

Waste discharges to the Matanza-Riachuelo River system, Buenos Aires: Burzaco Industrial Park and AySA municipal sewage treatment plant.

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Executive Summary

The Buenos Aires Municipal Area (BAMA) includes a number of industrial zones, incorporating a diverse mix of manufacturing, processing and servicing operations, often involving small or medium-sized enterprises. Many companies discharge waste effluent to surface waters feeding the Matanza-Riachuelo river system, which flows west to east through Buenos Aires before joining the Rio de la Plata. Some effluents, whether treated or untreated, are discharged to the Matanza or its tributaries through small discharge pipes serving either a single industrial facility or a small collection of facilities. Others dispose of their wastewaters under contract to one of four municipal sewage collection systems, each served by a common effluent treatment plant.

This study was designed to provide a snapshot of the quality of industrial effluents being discharged at two locations which may exemplify the more general situation, including a range of effluents being discharged to the Arroyo del Rey stream (which flows through the Parque Industrial Burzaco before joining the Riachuelo) and three samples (collected on different days) of the main effluent discharge from the southwest municipal treatment plant located at Aldo Bonzi, operated by Water and Sanitation Argentina (AySA) (and which discharges to the Matanza). A total of 28 samples (including river water, effluent discharges and associated sediments) were collected during January and February 2010 and returned to the Greenpeace Research Laboratories at the University of Exeter, UK, for quantitative analysis of toxic metals and qualitative analysis of both volatile and solvent-extractable organic contaminants.

Burzaco industrial park (Parque Industrial Burzaco)

Samples were collected from the Arroyo del Rey at 11 different locations as the stream flows northwards through the industrial park. Both water and sediment samples collected upstream were relatively clean, with little evidence of industrial or urban contamination. Evidence for significant inputs of waterborne contaminants was, however, detected at a number of points in the industrial park itself, including:-

- Effluent discharges from the Guiale meat packing and processing plant, which contained more than 70 organic compounds, including a range of chlorinated and phenolic compounds such as suspected endocrine disruptor triclosan, compounds which may be in use on site for purposes of disinfection. A sediment sample collected adjacent to this discharge pipe also showed some elevation of the toxic metals copper, zinc and lead above upstream levels and typical background concentrations, though the sources of such contaminants in this case are not clear.
- Effluent collected from a pipe running beneath Ortiz Street, of unknown origin, but again releasing a complex mixture of organic compounds to the el Rey stream, including residues of the weakly estrogenic synthetic musk chemical Galaxolide (HHCB), used as a fragrance enhancer in a wide variety of industrial and consumer products. Toxic metal concentrations in sediments at this location were particularly significant, with levels of chromium, copper and nickel between 10 and 20 times those found at the upstream site,

the chromium concentrations exceeding the threshold for “serious contamination” of sediments set in the Netherlands. Residues of di- and tri-chlorobenzene were also found in sediments here.

- Two separate wastewater discharges originating from the C.R.A radiator factory, which contained by far the highest concentrations of dissolved and suspended metals of all samples collected in this study, including total copper levels of between 2030 and 2770 ug/l. Effluent from one of the two pipes also contained very high concentrations of zinc (9240 ug/l), while that from the other was a source of both lead (483 ug/l) and cadmium (14 ug/l) to the stream. This second effluent also contained residues of numerous persistent organic compounds, including Galaxolide and the chlorinated phosphorus flame retardant tris(2-chloroisopropyl) phosphate (tradename Fyrol PCF).
- Sediment samples collected adjacent to the discharge from the C.R.A plant, which contained copper (up to 2.5% by weight of the sediment), zinc (up to 2% by weight), lead (up to 0.3% by weight) and cadmium at high concentrations, as well as traces of mercury. The highest copper and zinc levels recorded in these sediments exceeded Dutch threshold levels for “serious contamination” by around 130 and 30 times respectively. Residues of di- and trichlorobenzene and of the commonly used PVC plasticiser chemical DEHP were also found in one of the two sediments.
- Combined discharges from the Melian Street pluvial pipes which, though relatively free from dissolved and suspended metals, contained complex loadings of organic compounds, including phthalate plasticisers, organosulphur and organonitrogen compounds, traces of flame retardant and synthetic musk and of the chemical intermediate *p-tert*-butylphenol.

Samples of river water collected from the el Rey stream at a point downstream from the Burzaco industrial park still showed some signs of elevated copper and zinc concentrations, as well as some organic compounds, though inevitably diluted through mixing with the river flow by that point. Sediment samples from the same downstream location revealed somewhat greater accumulation of metals, as may be expected, including concentrations of copper, zinc, lead, chromium and nickel which were 15, 10, 6, 2 and 2 times higher respectively than the concentrations determined in sediment from the sample site upstream from the industrial park. This downstream sediment also contained detectable levels of cadmium (1mg/kg), a metal which had not been present at the upstream site.

The situation was qualitatively similar with respect to organic contaminants, which also may be expected to accumulate more readily in sediments than in flowing water and which were more numerous in samples collected downstream from Burzaco than those collected upstream. One additional significant finding was the presence of 5 isomers of the toxic, persistent and bioaccumulative compound nonylphenol in one of the downstream sediments, a potent hormone disrupting compound used in some detergent and dispersant formulations but of unknown origin in this case.

Taken together, these results demonstrate that the discharge of wastewaters from at least some of the industrial facilities located in the Burzaco area are leading to the contamination

of the waters and sediments of the Arroyo del Rey as it flows northwards through the industrial park. As waters and suspended sediments from this stream ultimately flow to the Riachuelo, it is clear even from this limited study that the Parque Industrial Burzaco is acting as one point source of toxic metals and persistent organic pollutants to the Matanza-Riachuelo basin overall. Although the Arroyo del Rey may not be the most polluted tributary in the system, it is clearly one of many such tributaries in the basin which receive a variety of industrial waste discharges and may, therefore, provide an example of what might also be happening elsewhere. Further, more detailed investigations would be necessary in order to trace the exact sources of the key contaminants identified in this study and to extend this work to other, similarly industrialised streams which feed the Matanza-Riachuelo system.

AySA municipal wastewater treatment plant, Aldo Bonzi

The three samples of treated effluent being discharged from the southwest AySA wastewater treatment plant at Aldo Bonzi, collected on three separate days between 26th January and 11th February 2010, revealed that this facility is also acting as a significant point source of metal and persistent organic pollution to the Matanza-Riachuelo river basin. Other than the heavily contaminated effluents originating from the C.R.A. radiator factory in Burzaco, the final treated effluents being released from this municipal wastewater treatment plant contained the highest concentrations of toxic metals recorded in this study. Levels ranged from 66 to 192 ug/l for chromium, from 59 to 205 ug/l for copper, from 22 to 95 ug/l for nickel and from 444 to 860 ug/l for zinc, though in all cases the major contribution was from metals attached to suspended particulate matter discharged with the effluent. Metal concentrations in the final sample, collected on 11th February, were around double those found in samples collected on the two previous occasions at the end of January, suggesting significant periodic variation in the quality of treated wastewater being discharged, a phenomenon apparent also from the official monitoring data for this facility in 2008, published under the ACUMAR programme. Overall, the ranges of metal concentrations determined in the current study were similar to those previously reported by ACUMAR.

Sediments collected on each occasion from a point in the river adjacent to the discharge point revealed metal contamination profiles which were similar to those in the treated effluents themselves. Once again, concentrations of copper and zinc in all three sediment samples, and of lead in the sample collected on 11th February, were above the thresholds set in the Netherlands for the identification of sediments as “seriously contaminated”. These same sediments also contained elevated levels of mercury, at around 30 times greater concentrations than might typically be expected for an uncontaminated water course.

Between 53 and 136 individual organic compounds were isolated from the three wastewater samples, with the broadest range found in the sample collected on February 11th, the sample which also showed the highest concentrations of metals of the three samples. The number of compounds which could be reliably identified ranged from 18 to 43, including the following compounds detected in every sample, irrespective of sampling date:

- Atrazine, one of the most widely used herbicides for the control of weeds and grasses;

- Traces of dichlorobenzenes;
- Steroid and terpenoid compounds;
- Aliphatic hydrocarbons

Compounds that were detected in the wastewater discharge on at least two occasions included:

- Fyrol PCF, a flame retardant;
- Polycyclic aromatic hydrocarbons (PAHs);
- Alkylated benzenes;
- Trace amounts of volatile chlorinated organic compounds including chloroform, trichloroethene and tetrachloroethene.

Additionally, several compounds were detected in only one of the three samples (i.e. on one of the three occasions), again reflecting periodic variations in the quality of the final treated effluent being discharged. Those chemicals included methylphenol, diisoadipate, decyltetraglycol and dichloromethane on 26th January, 12 isomers of nonylphenol in the sample collected 2 days later, and the PAH phenanthrene in the final sample, collected on 11th February. Despite these inevitable variations, the data set overall clearly indicates ongoing contamination of receiving waters with a range of toxic and persistent compounds, some portions of which are passing through the treatment process unchanged.

The results of analysis of the sediment samples collected at the same times and location lend further support to this observation, revealing the presence of residues of numerous persistent organic contaminants including the synthetic musk Galaxolide, the toxic organophosphate insecticide Chlorpyrifos, the phthalate ester DEHP and traces of chlorinated benzenes. Because of their environmental persistence and toxicity, both Chlorpyrifos and Atrazine (found in the effluents) are recognised as priority substances under the European Water Framework Directive.

Once again, while AySA's southwest municipal wastewater treatment plant is undoubtedly only one of many sources of effluent discharge to the Matanza-Riachuelo basin, it is a significant point source nonetheless. The fact that a wide range of common industrial pollutants can be identified, in some cases at significantly elevated concentrations, in the final treated effluent at the point of discharge to the aquatic environment provides an illustration of the inherent limitations of conventional wastewater treatment plants in handling and decontaminating wastewaters of industrial origin. Although it is impossible to say what proportion of the total load of toxic metals and persistent organic pollutants being directed to the treatment plant from industrial sources are being either degraded or retained in sludges, it is evident that neither degradation nor retention are capable of preventing these priority pollutants from being discharged to the Matanza-Riachuelo system and, therefore, contaminating the environment downstream. At the same time, it is likely that a significant proportion of those contaminants most resistant to degradation will routinely accumulate in the sludge wastes generated by the treatment plant, raising the potential for further, more widespread contamination as a result of subsequent disposal of treatment plant sludges.

Conclusions

As noted above, both the Burzaco industrial park and AySA's southwest treatment plant are merely case studies of what is likely to be a much wider and more generic problem of hazardous chemical pollution of water from industrial activities within the Buenos Aires Municipal Area. Together, they serve to illustrate the consequences of poorly controlled, possibly untreated, effluents from a wide range of industrial units within industrial zones and of the inability of conventional municipal wastewater treatment plants to deal effectively enough with toxic and persistent industrial chemical wastes, whatever their origin.

While this study has provided only a limited snapshot of sources of water pollution with hazardous chemicals within two areas of Buenos Aires, it also illustrates the urgent need for more extensive and more detailed technical investigation of the problem across the whole BAMA region, in order to determine its overall scale and severity. Such investigations, coupled with initiatives aimed at inventorising the current use and release of a whole range of hazardous substances by industries in the area, should provide the basis for a more sustainable approach to chemicals management and protection of water resources in the future. If environment and health protection goals are to be met in the long term, it will be vital in the more immediate term to establish targets of zero discharge for the most hazardous inorganic and organic compounds currently in use by industry, implemented where possible through an ongoing process of substitution of hazardous substances with less hazardous or preferably non-hazardous alternatives. Such policy objectives are scientifically defensible and technologically achievable and have been developed (and are now being implemented) in other parts of the world, including within the European Union and wider North-East Atlantic (OSPAR) and Baltic (HELCOM) regions.

