) sample and separately as (dissolved) concentrations in filtered samples. Concentrations of metals in sediments are reported as mg/kg dry weight. nd – not detected

Concentrations were either below limits of detection for the methods used or within the ranges expected for uncontaminated surface waters. A possible exception is zinc (whole concentration was 99 µg/l, dissolved concentration - 16 ug/l), which indicates a possible very slight contamination with this metal. Organic compounds detected in the wastewater were represented by three phthalate esters (DEHP, DBP and di-*iso*-butyl phthalate DiBP), three phenol derivatives (methyl- and ethylphenols), and three furan derivatives (1-furfuryl-2-acetyl pyrrole, 1-furfuryl-2-formyl pyrrole, and furan, 2,2'-[oxybis(methylene)]bis-). This sample also contained octanol, two indole derivatives, and range of aliphatic hydrocarbons.

Sediment sample PH10010, taken from the discharge channel at the point where it finally joins the Pasig River contained concentrations of copper very slightly higher than levels typically found in uncontaminated soils or freshwater sediments. This, however, is not considered indicative of contamination due to discharges of copper contaminated wastewater. No organic compounds were detected which could be identified with an acceptable degree of certainty.

3.5 Carmelray 1 Industrial Park

Wastewater sample PH10011 was collected from the pipe carrying wastes originating from the Carmelray 1 Industrial Park which predominantly hosts electronics and semiconductor manufacture industries. Sediment/soil sample PH10012 was taken below the wastewater discharge pipe which ends about 5 meters above the Cauang Cauang Creek surface. Sample PH10011 contained elevated levels of copper (whole concentration was 131 µg/l, dissolved concentration <20 ug/l), and lead (whole concentration was 85 µg/l, dissolved concentration 59 ug/l). However, these levels are not likely to be indicative of significant discharges of these metals. This sample did, however, contain a relatively high loading of detected organic compounds with 37 chemicals being reliably identified. Most of the identified chemicals are commonly identified in industrial wastewaters and included:

- 15 isomers of nonylphenol;
- phthalate ester DEHP;
- two esters of phosphoric acid (tributyl phosphate and triethyl phosphate);
- two chlorinated phenols detected, (at trace concentrations)
- several carboxylic acids, terpenoids, alcohol derivatives and caffeine;
- additionally, this sample contained butachlor, a selective pre-emergent herbicide from the class of acetanilides, together with its related compound, N-(2-phenylethyl)acetamide. The source of this herbicide in the wastewater discharge is unclear and needs to be further investigated.

In sample PH10012, the concentrations of copper and zinc were slightly higher than levels typically found in uncontaminated soils or freshwater sediments. Again, these levels were very similar to those detected in samples PH10004 & PH10005 suggesting that the copper and zinc levels may be due to locally elevated levels of these metals in soils in this area, rather than due to discharges. The load of organic compounds in the sediment was quite low with only aliphatic hydrocarbons detected, and these could be of natural origin.

3.6 Unilever-RFM Compound

Four samples were collected from around the Unilever-RFM Compound, within which both Hanson Papers and Banner Plasticard plants are located, among others. These samples comprised: two wastewater samples PH10013 and PH10015 from two pipes located 10m apart from each other and discharging into the Marikina River; a sediment sample PH1004 collected from the pipe from which

sample PH10013 was taken; and a soil sample PH10016 collected from the bank of the Marikina River about 1m from the end of the pipe from which wastewater sample PH10015 was taken.

Neither wastewater sample (PH10013 & PH10015) showed evidence of significant contamination with metals. Their concentrations were either below limits of detection for the methods used or within the ranges expected for uncontaminated surface waters. A possible exception to this was the zinc concentration in sample PH10013 (whole concentration was 99 µg/l, dissolved concentration <10 µg/l), indicating a very slight contamination with this metal. However, contamination of these wastewaters with organic compounds was significant and the pattern of their composition was almost identical in both samples suggesting that these pipes are carrying wastewater from the same source or combination of sources or processes. The range of organic contaminants detected in both samples of wastewater from the Unilever-RFM Compound included:

- three phthalate esters: DBP, DiBP and diethyl phthalate DEP;
- phenolic compounds: bisphenol A, bisphenol S, 4-tert-octylphenol and methylphenol;
- two biphenyl derivatives: o-hydroxybiphenyl and 2-methylbiphenyl;
- benzophenone and its derivative (2-hydroxy-4-methoxyphenyl)phenylmethanone, also known as oxybenzone, which is used in the pharmaceutical and personal care products;
- three glycol ethers which are primarily used as solvents: 2-(2-butoxyethoxy)ethanol also known as diethylene glycol monobutyl ether; 2-(hexyloxy)ethanol also known as ethylene glycol monohexyl ether; and 1,2-diphenoxyethane also known as ethylene glycol diphenyl ether;
- two alcohol derivatives: 2-ethyl-1-hexanol; and benzeneethanol;
- carboxylic acids: dodecanoic and hexadecanoic acids;
- esters of carboxylic acids: Propanoic acid, 2-methyl-, 3-hydroxy-2,4,4-trimethylpentyl ester, which is associated with acrylic paints; Benzoic acid, 2-benzoyl-, methyl ester, which is used in various UV curable systems, like UV coatings and inks; and Benzoic acid, 3-hydroxypropyl-;
- the phosphoric acid ester tri-*iso*-butyl phosphate, mainly used as a antifoam, but also employed as a plasticizer, wetting agent, and a pasting agent for pigment pastes;
- dehydroabiatic acid, a representative of resin acids occurring in pines, and a compound which is a major anionic contaminant of pulp mill effluents;
- a derivative of nitrogenous heterocyclic compound: 5,6-Dihydro-5,6-dimethylbenzo[c]cinnoline;
- and elemental sulfur.

Additionally, the following compounds were detected only in one of the two wastewater samples:

- a sulfur-containing compound 1,2,3,5,6-Pentathiepane (PH10013);
- the ester of carboxylic acid, Benzoic acid, 2-benzoyl-, methyl ester (PH10015);
- an insect repellent diethyltoluamide (PH10015);
- and a nitrogen- containing heterocyclic compound 1H-Indole (PH10015).

Sediment sample PH10014 and sediment/soil sample PH10016 contained copper and zinc at concentrations slightly higher than levels typically found in uncontaminated soils or freshwater sediments, but again very similar to levels detected in samples PH10004, PH10005 & PH10012 which may be due to locally elevated levels of these metals in the soils of the investigated area. Both sediment and soil samples PH10014 and PH10016 showed a high number of industrial organic compounds including:

- biphenyl derivatives: di-*iso*-propylbiphenyls, used as a dye solvent for carbonless copy paper (detected in both samples); and 3,3'-dimethylbiphenyl detected in sample PH10014 only;

- ditolyl alkanes: mixture of isomeric bis(methylphenyl)ethanes, also called di-tolyl-ethanes, 6 and 5 isomers of which were detected in samples PH10014 and PH10016 respectively; and di-*p*-tolyl-methane detected in sample PH10014 only;
- diphenyl alkanes: diphenylethane detected in both samples; diphenylmethane and diphenylpropane in sample PH10014 only; and 2 isomers of phenyl(dimethylphenyl)methane in sample PH1016 only;
- PAHs and their derivatives: mixture of di-*iso*-propylnaphthalenes, 6 isomers of which were detected in both samples; trimethylnaphthalenes, phenanthrene and methylphenanthrene in sample PH10014 only;
- additionally, both samples contained a derivative of indene, a polycyclic hydrocarbon: 1H - Indene, 2,3-dihydro-1-methyl-3-phenyl-.

Sample PH10014 contained a wider range of compounds from the same groups of organic compounds as were detected in both samples PH1014 and PH1016. (e.g. biphenyl derivatives, PAHs, diphenyl & ditolyl alkanes) which may be due to differences in the absorption capacity of the solid deposit inside the pipe (sample PH10014) and riverbank soil washed with the wastewater (sample PH10016). However, in both cases the contamination by organic compounds is quite obvious. This indicates that at least some industrial activities taking place within the Unilever-RFM industrial compound act as significant point sources of a diverse range of organic compounds to the Marikina River and the surrounding environment. Further, more detailed investigations would be needed in order to determine which of the various industrial enterprises located within the Unilever-RFM Compound were acting as point sources of the substances identified in the combined discharge.

4. Conclusions

The current study identified several point source discharges in Laguna Lake area which is one of the industrially important regions of the Philippines. The most prominent of these were: Mayer Textile, TNC Chemicals, Carmelray 1 Industrial Park and one or more of the facilities located within the Unilever-RFM Compound, all of which were found to be discharging into freshwater systems wastewater contaminated with a variety of toxic and persistent organic chemicals. Discharges from two other facilities sampled (namely PIS and Litton Mills) appeared to be somewhat less contaminated at the time of sampling.

Among the organic contaminants identified in the current study are several which have the potential to seriously impact environmental quality and hence the health of both humans and organisms in the wider ecosystems. Although a comprehensive survey of all wastewater discharges from facilities located around of the Laguna Lake basin was not possible, the results of this more limited study nonetheless provide a unique and valuable snapshot of the quality and complexity of discharges to water in this area. In addition to highlighting specific concerns surrounding four of the six discharges sampled, it is hoped that the findings can act as a catalyst for further investigation of discharges, emissions and losses of hazardous chemicals to the Laguna system, to be conducted under the appropriate authorities in the Philippines, in order to inform programmes aimed at progressive and substantive reductions in such inputs and their eventual cessation.

Appendix. Analytical methodology

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 5.

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 5. Limit of quantification (LOQ) is the lowest concentration in the linear regression (r^2 – 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 solvents were 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.

Analysis for metals

Preparation

A representative portion of each sediment or soil 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 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. In addition, a portion of each whole sample was filtered and then acidified in the same way. 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 2.0, 2.5 and 10 mg/l respectively for sediment/soil samples and at concentrations of 0.5, 1.0, 2.5 and 5 mg/l respectively for water samples, 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.

Quality control

For sediment samples, two samples were 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 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 manner 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.

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