Introduction

This study investigated the presence of hazardous chemicals in direct discharges of industrial wastewater to the aquatic environment from a range of facilities in the greater Buenos Aires area. Discharged wastewaters and associated sediment samples from the receiving rivers were collected for analysis from two areas; the el Rey stream (Arroyo del Rey) in the Burzaco area to the south of Buenos Aires, and the AySA municipal sewage treatment plant which receives a mix of municipal and industrial wastewater from the southwest basin of the Buenos Aires Metropolitan Area (BAMA) and discharges to the Matanza-Riachuelo River.

In the Burzaco area (Parque Industrial Burzaco), facilities involved in a wide range of industrial activities discharge wastewaters to the el Rey stream, a tributary which runs north to join the main channel of the Riachuelo. In some circumstances, wastewaters from individual facilities in this industrial park are discharged to communal underground pipes which subsequently discharge to the stream.

In the BAMA, the municipal sewage system is currently divided into four basins: Southwest, North, Ezeiza and Berazategui. Sewage from each basin flows into a separate treatment plant. The Southwest basin collects a portion of the total effluents generated in La Matanza region, which are sent to the Southwest plant for treatment. This plant is located in Aldo Bonzi, close to the Central Market. It is the oldest of the four treatment plants in BAMA, having been built in 1972.

The Southwest plant is operated by the state-owned Water and Sanitation Argentina (AySA) and is responsible for the collection, transportation, treatment and disposal of wastewaters, including those industrial discharges that the current system permits to be discharged to the sewer. This treatment plant serves a population of 575 000, with a treatment capacity is 170000 m³/day. It uses settling tanks to retain solids (primary treatment), with subsequent biological treatment of the remaining wastewater, followed by clarification to separate liquid and solid materials (secondary treatment). AySA reports that it performs quality control tests on received wastewaters to ensure that allowed parameters are met for the quality of the received wastewater.

Sampling program

The two areas investigated in this study (el Rey stream in the Burzaco area, and the AySA sewage treatment plant) were visited in January and February 2010, and a total of 28 samples (of wastewaters, stream waters and sediment) were collected. In the Burzaco area, wastewater samples were collected from various outfalls that discharge wastewaters into the el Rey stream. For each discharge point, a sample of sediment was also collected either from the el Rey stream adjacent to the outfall, or as a mixture of sediment from within the pipe and from the el Rey stream adjacent to the outfall. In addition, samples of water and sediment were collected from the el Rey stream at two locations, one upstream and one downstream from all discharge pipes included in this study. The AySA sewage treatment plant was

visited on three separate occasions, and on each occasion a sample of treated wastewater was collected from the outfall of the treatment plant at the point of discharge into the Matanza-Riachuelo River, along with sediment from the same river collected from a point adjacent to the discharge pipe.

In all cases, samples were collected and stored in pre-cleaned glass bottles that had been rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metal and organic residues. Wastewater and stream water samples were collected in 1 litre screw-cap bottle for use in the quantitative analysis of metals and qualitative analysis of solvent extractable (semi-volatile) organic compounds. A duplicate sample was collected in a separate 125 ml amber bottle with a ground-glass stopper (filled to leave no headspace) to be analysed for volatile organic chemicals. Sediment samples were collected in 100ml screw-cap bottles. All samples were immediately chilled and kept cool and dark during transit to the Greenpeace Research Laboratories at the University of Exeter in the UK for analysis. Detailed description of sample preparation and analytical procedures are presented in the Appendix.

Methodology

A number of different analyses were carried out on the wastewater, stream water and sediment samples collected. 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. Many water samples contained suspended solids and therefore, for all samples, both the total concentrations in the whole (unfiltered) sample and the concentrations of dissolved forms in a filtered sample were determined separately.

Extractable organic compounds were isolated from each sample and identified as far as possible using gas chromatography and mass spectrometry (GC/MS), following accelerated solvent extraction into a mixture of pentane and acetone for solid samples or solid phase extraction with ethyl acetate, pentane and toluene for wastewater samples. 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. A list of VOCs quantified in the water samples with limits of detection and quantification are presented in Table 6 in Appendix.

None of the VOCs investigated in this study were detected above the limit of quantification.

Results and discussion

The results from the analyses of wastewater and sediment samples are presented and discussed in the following sections, separately for each of the two areas investigated. Some key chemicals were identified in samples collected from more than one site, and therefore

background information on certain key pollutants detected during this study is presented in Boxes A-F through the discussion text.

It should be noted that all metals quantified in this study are naturally found at some level in uncontaminated environmental samples, such as sediments and surface waters, though generally at low concentrations. Inputs from point sources such as industrial discharges can, however, result in levels that far exceed natural background concentrations. The following sections focus on those metals found in the various samples at concentrations which are above typical background levels for uncontaminated waters and, therefore, indicative of significant inputs from industrial or other anthropogenic sources.

Burzaco

In the Burzaco area, wastewater samples were collected from various outfalls that discharge wastewaters into the el Rey stream. For each discharge point, a sample of sediment was also collected either from the el Rey stream adjacent to the outfall, or as a mixture of sediment from within the pipe and from the el Rey stream adjacent to the outfall. Details of all samples associated with wastewater discharges to the el Rey stream in the Burzaco area are presented in Table 1, along with a map showing the locations from which samples were collected (Figure 1).

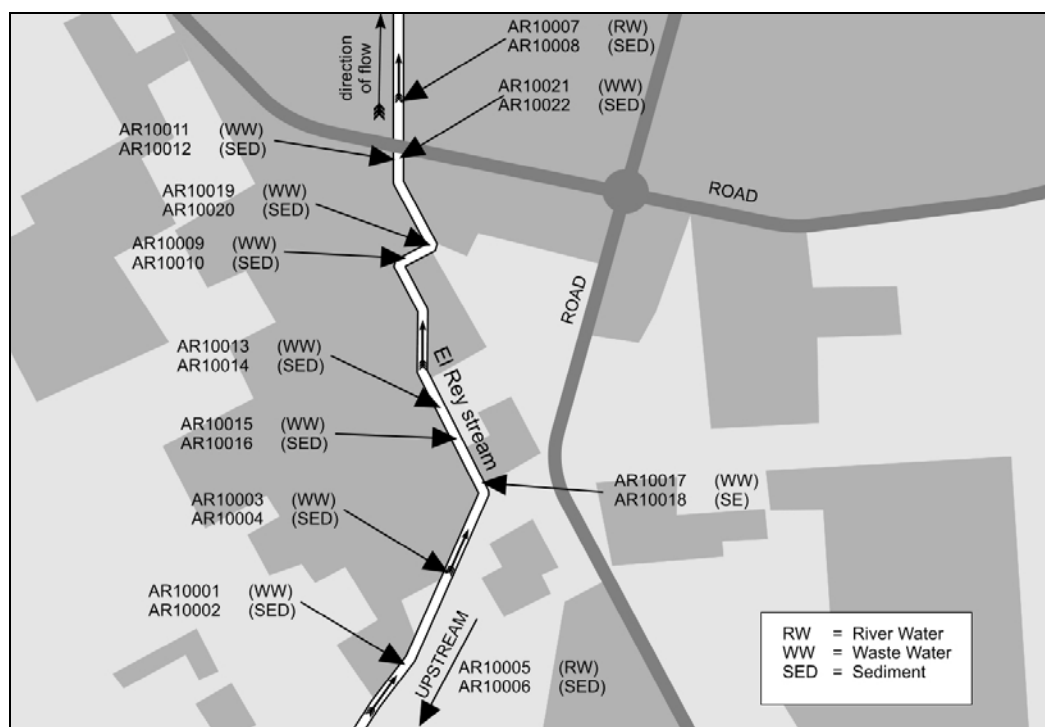


Figure 1. Sketch map of the el Rey stream in the Burzaco area Buenos Aires Argentina, showing the locations from which samples were collected, from pipes discharging to the stream and from the stream itself

Sample	Type	Description	Facility: main activity
AR10001	wastewater	discharge pipe from facility	Diransa: paint/varnish/adhesives
AR10002	sediment	el Rey stream adjacent to discharge pipe	
AR10003	wastewater	discharge pipe from facility	Guiale: meat packing/ processing
AR10004	sediment	el Rey stream adjacent to discharge pipe	
AR10005	stream water	upstream from the Burzaco industrial park	el Rey stream (upstream)
AR10006	stream sediment	upstream from the Burzaco industrial park (as 05)	
AR10007	stream water	downstream from the Burzaco industrial park	el Rey stream (downstream)
AR10008	stream sediment	downstream from the Burzaco industrial park (as 07)	
AR10009	wastewater	Viel street pluvial pipe	many
AR10010	sediment	el Rey stream adjacent to pluvial pipe	
AR10011	wastewater	Melian street pluvial pipe	many
AR10012	sediment	el Rey stream adjacent to pluvial pipe	
AR10013	wastewater	discharge pipe 1 (pipe closest to Cuyo Street)	C.R.A.: radiator factory
AR10014	sediment	el Rey stream adjacent to discharge pipe 1	
AR10015	wastewater	discharge pipe 2 (pipe closest to Ortiz Street)	C.R.A.: radiator factory
AR10016	sediment	mix of sediment from inside the pipe and from el Rey stream adjacent to discharge pipe 2	
AR10017	wastewater	concealed discharge pipe, from Ortiz street	unknown
AR10018	sediment	mix of sediment from inside the pipe and from el Rey stream adjacent to the pipe	
AR10019	wastewater	large cement discharge pipe from facility	Fradealco: alcohol & cleaning products, bleach, vinegar, sulfur
AR10020	sediment	el Rey stream adjacent to discharge pipe	
AR10021	wastewater	2 nd (smaller) pluvial pipe on Melian street (situated close to AR10011)	Many: Near to paint company & varnish, colour, pigment factory
AR10022	sediment	mix of sediment from inside the pipe and from el Rey stream adjacent to the pipe	

Table 1. Description of samples collected from outfalls in the vicinity of the el Rey stream, in the Burzaco area, Buenos Aires, Argentina, 2010

Results

The data from the analyses are summarised in Tables 2a-2c, and discussed in the following sections for each outfall or set of outfalls to the el Rey stream.

el Rey stream, upstream

The el Rey stream water (AR10005) and sediment (AR10006) collected upstream of the sampled discharges did not contain any metals at levels above those typically found in uncontaminated surface waters and sediments. Eight organic compounds were isolated from the sediment sample and only 4 of them, all aliphatic hydrocarbons, were identified to a high degree of reliability. The water sample has no detectable levels of organic compounds.

Diransa (paint/varnish/adhesives facility)

Moving downstream, the discharged wastewater from the Diransa facility (AR10001) did not contain elevated levels of the metals that were quantified, and the associated sediment (AR10002) contained similar levels for all metals to those found in the uncontaminated upstream sediment (AR10006). Both water and sediment samples from this location

contained only a small number of organic compounds (10 and 12 respectively) and only benzaldehyde (which might be of natural origin) was reliably identified in the sediment sample. Two organic compounds were identified in the water sample, both aliphatic hydrocarbons.

Sample	AR10005		AR10006	AR10001		AR10002	AR10003		AR10004	AR10017		AR10018
Type	stream water		stream sediment	wastewater		Sediment	wastewater		Sediment	Wastewater		Sediment
Brief description	el Rey, upstream		el Rey, upstream	Diransa pipe		stream by pipe	Guiale pipe		stream by pipe	pipe, Ortiz St.		pipe + stream
	tot	diss		tot	diss		tot	diss		tot	diss	
METAL	(µg/l)	(µg/l)	(mg/kg)	(µg/l)	(µg/l)	(mg/kg)	(µg/l)	(µg/l)	(mg/kg)	(µg/l)	(µg/l)	(mg/kg)
Antimony	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Arsenic	<50	<50	<20	<50	<50	<20	<50	<50	<20	<50	<50	<20
Barium	52	37	199	41	38	213	63	32	269	112	106	104
Cadmium	<10	<10	<1	<10	<10	<1	<10	<10	<1	<10	<10	<1
Chromium	<20	<20	26	<20	<20	23	<20	<20	71	<20	<20	514
Chromium (VI)	<50	<50	-	<50	<50	-	<50	<50	-	<50	<50	-
Cobalt	<20	<20	13	<20	<20	13	<20	<20	11	<20	<20	25
Copper	<20	<20	21	<20	<20	23	30	<20	93	22	<20	233
Lead	<50	<50	14	<50	<50	13	<50	<50	102	<50	<50	119
Manganese	59	<10	558	<10	<10	431	39	36	616	51	23	2100
Mercury	<2	<2	0.5	<2	<2	0.8	<2	<2	0.9	<2	<2	0.2
Nickel	<20	<20	11	<20	<20	13	<20	<20	31	<20	<20	152
Selenium	<200	<200	<30	<200	<200	<30	<200	<200	<30	<200	<200	<30
Vanadium	110	118	59	93	105	65	101	67	63	47	38	32
Zinc	20	<10	73	<10	<10	93	128	78	280	74	<10	164
pH	7		-	7		-	7		-	7		-
Organic compound isolated	5		8	12		10	79		10	28		12
No. reliably identified (% of total)	None		4(50%)	2(17%)		1(10%)	30(38%)		5(50%)	13(46%)		9(50%)
Chlorinated benzenes							1		(2)	(1)		(3)
Chlorinated phenols							4					
Other phenols							2					
Alkylbenzenes							2					
Indole & derivatives							4					1
PAHs							3					
Terpenoids							2					
Galaxolide										1		
Steroids							1					
Aliphatic hydrocarbons			4	2			6		3	9		5
Other compounds						1	3			2		
Volatile compounds:												
Disulfide, dimethyl							1					
Chloroform							(1)					

Table 2a. Organic chemicals identified, and concentrations of metals and metalloids, in samples of wastewater and sediment associated with wastewater outfalls in the vicinity of the el Rey stream, in the Burzaco area, Buenos Aires, Argentina, 2010. Samples from upstream locations to downstream are presented in the table from left to right. (..) signifies organic compounds identified at trace levels using a selective SIM method. Concentrations in wastewater and river water samples are given as µg/l for both the (tot)al concentrations in the whole sample and separately as (diss)olved concentrations in filtered samples, concentrations in sediments are given as mg/kg dry weight.

Sample	AR10015		AR10016		AR10013		AR10014		AR10009		AR10010		AR10019		AR10020	
Type	Wastewater		Sediment		Wastewater		Sediment		wastewater		stream sediment		wastewater		Sediment	
Brief description	C.R.A. pipe 2		pipe 2+ stream		C.R.A. pipe 1		pipe 1 + stream		Viel St pluvial		stream by pipe		Fradealco pipe		stream by pipe	
	tot	diss			tot	diss			tot	diss			tot	diss		
METAL	(µg/l)	(µg/l)	(mg/kg)		(µg/l)	(µg/l)	(mg/kg)		(µg/l)	(µg/l)	(mg/kg)		(µg/l)	(µg/l)	(mg/kg)	
Antimony	<20	<20	<20		<20	<20	<20		<20	<20	<20		<20	<20	<20	
Arsenic	<50	<50	<20		<50	<50	45		<50	<50	<20		<50	<50	<20	
Barium	92	102	213		36	141	187		175	67	229		55	55	207	
Cadmium	14	<10	12		<10	<10	2		<10	<10	<1		<10	<10	<1	
Chromium	<20	<20	35		<20	<20	86		<20	<20	44		<20	<20	14	
Chromium (VI)	<50	<50	-		<50	<50	-		<50	<50	-		<50	<50	-	
Cobalt	<20	<20	10		<20	<20	11		<20	<20	13		<20	<20	10	
Copper	2770	1215	24700		2030	935	8870		<20	<20	32		<20	<20	17	
Lead	483	171	300		250	<50	2780		<50	<50	15		<50	<50	7	
Manganese	106	102	333		<10	<10	520		25	<10	588		<10	<10	501	
Mercury	<2	<2	0.8		<2	<2	4.1		<2	<2	0.3		<2	<2	0.6	
Nickel	<20	<20	20		<20	<20	39		<20	<20	14		<20	<20	8	
Selenium	<200	<200	<30		<200	<200	<30		<200	<200	<30		<200	<200	<30	
Vanadium	44	41	119		86	69	152		63	70	63		88	95	41	
Zinc	429	331	957		9240	7070	20000		34	14	98		14	<10	51	
pH	7		-		7		-		7		-		7		-	
Organic compounds isolated	32		23		35		14		34		11		24		11	
No. Reliably identified (% of total)	12(38%)		17(74%)		11(31%)		7(50%)		9(26%)		4(36%)		8(33%)		4(36%)	
Chlorinated benzenes			(4)				(1)									
Alkylbenzenes					1											
Phthlates							1									
Terpenoids	5															
Galaxolide	1															
Fyrol PCF	1															
Steroids	2															
Aliphatic hydrocarbons	3		11		9		6		9		4		8		4	
Other compounds			1													
Volatile compounds:																
Trichloroethene					(1)											

Table 2b. Organic chemicals identified, and concentrations of metals and metalloids, in samples of wastewater and sediment associated with wastewater outfalls in the vicinity of the el Rey stream, in the Burzaco area, Buenos Aires, Argentina, 2010. Samples from upstream locations to downstream are presented in the table from left to right. (..) signifies organic compounds identified at trace levels using a selective SIM method. Concentrations in wastewater and river water samples are given as µg/l for both the (tot)al concentrations in the whole sample and separately as dissolved concentrations in filtered samples, concentrations in sediments are given as mg/kg dry weight.

Sample	AR10011		AR10012	AR10021		AR10022	AR10007		AR10008
Type	wastewater		Sediment	Wastewater		Sediment	stream water		stream sediment
Brief description	Melian St pluvial		stream by pipe	Melian St pluvial 2		pipe + stream	el Rey, down		el Rey, down
	tot	diss		tot	diss		tot	diss	
METAL	(µg/l)	(µg/l)	(mg/kg)	(µg/l)	(µg/l)	(mg/kg)	(µg/l)	(µg/l)	(mg/kg)
Antimony	<20	<20	<20	<20	<20	<20	<20	<20	<20
Arsenic	<50	<50	<20	<50	<50	<20	<50	<50	<20
Barium	50	54	128	99	64	177	66	69	194
Cadmium	<10	<10	<1	<10	<10	<1	<10	<10	1
Chromium	<20	<20	47	<20	<20	17	<20	<20	55
Chromium (VI)	<50	<50	-	<50	<50	-	<50	<50	-
Cobalt	<20	<20	7	<20	<20	9	<20	<20	11
Copper	<20	<20	75	30	<20	22	59	23	326
Lead	<50	<50	41	<50	<50	7	<50	<50	81
Manganese	53	30	384	136	17	494	64	56	368
Mercury	<2	<2	0.7	<2	<2	0.2	<2	<2	1
Nickel	<20	<20	13	<20	<20	9	<20	<20	22
Selenium	<200	<200	<30	<200	<200	<30	<200	<200	<30
Vanadium	87	77	31	41	31	56	68	61	87
Zinc	22	12	167	200	27	67	117	49	755
pH	7		-	7		-	7		-
Organic compounds isolated	28		124	33		10	12		82
No. Reliably identified (% of total)	9(32%)		47(38%)	14(42%)		5(50%)	2(17%)		36(44%)
Chlorinated benzenes			(2)	(1)					(2)
DiNP			17						
Other phthalates									3
PAHs			2						1
Indole & derivatives			1						1
Benzothiazole derivs			1						
Cyclic diene derivs									1
Nonylphenol									5
Other phenols				1					1
Galaxolide				1					
Fyrol PCF				1					
Terpenoids	1			1					1
Steroids			1	2					1
Aliphatic hydrocarbons	8		22	6		5	1		19
Other compounds			1	1			1		1

Table 2c. Organic chemicals identified, and concentrations of metals and metalloids, in samples of wastewater and sediment associated with wastewater outfalls in the vicinity of the el Rey stream, in the Burzaco area, Buenos Aires, Argentina, 2010. Samples from upstream locations to downstream are presented in the table from left to right. (..) signifies organic compounds identified at trace levels using a selective SIM method. Concentrations in wastewater and river water samples are given as µg/l for both the (tot)al concentrations in the whole sample and separately as dissolved concentrations in filtered samples, concentrations in sediments are given as mg/kg dry weigh

Guiale meat packing & processing

Discharged wastewater from the Guiale meat packing & processing facility (AR10003) contained total copper and zinc concentrations that were slightly elevated compared to background surface water levels, although the dissolved concentration of these metals, were both somewhat lower. In contrast, the load of organic compounds in this sample was quite

high with 79 compounds isolated. Among those, 30 organic compounds have been reliably identified including a range of chlorinated compounds. 6 phenolic compounds were detected in this sample: phenol; its methylated derivative 4-methylphenol; two chlorinated methylphenols and chlorinated phenoxyphenol also known as Triclosan. Although the precise origins of such compounds in wastewater from a meat packing and processing plant are not known, it is possible they arise from the use of antibacterial or disinfectant preparations on site.

Triclosan, an antimicrobial disinfectant agent that is used in a wide array of consumer products, has been detected in various environmental compartments in other parts of the world, including in surface river waters (Hua *et al.* 2005), treated wastewaters and sludge biosolids (Coogan *et al.* 2007) and also in the human body including in breast milk (Allmyr *et al.* 2006a), in plasma (Allmyr *et al.* 2006b) and in urine (Calafat *et al.* 2008). Due to incomplete removal of Triclosan during wastewater treatment, it is ubiquitous in the environment. Recently it was shown that Triclosan is a potent inhibitor of estradiol and estrone sulfonation in sheep placenta (James *et al. in press*). Results of this study suggested that exposure of pregnant sheep and, by analogy, pregnant women to Triclosan might endanger the pregnancy by reducing total placental estrogen secretion and thereby reducing estrogen action in target tissues critical for maintenance of the pregnancy.

Another chlorinated compound, 1,4-dichlorobenzene, well known environmental contaminant widely used as a deodorizer and disinfectant in sanitary products, was also identified. More information on chlorinated benzenes is presented in Box A. Dimethyl disulfide, a toxic and highly odorous volatile organic compound with action similar to hydrogen sulphide, was also detected in this sample, possibly arising from the degradation of organic material and/or from the use of sulphur compounds during meat processing. Three polycyclic aromatic hydrocarbons (PAHs) were detected in this sample, namely phenanthrene, naphthalene and a hydrogenated derivative of naphthalene. Other aromatic compounds present included Indole and three of its derivatives, together with two alkylated benzenes. This sample has also shown the presence of chloroform at trace levels. Additionally, the sample contained several aliphatic hydrocarbons, natural terpenoids and steroid cholesterol.

The associated sediment (AR10004) also contained copper and zinc, as well as lead, at somewhat higher levels compared to the upstream sediment (AR10006), which may indicate the accumulation of copper and zinc in the sediment at this location due to ongoing discharges of these metals in wastewater. The source of lead is not clear. The levels of these three metals in the sediment (AR10004), however, are only 2-3 times higher than concentration ranges expected for uncontaminated river sediments. Though present at higher levels compared to the upstream sediment (AR10006), the levels of chromium and nickel in the sediment by the Guiale discharge are within the concentration ranges expected for uncontaminated river sediments in other locations. Only 10 organic compounds were isolated from the sediment sample. Nonetheless, two of them were reliably identified as dichlorobenzenes, one of which, 1,4-dichlorobenzene, was also detected in the wastewater

Box A. Chlorinated Benzenes

Chlorinated benzenes, or chlorobenzenes, are simple chlorinated derivatives of benzene, possessing between one and six chlorine atoms (i.e. mono- to hexachlorobenzene). Chlorobenzenes, especially mono-, di-, tri- and hexachlorinated forms, have had a variety of uses, including as solvents (e.g. in commercial PCB formulations) and intermediates in the manufacture of other chemicals such as antioxidants, dyes and pigments, pharmaceuticals and agricultural chemicals. Today only mono- and dichlorobenzenes continue to be manufactured in substantial quantities.

Chlorobenzenes are relatively persistent in the environment and can bioaccumulate in both terrestrial and aquatic systems. Both acute and chronic effects have been reported in a wide range of aquatic organisms and in mammals. Effects of exposure vary depending on the chlorobenzene in question, though common impacts include those on the liver, thyroid and central nervous system (CNS). In general terms, toxicity tends to increase with increasing degree of chlorination (WHO 2004).

For example, human exposure to monochlorobenzene causes CNS depression and respiratory tract irritation, while animal studies have reported liver necrosis, renal toxicity and effects on the pancreas, blood and lymph and adrenal glands (Ware 1988a, Meek *et al.* 1994). Effects reported for dichlorobenzenes in humans include anaemia, skin lesions, vomiting, headaches and eye and respiratory tract irritation (Ware 1988b). More recent study (Yan *et al.* 2008) reported that 1,4-dichlorobenzene can effect neuronal signal transduction in human neuroblastoma SH-SY5Y cells by interfering with the functional activities of acetylcholine receptors.

For tri- and tetrachlorobenzenes, impacts on liver, kidney and thyroid are among the most commonly reported in mammals (Giddings *et al.* 1994a, b). Some evidence for fetal and developmental toxicity has been reported for both tetra- and pentachlorobenzenes (Giddings *et al.* 1994c).

sample AR10003. More information on chlorinated benzenes is presented in Box A. Other organic compounds identified in this sample were aliphatic hydrocarbons.

Pipe on Ortiz street

Wastewater of unknown origin discharged *via* a concealed pipe originating from Ortiz street (AR10017) also contained total copper and zinc concentrations that were slightly elevated compared to background surface water levels, though at slightly lower levels compared to the Guiale wastewater. The dissolved concentrations of these metals, however, were below limits of detection for the methods used. 28 organic compounds were isolated from this wastewater sample. Of 13 compounds that were reliably identified, aliphatic hydrocarbons were predominant. Once again, however, trace levels of 1,4-dichlorobenzene were detected. This sample also contained Galaxolide (HHCb), a polycyclic musk (also known as white musk) which is used as a fragrance enhancer in the perfume industry and in a wide range of personal care products. This chemical has been detected in sewage discharges and surface waters in other countries (Rimkus 1999), and was recently reported to be the most abundant synthetic musk present in discharges to the Tamar and Plym estuaries in the UK (Sumner *et al.* 2010). Indeed, discharges from sewage treatment plants are considered to be the primary route by which such compounds enter aquatic systems. Galaxolide has been also detected in the human body including in the blood (Hutter *et al.* 2005). It is known to possess weak estrogenic activity *in vitro*, the significance of which *in vivo* is now thought by some to have

been underestimated to date, especially when present as one component of complex mixtures of hormonally active compounds (van der Burg *et al.* 2008).

Two fatty acid alcohols were also detected in this sample, 1-dodecanol and 2-ethylhexanol (2-EH). Dodecanol, also known as dodecyl alcohol or lauryl alcohol, is usually obtained from natural plant oils by reduction and has a variety of uses including manufacture of surfactants, lubricating oils, and pharmaceuticals. The primary use of 2-ethylhexanol is in manufacture of the phthalate ester bis(2-ethylhexyl) phthalate (DEHP), a plasticizer commonly used to soften PVC plastic and which is regulated in Europe as “toxic to reproduction”. 2-ethylhexanol itself is a toxic compound which can irritate skin, eyes and respiratory tract. It can also cause nausea and headache after inhalation, and diarrhoea and vomiting after ingestion.

The associated sediment sample (AR10018), a mixture of sediment from inside the pipe and from el Rey stream adjacent to the pipe, contained elevated levels of chromium, copper and nickel, and to a lesser extent lead, manganese and zinc. The levels of chromium, copper and nickel were between 10 and 20 times the respective levels found in the upstream sediment from the el Rey stream (AR10006). The concentrations of chromium and nickel were the highest for all sediment samples in this study. Standards defining thresholds for acceptable levels of metals in river sediments have not been defined in Argentina. However the chromium concentration exceeds the threshold levels for seriously contaminated sediments in the Netherlands (see Table A1 in Box B (NMHSPE 2000)).

Although only a relatively low number of organic compounds was isolated from this sediment sample (12 compounds), three of the 9 compounds which were reliably identified were chlorinated benzenes, including two dichlorobenzenes and one trichlorinated benzene. One of these dichlorobenzenes, 1-4-dichlorobenzene, was also detected (albeit at trace levels) in the corresponding wastewater sample AR10017. More information on chlorinated benzenes is presented in Box A. It is quite common that sediment samples at the place of wastewater discharges accumulate chemicals that were discharged over a period of time, hence providing a picture of contaminant inputs integrated over time. It is possible that this is the case here, though with no clear information on the industrial origins of this particular discharge, it is impossible to say.

C.R.A. radiator factory

Of all the wastewater samples analysed, those discharged from the C.R.A. radiator factory were the most contaminated with metals. Wastewaters from both pipes contained similar high concentrations of total copper (2030-2770 µg/l), with dissolved copper accounting for just under half the total copper load in both samples. The wastewater discharged via the pipe located closest to Cuyo Street (AR10013) also contained a high concentration of zinc (9240 µg/l) predominantly in dissolved forms, and to a lesser extent lead. Wastewater discharged via the pipe located closest to Ortiz Street (AR10015) contained approximately double the total concentration of lead (483 µg/l), though a far lower zinc concentration. This wastewater

Box B. Metals.

Cadmium (Cd) is a rare metal, found naturally in the environment at very low concentrations, typically below 2 mg/kg in sediments (Alloway 1990, ATSDR 2008). When released to aquatic environments cadmium is more mobile than most other metals (ATSDR 2008). Cadmium has many uses, including in metal alloys and for metal plating processes (ATSDR 2008, Hawkins *et al.* 2006). Cadmium has no known biochemical or nutritional function and is highly toxic to plants, animals and humans (ATSDR 2008, WHO 1992). Cadmium is a cumulative toxicant and long-term exposure can result in damage to the kidneys and bone toxicity (Godt *et al.* 2006, WHO 1992). Studies have relatively recently demonstrated kidney damage in humans at lower levels of exposure than previously anticipated (Hellstrom *et al.* 2001). Other health effects from cadmium exposure include disruption to calcium mechanisms causing bone effects, as well as the development of hypertension (high blood pressure) and heart disease. In the short term, inhalation of cadmium oxide fumes or dusts can also affect the respiratory system (ATSDR 2008, Godt *et al.* 2006, WHO 1992). Furthermore, cadmium and its compounds are known to be human carcinogens, primarily for lung cancer following inhalation (DHSS 2005).

Chromium (Cr) is primarily used in the metallurgical industry (in stainless steel and other alloys), as well as in various industrial processes including leather tanning. Hexavalent chromium compounds are used in metal finishing (chrome plating), in wood preservatives and as corrosion inhibitors (ATSDR 2008b). Chromium normally exists in the environment in trivalent Cr(III) forms, which generally have very low solubility in water and tend to rapidly precipitate or adsorb onto suspended particles and bottom sediments. Hexavalent Cr(VI) forms can exist, though far less frequently, and these compounds are usually converted rapidly to trivalent Cr(III) compounds by reducing compounds. Hexavalent forms tend to be readily soluble in water and therefore can be highly mobile in aquatic environments (ATSDR 2008b, DeLaune *et al.* 1998, Lin 2002). Chromium (III) is an essential nutrient for animals and plants, though large doses may be harmful. In contrast, hexavalent chromium is highly toxic even at low concentrations, including for many aquatic organisms (Baral *et al.* 2006). Hexavalent chromium compounds are also corrosive, and in humans allergic skin reactions readily occur following exposure, independent of dose (ATSDR 2008b). Furthermore, hexavalent chromium is a known human carcinogen under some circumstances (IARC 1990).

Copper (Cu) is a widely used metal, primarily as a pure metal or as part of mixtures (alloys) with other metals, though there are also many other uses of copper compounds, including within metal finishing processes. The manufacture of plumbing materials is one of the main uses of copper metal and alloys, in part due to the malleability and thermal conductivity of copper (ATSDR 2004). Levels of copper in the environment are typically quite low, commonly less than 50 mg/kg in uncontaminated freshwater sediments (ATSDR 2004) and below 30 mg/kg in soils (Alloway 1990). Background concentration of soluble copper in uncontaminated surface waters can vary significantly, but levels are typically below 10 µg/l, and often far lower (ATSDR 2004, Comber *et al.* 2008). Copper is an important element for humans and animals in low doses. However, exposure to high levels of bioavailable copper can lead to bioaccumulation and toxic effects (ATSDR 2004). Releases of copper to aquatic systems are of particular concern as many aquatic organisms are extremely sensitive to copper, particularly in soluble forms which are generally far more bioavailable and toxic to a wide range of aquatic plants and animals (ATSDR 2004, Adams & Chapman 2006), with some effects occurring even at very low concentrations (Sandahl *et al.* 2007).

Lead is a metal that is found naturally in the environment, though usually at very low concentrations unless at locations affected by inputs from human activities. Uncontaminated soils and freshwater sediments typically contain less than 30 mg/kg of lead (Alloway 1990, ATSDR 2007). Lead has no known biochemical or nutritional function and is highly toxic to humans as well as many animals and plants (ATSDR 2007, Adams & Chapman 2006, WHO 1989). Levels can build up in the body through repeated exposure and have irreversible effects on the nervous system, which is of particular concern for the developing nervous system in young humans, with impacts occurring even at very low levels of exposure. Other effects include damage to the blood system, and impacts on the kidneys and on reproduction (ATSDR 2004, Jusko *et al.* 2008, Sanders *et al.* 2009). Some studies have indicated that there may be no safe level of exposure, particularly in the developing central nervous system in humans (Canfield *et al.* 2003).

Mercury (Hg) and its compounds have been used in numerous products and industrial processes, including use in batteries, thermometers and other measuring and control instruments, as well as in dental restorations which is known to contribute to municipal wastewater inputs (ATSDR 1999, Danish EPA 2004, UNEP 2002). The main industrial processes that employ mercury is the chlor-alkali mercury cell process (ATSDR 1999, UNEP 2002). In many countries, however, most historical uses of mercury are being increasingly restricted or phased out due to environmental and health concerns (UNEP 2002). Mercury is generally found in the environment at extremely low levels. Level in uncontaminated river sediments can vary, but levels are typically below 0.4 mg/kg (Salomons & Forstner 1984). Surface freshwaters without known sources of mercury contamination generally contain less than 1ng/l (0.001µg/l) of total mercury (Hope & Rubin 2005). Following release to the aquatic environment, mercury can become transformed into methyl mercury, a highly toxic form that can

bioaccumulate and biomagnify (progressively concentrate) to high levels in food chains, particularly in fish (WHO 1989, UNEP 2002). Mercury and its compounds are highly toxic and this metal that has no biochemical or nutritional value (WHO 1989). For the general population, the primary route of exposure to mercury is through diet in the form of methyl-mercury (UNEP 2002). This form of mercury can accumulate in the body and its main impact is damage to the nervous system. Methyl-mercury can readily pass through the placental barrier and the blood-brain barrier, and can have adverse effects on the developing brain and central nervous system in fetuses and children, even at levels to which many people are currently exposed in some countries (Mahaffey *et al.* 2004, UNEP 2002). Recent research also indicates that exposure can increase cardiovascular and heart disease (Virtanen *et al.* 2005).

Nickel as a metal and its alloys, as well as nickel compounds, have many industrial uses, including in metal plating, the manufacture of plumbing and electronic devices, in catalysts, batteries, pigments and ceramics (ATSDR 2005, DHHS 2005). Levels of nickel in the environment are typically low, with uncontaminated freshwater sediments generally containing below 60 mg/kg nickel (Alloway 1990, ATSDR 2005). Although nickel bound to sediments and soils is generally persistent, water-soluble nickel compounds can be quite mobile. Very small amounts of nickel are essential for normal growth and reproduction in most animals and plants, and this is most likely also true for humans (ATSDR 2005, Alloway 1990). However, toxic and carcinogenic effects can result from exposure to higher concentrations for a wide range of life forms, including gastrointestinal and cardiac effects (ATSDR 2005, Cempel & Nickel 2006). In humans, a significant proportion of the population (2-5%) are also nickel sensitive, and effects can occur in sensitised individuals at far lower concentrations (ATSDR 2005). For some aquatic organisms, impacts can occur at very low nickel concentrations (Deleebeeck *et al.* 2008). Furthermore, some nickel compounds have been classified as carcinogenic to humans, and there is also evidence of carcinogenicity in animals (DHHS 2005, IARC 1990).

Zinc (Zn) and its compounds have numerous industrial uses. As a metal, zinc is primarily used as a protective coating of iron and steel and other metals/alloys, particularly through galvanizing, including in the manufacture of plumbing materials and electronic devices. Zinc compounds also have numerous uses, including in paints and pigments, batteries and catalysts (ATSDR 2005b). Levels of zinc are generally quite low in the environment; with levels typically below 100 mg/kg in uncontaminated soils and freshwater sediments (ATSDR 2005b). Zinc is an essential nutrient for humans and animals, however exposure to high concentrations of bioavailable zinc can result in significant bioaccumulation with possible toxic effects, including for aquatic organisms (Adams & Chapman 2006, ATSDR 2005). Symptoms of high doses in humans include pancreatic damage, anaemia and gastrointestinal distress, with similar effects also reported for animals (ATSDR 2005, IPCS 2001).

Contaminated sediments threshold levels and local background levels for metals

Standards defining thresholds for acceptable levels of metals in river sediments have not been defined in Argentina. As a result, certain thresholds from other countries are presented below, including threshold levels for seriously contaminated sediments in the Netherlands (NMHSPE 2000), and levels defined by the National Oceanic and Atmospheric Administration (NOAA) of America, above which adverse biological effects have been usually observed in aquatic organisms (Long & Morgan 1990). For comparison, data is also included from the sediment sample (AR10006) collected from the upstream site of the el Rey stream in Burzaco, as an indication of local background levels for freshwater sediments.

Metal (mg/kg)	Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Zinc
highest value, this study	12 (AR10016)	514 (AR10018)	24700 (AR10016)	2780 (AR10014)	10.7 (AR10028)	152 (AR10018)	20000 (AR10014)
Dutch threshold (a)	12	380	190	530	10	210	720
NOAA level (b)	9.6	145	390	110	1.3	50	270
AR10006 (local background)	<1	26	21	14	0.5	11	73

Table A1. Contaminated sediments threshold levels and local background levels for certain metals, in mg/kg. (a) NMHSPE 2000, (b) Long & Morgan 1990.

also contained cadmium at 14 µg/l, a level elevated above background for this toxic metal which is usually present in the environment at very low concentrations.

The metals present at high concentrations in the discharged wastewaters can be toxic to aquatic life. Of particular concern is the high level of copper as many aquatic organisms are highly sensitive to this metal, particularly when it is present in dissolved forms, and impacts can occur at very low concentrations (ATSDR 2004, Bryan & Langston 1992, Sandahl *et al.* 2007).

The patterns of the organic compounds identified in wastewater samples AR10013 and AR10015 were quite different. The sample that was collected from the pipe located closest to Cuyo Street (AR10013) contained mostly aliphatic hydrocarbons with traces of the volatile chlorinated compound trichloroethene. Trichloroethene is a toxic organic compound that is used as a solvent. It has commonly been found in discharges from industrial sites in other parts of the world, including those involved in production of chlorinated solvents, as well as in the discharges from metal degreasing operations. Trichloroethene has been classified by International Agency for Research on Cancer in Group 2A (i.e. “probably carcinogenic to humans”). The sample collected from the pipe located closest to Ortiz Street (AR10015) contained the following chemicals: the polycyclic musk Galaxolide; the chlorinated-phosphorous flame retardant tris-(2-chloroisopropyl) phosphate (trade name Fyrol PCF); tricyclodecenol, one of the components of immersion oil used in microscopy; the steroid compounds stigmasta-5,22-dien-3-ol and cholest-5-en-3-ol; and natural occurring compounds including (1,1-dimethylethyl)cyclohexanone and the terpenoids squalene, dihydromyrcenol and dihydromethyl jasmonate. Note that the polycyclic musk Galaxolide was also detected in the discharge from the pipe (sample AR10017) located upstream of AR10015. For more information on Fyrol PCF see Box C.

The elevated concentrations of metals in the wastewaters were reflected in their associated sediments samples. The levels of these metals in the sediments suggest their accumulation over time as a result of ongoing discharge of contaminated wastewaters from the C.R.A facility. Both sediment samples contained high levels of copper (8870-24700 mg/kg, 0.9-2.5% by weight), particularly in that sample associated with the outfall closest to Ortiz Street (AR10016). The sediment associated with the pipe located closest to Cuyo Street (AR10014) also contained high levels of zinc (20000 mg/kg, or 2.0% by weight) and lead (2780 mg/kg, or 0.3% by weight). These two metals were also present at lower, though still elevated, levels in the other sediment (AR10016), which also contained cadmium at a concentration higher than background levels of this metal in sediments. The concentrations of copper, lead and zinc in these two samples were the highest for all sediment samples in this study. The concentrations of copper and zinc in both, and lead in AR10014, exceeded the threshold levels for seriously contaminated sediments in the Netherlands (see Table A2 in Box A (NMHSPE 2000)). The level of copper in AR10016 exceeded this threshold value by 130 times, while that of zinc in AR10014 exceeded the threshold by 30 times.

AR10014 also contained an elevated concentration of mercury, and both sediment samples contained vanadium at levels somewhat higher than those found in other sediments analysed from this area. Mercury and vanadium were not present in the wastewaters being discharged *via* either pipe at the time of sampling, and therefore their sources at these locations are not clear. The sediment levels may reflect discharge of wastewaters that vary in quality over

Box C: Fyrol PCF or Tris(monochloroisopropyl) phosphates (TMCPPs)

Tris(monochloropropyl) phosphates (TMCPPs) are four isomers having the molecular formula $C_9H_{18}Cl_3O_4P$ which belong to the class of chlorinated alkyl phosphate esters. The most abundant isomer in commercial products is the completely branched isomer, tris(1-chloro-2-propyl) phosphate and the least abundant form is the completely linear isomer, tris(2-chloropropyl) phosphate. Variations in manufacturing methods result in commercial formulations that contain different proportions of four isomers. Although tris(1-chloro-2-propyl) phosphate is the most abundant isomer, companies have tended to refer to their product by the name tris(2-chloropropyl) phosphate.

TMCPPs are not known to occur naturally but are manufactured from propylene oxide and phosphorous oxychloride (IPCS 1998). TMCPPs are used as a flame retardants in rigid and flexible polyurethane foams, although they may also be used for textile (non-apparel) finishes (NRC 2000). TMCPP mixtures are sold under various trade names including Antiblaze 80, Amgard TMCP, Fyrol PCF, and Hostaflam PO 820.

Tris(1-chloro-2-propyl) phosphate is not readily biodegraded in sewage sludge inocula though it is rapidly metabolised by fish (IPCS 1998). These compounds are relatively stable and undergo only slow hydrolysis under weak alkaline or acid conditions. Traces of tris(1-chloro-2-propyl) phosphate have been detected in industrial and domestic effluents, but not in surface waters and sediments (IPCS 1998). Also three isomers of TMCPP have been detected in air samples from some common indoor work environment, i.e., an office building, a day care center, and a school building (Carlsson *et al.* 1997).

Tris(1-chloro-2-propyl) phosphate is of low to moderate acute toxicity by oral (LD_{50} in rats is 101-4200 mg/kg body weight), dermal (LD_{50} in rats and rabbits is > 5000 mg/kg body weight) and inhalation routes (LD_{50} in rats is > 4.6 mg/litre) (IPCS 1998). Rabbit eye and skin irritant studies have indicated that tris(1-chloro-2-propyl) phosphate is either non-irritant or mildly irritant.

The reproductive toxicity, immunotoxicity and carcinogenic potential of tris(1-chloro-2-propyl) phosphate have not been investigated. There are no data on the subchronic or chronic toxicity of TMCPPs for dermal, inhalation, or oral routes of exposure (NRC 2000). The National Research Council (NRC) recommends that further studies need to be carried out into the effects of the release of TMCPPs vapours into air and into saline from treated fabric (NRC 2000). In addition, no studies of the effects of this flame retardant on humans are available. However, acute toxicity values for other organisms in the environment are available, with LD_{50} values ranging from 3.6 to 180 mg/litre. Aquatic toxicity information shows that changes occur in algae, daphnids and fish at concentrations of 6, 32, and 9.8 mg/litre, respectively (IPCS 1998).

Despite the lack of information on the carcinogenic potential of the TMCPPs identified, studies on a very similar compound, tris(2-chloroethyl) phosphate, showed that it possesses carcinogenic properties when tested on mice and rats (IPCS 1998) and recently it has been added to the list of candidates as 'substances of very high concern' under the REACH Regulation (ECHA 2010).

time, or result from historic releases that no longer take place. Further, more detailed, investigations would be necessary in order to determine the origins of this contamination.

Both sediment samples AR10014 and AR10016 contained a range of aliphatic hydrocarbons, as well as the seemingly ubiquitous 1,4-dichlorobenzene (though only at trace levels in these samples). Additionally, sample AR10016 (containing a combination of sediment from el Rey stream and deposits from the discharge pipe closest to Ortiz Street) showed the presence of trace amounts of 1,2-dichlo-, 1,2,3-trichloro- and 1,2,4-trichlorobenzene. Also, residues of

the plasticizer bis(2-ethylhexyl) phthalate (DEHP) itself were identified in sample AR10016. More information on DEHP is presented in Box D.

Viel street pluvial pipe

The wastewater sample collected from the Viel street pluvial pipe discharge (AR10009), and the associated sediment (AR10010) did not contain any metals at levels above levels typically found in uncontaminated surface waters and sediments. Organic compounds identified in both samples were represented only by aliphatic hydrocarbons, which could simply reflect a background of urban contamination.

Fradealco

Neither the wastewater sample collected from the Fradealco facility discharge pipe (AR10019) nor the associated sediment (AR10020) contained any metals at levels above those typically found in uncontaminated surface waters and sediments. Again, in the samples from this site, only a limited number of aliphatic hydrocarbons were identified..

Melian street pluvial pipes

The wastewater sample collected from the Melian street pluvial pipe (AR10011) did not contain any metals at levels above levels typically found in uncontaminated surface waters. Organic compounds identified in this sample were again only aliphatic hydrocarbons and squalene, which could have natural origins. The associated sediment sample (AR10012) was also largely uncontaminated, with metal concentrations similar to those in the upstream sediment (AR10006). Although copper, lead and zinc were present in sediment AR10012 at concentrations 2-3 times higher than for the upstream sediment, these levels were still only slightly above concentration ranges typically found in uncontaminated river sediments.

In contrast, the load of organic compounds in this sediment sample was very high, with 124 compounds isolated, from which 47 have been reliably identified. Sample AR10012 contained 17 isomers of the plasticizer diisononyl phthalate (DiNP), often used as a replacement for other, more toxic, forms of phthalate ester, including DEHP. More information on both DiNP and DEHP is presented in Box D.

This sample also contained a high number of aliphatic hydrocarbons, together with aromatic hydrocarbons including a sulphur-containing compound (a benzothiazole derivative), the polycyclic aromatic hydrocarbon phenanthrene and a nitrogen-containing compound (indole derivative), which together may suggest some recent or historic oil contamination on the site investigated.

The wastewater sample collected from the 2nd (smaller) Melian street pluvial pipe (AR10021) was largely uncontaminated with metals, though it did contain total copper and zinc concentrations that were slightly elevated compared to typical background surface water levels. The dissolved concentrations of both these metals were, however, far lower and within background concentration ranges. Moreover, metal concentrations in the associated

Box D: Phthalates (phthalate esters)

Phthalates (or, more accurately, phthalate diesters) are nonhalogenated chemicals with a diversity of uses, dominated by use as plasticizers (or softeners) in plastics, especially PVC (e.g. in cables and other flexible components). Other applications included uses as components of inks, adhesives, sealants, surface coatings and personal care products. Some phthalates are discrete chemicals, such as the well known di(2-ethylhexyl) phthalate (DEHP), while others are complex mixtures of isomers, such as diisononyl phthalate (DINP).

All uses of phthalates, especially the major use as PVC plasticisers, result in large-scale losses to the environment (both indoors and outdoors) during the lifetime of products, and again following disposal. Within the European Union (EU) alone, this amounts to thousands of tonnes per year (CSTEE 2001a). As a result, phthalates are among the most ubiquitous man-made chemicals found in the environment. They are widely found in the indoor environment, including in air and dust (Otake *et al.* 2001, Butte & Heinzow 2002, Fromme *et al.* 2004) at concentrations which commonly reflect the prevalence of plastics and certain textiles within the rooms sampled (Abb *et al.* 2009). Phthalates are commonly found in human tissues, including in blood and, as metabolites, in urine (Colon *et al.* 2000, Blount *et al.* 2000, Silva *et al.* 2004), including reports of significantly higher levels of intake in children (Koch *et al.* 2006). In humans and other animals they are relatively rapidly metabolised to their monoester forms, but these are frequently more toxic than the parent compound (Dalgaard *et al.* 2001).

Substantial concerns exist with regard to the toxicity of phthalates to wildlife and humans. For example, DEHP, one of the most widely used to date, is known to be toxic to reproductive development in mammals, capable (in its monoester form MEHP) of interfering with development of the testes in early life, thought to be mediated through impacts on testosterone synthesis (Howdeshell *et al.* 2008, Lin *et al.* 2008). Even at low doses, exposure to mixtures of phthalates can result in cumulative effects on testicular development in rats (Martino-Andrade *et al.* 2008). In addition, adverse impacts on female reproductive success in adult rats and on development of the young have been reported following exposure to this chemical (Lovekamp-Swan & Davis 2003, Grande *et al.* 2006, 2007, Gray *et al.* 2006).

Butylbenzyl phthalate (BBP) and dibutyl phthalate (DBP) have also been reported to exert reproductive toxicity (Ema & Miyawaki 2002, Mylchreest *et al.* 2002, Aso *et al.* 2005). Both DEHP and DBP are classified as “toxic to reproduction” within Europe. Other research has revealed a correlation between phthalate exposure during pregnancy and decreased ano-genital index (distance from the anus to the genitals) in male children (Swan *et al.* 2005). Decreased AGI correlated with concentrations of four phthalate metabolites, namely monoethyl phthalate (MEP), mono-n-butyl phthalate (MBP), monobenzyl phthalate (MBzP), and monoisobutyl phthalate (MiBP). It was also found that DBP can not only be taken up by crops and enter the food chain, but also affects proteome formation as well as the physiology and the morphology of some crops during growth (Liao 2006). Other commonly used phthalates, including the isomeric forms DINP and DIDP (diisodecyl phthalate), are of concern because of observed effects on the liver and kidney, albeit at higher doses.

At present, there are relatively few controls on the marketing and use of phthalates, despite their toxicity, the volumes used and their propensity to leach out of products throughout their lifetime. Of the controls which do exist, however, probably the best known is the EU-wide ban on the use of six phthalates in children’s toys and childcare articles, first agreed as an emergency measure in 1999 and finally made permanent in 2005 (EC 2005). While this addresses one important exposure route, exposures through other consumer products have so far largely escaped regulation. Within Europe, three phthalates (DBP, BBP and DEHP) were proposed to be included into the first shortlist of seven substances for which detailed justification and authorization will be required for any proposed continued uses (ECHA 2009). These phthalates, together with recently added di-isobutyl phthalate (DiBP), have been included into the list of candidates as ‘substances of very high concern’ under the REACH Regulation (ECHA 2010).

Within the EU DEHP is listed as a priority substance under the Water Framework directive, a regulation designed to improve the quality of water within the EU (EU 2008). DEHP and DnBP have also been identified as substances for priority action under the OSPAR convention, under which signatory countries have agreed a target of cessation of discharges, emissions and losses of all hazardous substances to the marine environment of the North-East Atlantic by 2020, the “one generation” cessation target (OSPAR 1998).

sediment (AR10022) were equivalent to the upstream, uncontaminated, stream sediment (AR10006).

The pattern of organic compounds identified in the wastewater sample AR10021 was very similar to that in the sample AR10015. The range of compounds detected in both samples included, once again, the polycyclic musk Galaxolide, the flame retardant Fyrol PCF, a number of steroid compounds and aliphatic hydrocarbons. Additionally, sample AR10021 also contained traces of 1,4-dichlorobenzene and of 4-(1,1-dimethylethyl)phenol, also known as p-tert-butylphenol. This latter chemical is used as an intermediate for the production of phenolic resins, although its precise origins in this particular sample cannot be determined.

el Rey stream, downstream

Samples of water (AR10007) and sediment (AR10008) were also collected from the el Rey stream at a location downstream of all sampled discharges described above. At this point, the stream water contained both total and dissolved concentrations of copper and zinc that were higher than those found in the stream water sample collected from the upstream site (AR10005).

In addition, the downstream sediment (AR10008) contained higher concentrations compared to the upstream sediment (AR10006) for many of the metals that have been highlighted for samples associated with the various outfalls to the el Rey stream. Most notably, the concentrations of copper and zinc in the downstream sediment were 15 and 10 times higher than the upstream sediment concentrations respectively. The concentration of lead was 6 times higher, and those of chromium and nickel were both 2 times higher. In addition cadmium was detected in the downstream sediment (albeit only a 1 mg/kg), but not in the upstream sediment. Although considerable variation was evident in levels of metal contamination of sediments in the el Rey stream at the various different points sampled, the generally higher levels found in the final downstream sample than in the initial upstream sample may reflect the combined contribution of waste inputs and run-off from all point and diffuse sources to the stream as it passes through the Burzaco Industrial Park.

A rather limited number of organic compounds was isolated from the stream water sample, with only one aliphatic hydrocarbon and molecular sulphur being reliably identified. However, the sediment sample AR10008 did show signs of greater loading with organic compounds than the sediment sample collected upstream of all sites (AR10006). Those identified in this final downstream sample included many which were also detected in the sediment samples collected close to discharge outfalls upstream, including residues of chlorinated benzenes, steroids, aliphatic and aromatic hydrocarbons, and the plasticizer DEHP. This sample also contained two more phthalate esters, which were not detected in the upstream samples, namely diisobutyl and butyl benzyl phthalate. More information on phthalates is presented in Box D. Several phenolic compounds were also conspicuous in this downstream sediment sample, including 5 isomers of the persistent, hormone-disrupting compound nonyl phenol. The presence of this compound suggests an additional point source to the stream other than those specifically sampled in this study, or perhaps an historical

contamination incident. Given the known aquatic toxicity of this chemical, its presence and possible source deserves urgent investigation.

The elevated levels of certain metals and presence of organic contaminants in the el Rey stream sediment sample that was collected downstream of all investigated outfalls indicates contamination of the stream as a result of ongoing inputs of contaminated wastewaters.

AySA sewage treatment plant

On three separate occasions between 26th January and 11th February 2010, samples of the treated wastewater being discharged from the AySA facility were collected, along with sediment from the edge of the Matanza-Riachuelo River adjacent to the discharge pipe. Details of all samples are presented in Table 3.

Sample	Date	Type	Description
AR10023	26/01/2010	wastewater	Discharge pipe into Matanza-Riachuelo River
AR10024		sediment	from the edge of the Matanza-Riachuelo River adjacent to the discharge pipe
AR10025	28/01/2010	wastewater	Discharge pipe into Matanza-Riachuelo River
AR10026		sediment	from the edge of the Matanza-Riachuelo River adjacent to the discharge pipe
AR10027	11/02/2010	wastewater	Discharge pipe into Matanza-Riachuelo River
AR10028		sediment	from the margin of the Matanza-Riachuelo River adjacent to the discharge pipe

Table 3. Description of samples associated with the AySA sewage treatment plant, Aldo Bonzi, La Matanza, Argentina, 2010

Results

The data from the analyses are summarised in Table 4, and discussed below.

The three samples of treated wastewater (AR10023, 25 & 27) contained notable total concentrations of chromium (66-192 µg/l), copper (59-205 µg/l), nickel (22-95 µg/l) and zinc (444-860 µg/l). Of these four metals, only zinc was present in dissolved forms above limits of detection for the methods used, in the range 33 – 58 µg/l. The total (whole sample) concentrations of these four metals in the treated wastewater samples were the highest total levels of all wastewater samples included in this study, other than the two samples of wastewater discharged from the C.R.A. radiator factory. The concentrations of these metals are many times higher than background levels typically found in surface waters.

In addition to the high total concentrations, this study has demonstrated significant variations in the concentrations of certain metals in the discharged treated wastewater on separate occasions. Wastewater collected on the 11th February (AR10027) contained total concentrations of chromium, copper, nickel and zinc that were two times higher than levels in the samples collected on earlier occasions (AR10023, 25).

Sample	AR10023		AR10025		AR10027		AR10024	AR10026	AR10028
Type	Wastewater						Sediment		
Brief description	Discharge pipe						M-R River by pipe		
Date	26/01/2010		28/01/2010		11/02/2010		26/01/2010	28/01/2010	11/02/2010
	total	diss	total	diss	total	diss			
pH	7	7	7	7	7	7	-	-	-
METAL	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(mg/kg)		
Antimony	<20	<20	<20	<20	<20	<20	<20	<20	<20
Arsenic	<50	<50	<50	<50	<50	<50	<20	<20	<20
Barium	200	93	174	92	291	94	322	288	245
Cadmium	<10	<10	<10	<10	<10	<10	1	2	1
Chromium	66	<20	71	<20	192	<20	271	268	194
Chromium (VI)	<50	<50	<50	<50	<50	<50	-	-	-
Cobalt	<20	<20	<20	<20	<20	<20	6	6	6
Copper	59	<20	82	<20	205	<20	731	494	1570
Lead	<50	<50	<50	<50	<50	<50	498	405	1020
Manganese	108	76	128	75	250	107	200	205	265
Mercury	<2	<2	<2	<2	<2	<2	5.8	6.6	10.7
Nickel	22	<20	43	<20	95	<20	119	138	78
Selenium	<200	<200	<200	<200	<200	<200	<30	<30	<30
Vanadium	25	<20	32	<20	59	<20	86	105	69
Zinc	444	58	427	39	860	33	1050	1090	984
Organic compounds isolated	53		75		136		41	63	82
No. reliably identified (% of total)	18(34%)		38(51%)		43(32%)		18(44%)	33(52%)	30(37%)
Chlorinated benzenes	(2)		(1)		1(1)		(2)	(2)	(2)
Chlorpyrifos								1	1
Atrazine	1		1		1				
Galaxolide							1	1	1
Phthalates								1	1
Fyrol PCF	1		1						
Nonylphenol			12						
Other phenols					1				
PAHs	1				6		1		
Alkylbenzenes			5		7				3
Cyclic diene derivs								2	
Terpenoids	1		1		1		1	1	
Steroids	1		2		1				4
Decyltetraglycol					1				
Diisooctyl adipate					1				
Indole & derivatives								2	1
Aliphatic hydrocarbons	10		11		16		13	21	14
Other compounds	1		1		2			2	2
Volatile compounds:									
Chloroform			(1)		(1)				
Trechloroethene			(1)		(1)				
Tetrachloroethene			(1)		(1)				
Dichloromethane					(1)				

Table 4. Organic chemicals identified, and concentrations of metals and metalloids, in samples of wastewater and sediment associated with the AySA sewage treatment plant, Aldo Bonzi, La Matanza, Argentina, 2010. (..) signifies organic compounds identified at trace levels using a selective SIM method. Concentrations in wastewater samples are given as µg/l, for both the total concentrations in the whole sample and separately as (diss)olved concentrations in a filtered sample; concentrations in sediments are given as mg/kg dry weight.

Data have been published on the composition of discharged wastewater from the AySA sewage treatment plant for the period between autumn 2008 to summer 2009, under the

Program of integrated monitoring of the quality of superficial water and sediments of the Matanza-Riachuelo River basin and the South Coastal Strip of the Río de la Plata (ACUMAR 2009). Those data also demonstrate variations in treated wastewater metal concentrations for this facility. On one occasion, a sample of treated wastewater discharged in autumn 2008 contained total and dissolved concentrations of nickel that were over 40 times and 4 times higher respectively than levels in three samples collected by ACUMAR on other occasions.

The metal concentrations found in the current study for the three samples of discharged wastewaters (AR10023, 25, 27) are, for the majority of metals, consistent with those data previously published by ACUMAR for wastewater samples collected from the same outfall on four occasions between autumn 2008 to summer 2009 (ACUMAR 2009), as summarised in Table 5. A few minor differences do exist between the two sets of data, which were collected during different periods of time. The average total chromium and zinc concentrations found in this study were approximately two times higher than the corresponding levels published by ACUMAR. The average total nickel concentration published by ACUMAR was far higher than the corresponding data from this study, but this difference was due to the single high value in the ACUMAR data from autumn 2008 noted above. Excluding this one sample, the average total nickel concentration for the ACUMAR data would be similar to that determined in the current study.

A diverse range of organic compounds were detected in all three samples of treated wastewater (AR10023, AR10025 and AR10027), with a number of compounds isolated ranging from 53 in sample AR10023 to 136 in sample AR10027. The number of compounds which could be reliably identified ranged from 18 to 43. Among those, the following compounds were detected in every sample, irrespective of sampling date:

- Atrazine, one of the most widely used herbicides for the control of weeds and grasses (see Box E);
- Traces of chlorinated dichlorobenzenes;
- Steroid and terpenoid compounds;
- Aliphatic hydrocarbons

Compounds that were detected in the wastewater discharge on at least two occasions included:

- Fyrol PCF, a flame retardant;
- Polycyclic aromatic hydrocarbons (PAHs);
- Alkylated benzenes;
- Trace amounts of volatile chlorinated organic compounds including chloroform, trichloroethene and tetrachloroethene.

Additionally, several compounds were detected in only one of the three samples (i.e. on one of the three occasions), again reflecting periodic variations in the quality of the final treated effluent being discharged. Those chemicals included methylphenol, diisoadipate, decyltetraglycol and dichloromethane in sample AR10027, 12 isomers of nonylphenol in

Box E: Atrazine

Atrazine, a selective triazine herbicide, is a synthetic chemical which is used to control residual weeds in maize and sweet corn, grass in forest, non-crop areas and weeds in raspberries and roses. The full chemical name of this compound is 6-chloro-N-ethyl-N-isopropyl-1,3,5-triazinediyl-2,4-diamine. Other trade names include Atrazine granules, New chlorea, Residox, Weedex, Primatol A, Tripart Atrazine.

Atrazine is the most widely used herbicide from the family of triazines worldwide, in the United States alone approximately 70 million pounds of active ingredient is applied domestically per year (US EPA 2009a). This chemical relatively persistent in soil (up to 1 year) and, as it is moderately soluble in water, may migrate to surface and ground waters.

Conventional methods for both wastewater treatment and drinking water treatment processes are largely ineffective in removing atrazine (Ghosh & Philip 2004; William & Lauren 1996; Ternes *et al.*, 2002; Verstraeten *et al.*, 2002). Therefore, it has been frequently detected in surface waters, groundwater and also in drinking water (Battaglin & Hay 1996; Paul & Steven 2001; Cerejeira *et al.* 2003; Hua *et al.* 2006). Atrazine has been classified as a Restricted Use Pesticide in the USA due to its potential for groundwater contamination.

Atrazine may degrade into one of many metabolites, each of varying persistence and toxicity. The most common metabolites of atrazine are hydroxyatrazine (HA), deethylatrazine (DEA), deisopropylatrazine (DIA), didealkylatrazine (DDA), and deethylhydroxy atrazine (DEHA), which may form through five different degradation processes: hydrolysis, adsorption, volatilisation, photodegradation, and microbial degradation. Some toxicological evidence indicated that only the chlorinated metabolites DEA, DIA, and DDA, in addition to atrazine, pose a risk to human health (Winkelmann & Klaine 1991). Whilst the toxic effects of atrazine are currently under review, little is known regarding the effects of many of its metabolites, particularly in the aquatic environment.

Atrazine is included into Annex X "List of priority substances in the field of water policy" of the EU Parliament and Council Decision (EC 2001), which amended Water Framework Directive 2000/60/EC (EC 2000), as possible "priority hazardous substance" due to their widespread distribution in the environment and toxic effects they may exhibit on living organisms.

High mobility of atrazine in soil and its potential for groundwater contamination may represent a serious human health hazard because of potential toxic effects of this herbicide. Atrazine has been identified as disruptor of endocrine system in numerous experimental studies in laboratory animals and aquatic organisms (Salaberria *et al.* 2009; Freeman *et al.* 2005; Victor-Costa *et al.* 2010; Friedmann 2002; Song *et al.* 2009). It may also affect nervous and reproductive systems (Cooper *et al.* 2000; Narotsky *et al.* 2001; Rodriguez *et al.* 2005). Excessive exposure to atrazine may affect the digestive system, eye, heart, kidney, liver and skin.

In 2009, the U.S. Environmental Protection Agency started a comprehensive new evaluation of atrazine to determine its effects on humans (US EPA 2009b). At the end of this process, the agency will decide whether to revise its current risk assessment of the pesticide and whether new restrictions are necessary to better protect public health. EPA will evaluate the pesticide's potential cancer and non-cancer effects on humans. Included in this new evaluation will be the most recent studies on atrazine and its potential association with birth defects, low birth weight, and premature births. EPA will consider the potential for atrazine cancer and non-cancer effects, and will include data generated since 2003 from laboratory and population studies. On April 26 - 29, 2010, the FIFRA Scientific Advisory Panel had a meeting to review and consider the "Reevaluation of the Human Health Effects of Atrazine: Review of Experimental Animal and In Vitro Studies and Drinking Water Monitoring Frequency." There is still no information available on the outcomes of this meeting.

sample AR10025, and the PAH phenanthrene in sample AR10023. Despite these inevitable variations, the data set overall clearly indicates ongoing contamination of receiving waters with a range of toxic and persistent compounds, residues of some of which are passing through the treatment process unchanged.

metal (µg/l)	ACUMAR				This study (AR10023, 25, 27)			
	total		dissolved		total		dissolved	
	range	average	range	average	range	average	range	average
arsenic	<18	<18	<18	<18	<50	<50	<50	<50
cadmium	0.5 - 1.4	0.8	nd - 0.4	0.4	<10	<10	<10	<10
chromium	26 - 83	54	12 - 16	14	66 - 192	110	<20	<20
copper	26 - 128	70	6 - 24	14	59 - 205	115	<20	<20
mercury	0.039 - 0.062	0.051	0.008	0.008	<2	<2	<2	<2
nickel	30 - 1705	452 (34*)	7 - 117	43 (18*)	22-95	53	<20	<20
lead	4 - 31	19	3 - 6	5	<50	<50	<50	<50
zinc	102 - 519	310	23 - 84	45	427-860	577	33-58	43

Table 5. Comparison of metal concentrations in discharged wastewater samples from this study (AR1023, 25, 27) with data published by ACUMAR (ACUMAR 2009), showing the range and average values for both the total concentrations in the whole sample and dissolved concentrations in a filtered sample. * one high value outlier removed

The concentrations of metals in the three sediment samples collected from the Matanza-Riachuelo River immediately adjacent to the AySA outfall (AR10024, 26, 28) generally reflected the profiles of metals in the wastewater samples (AR10023, 25, 27). All the sediment samples contained high levels of copper and zinc, at between 10 and 30 times higher than concentrations expected for uncontaminated river sediments. To a lesser extent, the sediment samples contained chromium and nickel, at 2-3 times higher than typical background levels for freshwater sediments. The concentrations of copper and zinc in all three sediments, and lead in AR10028, exceeded the threshold levels for seriously contaminated sediments in the Netherlands (see Table A1 in Box B (NMHSPE 2000)).

In addition, all sediment samples contained elevated levels of lead and mercury, with both metals present in the three samples at concentrations between 15 and 30 times higher than concentrations typically found in uncontaminated river sediments. The concentration of mercury in AR10028 was the highest for all sediment samples in this study, and the levels of mercury and lead in this sample exceeded the threshold levels for seriously contaminated sediments in the Netherlands, (again, see Table A1 in Box B (NMHSPE 2000)). Lead and mercury were not present in any of the wastewater samples at levels above limits of detection for the methods used.

The elevated levels of these metals in the river sediments indicate their accumulation at this location due either to their ongoing discharges in treated wastewaters, or possibly from historic releases via this outfall.

The number of organic compounds isolated from the same three sediment samples AR10024, AR10026 and AR10028 was proportional to the number of compounds isolated from the corresponding wastewaters (AR10023, AR10025 and AR10027) and consisted of 41, 63 and 82 compounds respectively. In another words, the sediment and wastewater samples AR10028 and AR10027 collected at the same time had the highest load of organic compounds. Nonetheless, several groups of organic compounds were present in all three sediment samples:

- Galaxolide, a synthetic polycyclic musk;
- Traces of dichlorobenzenes;
- Aliphatic hydrocarbons

Compounds that were detected in at least two samples were:

- Chlorpyrifos, an organophosphate insecticide that is used to control insect pests. Trade names include Brodan, Detmol UA, Dowco 179, Dursban, Empire, Eradex, Lorsban, Paqeant, Piridane, Scout, and Stipend. Chlorpyrifos is moderately toxic chemical and chronic exposure has been linked to neurological effects, developmental disorders, and autoimmune disorders. More information of chlorpyrifos is presented in Box F;
- The phthalate ester DEHP, regulated as “toxic to reproduction” in Europe;
- Terpenoids;
- Indole and its derivatives.

Additionally, several organic compounds have been detected in only one of the three sediment samples, including alkylated benzenes and steroid compounds in sample AR10028, two derivatives of cyclic dienes (cyclododecadiene and alkylated cycloheptadiene) in sample AR10026 and phenanthrene in sample AR10024.

Neither Chlorpyrifos nor Galaxolide were detected in the corresponding wastewater samples at the time of the sampling. Their presence in the sediments in the vicinity of the outfall may indicate past or periodic releases of these chemicals from the AySA sewage treatment plant.

Both Atrazine and Chlorpyrifos are included into Annex X “List of priority substances in the field of water policy” of the EU Parliament and Council Decision (EC 2001), which amended Water Framework Directive 2000/60/EC (EC 2000), as possible “priority hazardous substance” due to their widespread distribution in the environment and toxic effects they may exhibit on living organisms. Moreover, joint toxicity tests in fish between atrazine and chlorpyrifos have shown greater than additive responses in invertebrates, suggesting complex and more severe impacts may arise from the presence of mixtures of hazardous chemicals in the environment, though the interactions in vertebrates were less pronounced (Mehler *et al.* 2008).

Conclusions

The results of this study demonstrate that the discharge of wastewaters from at least some of the industrial facilities located in the Burzaco area are leading to the contamination of the waters and sediments of the Arroyo del Rey as it flows northwards through the industrial park. As waters and suspended sediments from this stream ultimately flow to the Riachuelo, it is clear even from this limited study that the Parque Industrial Burzaco is acting as one point source of toxic metals and persistent organic pollutants to the Matanza-Riachuelo basin overall. Although the Arroyo del Rey may not be the most polluted tributary in the system, it is clearly one of many such tributaries in the basin which receive a variety of industrial waste

Box F: Chlorpyrifos

Chlorpyrifos belongs to the class of organic compounds called organophosphates (OPs). OP is the currently used generic term that includes all insecticides containing phosphorus. All organophosphates are derived from one of the phosphorus acids, and as a class are generally the most toxic of all pesticides to vertebrates. Because of the similarity of OP chemical structures to the “nerve gases”, their modes of action are also similar. Their insecticidal qualities were observed in Germany during World War II in the study of the extremely toxic OPs nerve gases sarin, soman, and tabun. Initially, the discovery was made in search of substitutes for nicotine to control aphids (Metcalf 1995).

Chlorpyrifos is a heterocyclic organophosphate. Trade names for chlorpyrifos include Dursban, Lorsban, Loxiran, Zidil, Detmol, Perinex, Brodan, Eradex and Spannitt. In pure form, chlorpyrifos is white crystal compound with a mild mercaptan odour. It is soluble in water to 2mg/l (Galo & Lawryk 1991). It is stable in neutral and weekly acidic media and hydrolysed by strong alkalis.

Chlorpyrifos is a broad-spectrum insecticide (Metcalf 1995). Chlorpyrifos is one of the most commonly used pesticides in the indoor environment today. It has been used as an active ingredient in agricultural formulations on wide range of crops including pome fruit, stone fruit, citrus fruit, nut crops, strawberries, figs, bananas, vines, vegetables, potatoes, beet, tobacco, soya beans, sunflowers, groundnuts, rice, cotton, lucerne, cereals, maize, outdoor ornamentals, turf and in forestry (RSC 1987). It is also used in flea collars and dips, animal sprays and shampoos, carpets, crack and crevice sprays, and for subterranean termite treatment. According to the US Environmental Protection Agency, 972 registered products contain chlorpyrifos for widespread uses for termite and roach control and home and garden use (US EPA 1997).

OPs have two distinctive features: they are generally much more toxic to vertebrates than other classes of insecticides, and chemically they are the most unstable or non-persistent. It is this latter characteristic that brought them into agricultural use as substitutes for the persistent organochlorines. Organophosphorus insecticides are reactive compounds and readily degrade by oxidation, hydrolysis, and in living organisms (Saint-Fort 1991). The half-life of chlorpyrifos in soil is 80-100 days. The main metabolite is 3,5,6-trichloro-2-pyridinol, which is subsequently degraded to organochlorine compounds and carbon dioxide (RSC 1987). In animals rapid metabolism occurs following oral administration of chlorpyrifos with the principal metabolites being 3,5,6-trichloro-2-pyridinol and 23monoethyl chlorpyrifos.

Thus, OPs are general biocides that are toxic to nearly all animals. The oral LD50 values (mg/kg) of chlorpyrifos to mallard and pheasants are 75 and 12 respectively (Metcalf 1995). Mullie & Keith (1993) reported that aerial application of chlorpyrifos resulted in temporary decrease in the abundance of birds, bird foods and cholinesterase levels in several bird species. Chlorpyrifos is also highly toxic to fish, bees and to beneficial parasites and predators (RSC 1987). The LC50 (96 hours) of chlorpyrifos for rainbow trout is 0.003mg/l. Even if it does not provoke any mortality, sublethal doses may be an important threat for species and population equilibrium by modifying physiological or behavioural parameters such as pheromonal communications (Delpuech *et al.* 1998). As a result, pollution of the environment by this insecticide could lead to a global modification of the biodiversity. In 2009, US EPA has set new limitations on the use of chlorpyrifos to protect endangered and threatened salmon and steelhead in California, Idaho, Oregon and Washington (US EPA 2009).

Recent experimental data on rats suggest that chlorpyrifos may be a developmental neurotoxicant and that exposure *in utero* may cause biochemical and functional aberrations in foetal neurones as well as deficits in the number of neurones (Landrigan *et al.* 1999; Slotkin 1999; Brimijoin & Koenigsberger 1999). It was also reported (US EPA 2006) that Chlorpyrifos can cause cholinesterase inhibition in humans; that is, it can over stimulate the nervous system causing nausea, dizziness, confusion, and at very high exposures (e.g., accidents or major spills), respiratory paralysis and death.

At the present time, the greatest concern about uses of formulations containing chlorpyrifos relates to toxic effects on humans, especially children (Landrigan 2001; Szpir 2006; Colborn 2006, Rauh 2006). An extensive and unusual pattern of birth defects including defects of brain, eyes, ears, palate, teeth, heart, feet, nipples and genitalia were reported in the earlier study of four children exposed *in utero* to chlorpyrifos (Sherman 1996). Studies of indoor exposure to chlorpyrifos indicate that young children are at higher risks to the semivolatile pesticide than had been previously estimated (Davis & Ahmed 1998; Gurunathan *et al.* 1998). The study showed that after a single broadcast use of the pesticide by certified applicators in apartment rooms, chlorpyrifos continued to accumulate on children's toys and hard surfaces 2 weeks after spraying. Based on the findings of this and other research studies, the estimated chlorpyrifos exposure levels from indoor spraying for children are approximately 21-119 times above the current recommended reference dose of 3µg/kg/day from all sources. Furthermore, it was found that chlorpyrifos is readily absorbed through the skin and decontamination procedures that rely on soap and water have low removal efficiencies (Fenske & Lu 1994).

discharges and may, therefore, provide an example of what might also be happening elsewhere. Further, more detailed investigations would be necessary in order to trace the exact sources of the key contaminants identified in this study and to extend this work to other, similarly industrialised streams which feed the Matanza-Riachuelo system.

Likewise, while AySA's southwest municipal wastewater treatment plant is undoubtedly only one of many sources of effluent discharge to the Matanza-Riachuelo basin, it is a significant point source nonetheless. The fact that a wide range of common industrial pollutants can be identified, in some cases at significantly elevated concentrations, in the final treated effluent at the point of discharge to the aquatic environment provides an illustration of the inherent limitations of conventional wastewater treatment plants in handling and decontaminating wastewaters of industrial origin. Although it is impossible to say what proportion of the total load of toxic metals and persistent organic pollutants being directed to the treatment plant from industrial sources are being either degraded or retained in sludges, it is evident that neither degradation nor retention are capable of preventing these priority pollutants from being discharged to the Matanza-Riachuelo system and, therefore, contaminating the environment downstream. At the same time, it is likely that a significant proportion of those contaminants most resistant to degradation will routinely accumulate in the sludge wastes generated by the treatment plant, raising the potential for further, more widespread contamination as a result of subsequent disposal of treatment plant sludges.

As noted above, both the Burzaco industrial park and AySA's southwest treatment plant are merely case studies of what is likely to be a much wider and more generic problem of hazardous chemical pollution of water from industrial activities within the Buenos Aires Municipal Area. Together, they serve to illustrate the consequences of poorly controlled, possibly untreated, effluents from a wide range of industrial units within industrial zones and of the inability of conventional municipal wastewater treatment plants to deal effectively enough with toxic and persistent industrial chemical wastes, whatever their origin.

While this study has provided only a limited snapshot of sources of water pollution with hazardous chemicals within two areas of Buenos Aires, it also illustrates the urgent need for more extensive and more detailed technical investigation of the problem across the whole BAMA region, in order to determine its overall scale and severity. Such investigations, coupled with initiatives aimed at inventorising the current use and release of a whole range of hazardous substances by industries in the area, should provide the basis for a more sustainable approach to chemicals management and protection of water resources in the future. If environment and health protection goals are to be met in the long term, it will be vital in the more immediate term to establish targets of zero discharge for the most hazardous inorganic and organic compounds currently in use by industry, implemented where possible through an ongoing process of substitution of hazardous substances with less hazardous or preferably non-hazardous alternatives. Such policy objectives are scientifically defensible and technologically achievable and have been developed (and are now being implemented) in other parts of the world, including within the European Union and wider North-East Atlantic (OSPAR) and Baltic (HELCOM) regions.

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Appendix 1. Analytical methodology

Analysis for Volatile Organic Compounds (VOCs)

Method

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 35⁰C (held for 4min), rising to 55⁰C at 5⁰C/min, and then to 210⁰C at 15⁰C/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. Halogenated VOCs quantified in the water samples with limits of detection and quantification are presented in Table 6.

Quality control

Standard deviation (SD), relative standard deviation (RSD) and limits of detection (LOD) were calculated using data from the analysis of seven replicates of a standard mixture of commonly occurring VOCs, containing 1ppb of each analyte. 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 analysing a calibration standard at a concentration near the midpoint concentration for the calibration range of the GC-MS.

Compound	LOQ, µg/l	LOD, µg/l	SD, µg/l	RSD, %	r ²
Chloroform	0.3	0.3	0.05	4.5	0.999
Bromoform	0.5	0.4	0.06	6.6	0.999
Ethene, dichloro-	0.4	0.4	0.06	5.6	1.000
Ethene, 1,2-dichloro-, cis- *	1.0	1.0	0.20	10.1	0.999
Ethene, trichloro-	0.4	0.4	0.06	7.1	0.999
Ethene, tetrachloro-	0.3	0.3	0.05	5.1	0.999
Ethane, 1,1,1-trichloro-	0.3	0.3	0.05	4.3	0.999
Ethane, 1,2-dichloro-*	1.0	1.0	0.21	9.4	1.000
Ethane, 1,1,2,2-tetrachloro-	0.2	0.2	0.04	6.1	1.000
Methane, bromodichloro-*	0.5	0.5	0.09	3.7	0.997
Methane, dibromochloro-	0.5	0.2	0.03	3.9	0.999
Methane, dichloro-	0.2	0.2	0.03	4.3	0.999
Methane, tetrachloro-	0.3	0.3	0.05	3.9	0.999

Table 6. Standard deviation (SD), relative standard deviation (RSD) and limit of detection (LOD) were calculated using concentration of the seven replicas of the standard mixture containing 1ppb of each analyte. Limit of quantification (LOQ) is the lowest concentration in the linear regression (r² – corresponding correlation coefficient) used for quantification. * - 2ppb of analyte was used.

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 5890 Series II GC with Restek Rtx-XLB column (30m, 0.25mm ID, 0.25 µm film thickness) linked to an Agilent 5972 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 and metalloids

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 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 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 ug/l and 100 ug/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, three whole samples and four filtered 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 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 ug/l and 80 ug/l), prepared internally from different reagent stock.

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