

Matanza-Riachuelo Basin Part 2: Industrial Samples

Identification and environmental significance of organic pollutants and heavy metal contaminants found in industrial wastewaters and sediments collected from the Matanza-Riachuelo Basin area, Argentina 1997-1998

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Introduction

The Matanza-Riachuelo Basin runs through a highly industrial and urbanised area of Argentina, to the south of the city of Buenos Aires. Sections of both rivers are already highly polluted, yet they continue to receive unknown quantities of industrial waste, domestic sewage and urban runoff. A recent report to the press by the Argentine Secretary of Natural resources and Sustainable Development (Programa de Obras 1997), listed domestic sewage, and wastes generated from the chemical, petrochemical, pharmaceutical, metallurgical, leather, food, textile and paper industries, as the primary contributors and sources of the pollution.

In November 1997 and March 1998, seventeen samples of industrial effluent and associated sediment were collected from the Matanza-Riachuelo Basin area, with the aim of identifying the range of organic pollutants and heavy metal contaminants present (see Table 1). All samples were collected and stored in glass bottles, previously rinsed with nitric acid and pentane, to remove all heavy metal and organic residues (Keith 1991). Solid samples were collected with wooden spoons, previously rinsed with deionised water, nitric acid and pentane. Aqueous samples were collected in 1-litre bottles, rinsed three times with the sample before the final collection. Bottles were filled completely, ensuring no air bubbles were present. They were then transported to the Greenpeace Research Laboratory, kept cold during transit, and refrigerated immediately on arrival. Organic compounds were identified qualitatively using Gas Chromatography Mass Spectrometry (GC-MS). Heavy metals were determined quantitatively using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

Materials and Methods

1. Organic Screen Analysis

All solvents were of High Purity Grade (PRAG or low haloform). Glassware used in extraction and cleaning up procedures was cleaned in detergent, rinsed with tap water and deionised water, dried in the oven overnight at 105⁰C, and rinsed three times with low haloform pentane.

Solid Samples

For each sample, approximately 30g (wet weight) was weighed and transferred to a clean 100 ml glass bottle. Samples were spiked with deuterated (d8) naphthalene (an internal standard) at a concentration of 4.7 mg/kg. 15 ml of pentane was added, followed by 5 ml of acetone. All samples were then sonicated for 2 hours.

Extracts were decanted, filtered through a pre-cleaned hydrophobic phase separator filter and collected in reagent tubes. They were then acidified to pH 2 with 10% nitric acid. Following this, a second portion of 15 ml pentane / 5ml acetone was added and the extraction procedure repeated. Finally, both extracts obtained for each sample were combined and evaporated to a volume of approximately 3 ml. The concentrated extract was cleaned through Florisil column, eluted with a 95:5 mixture of pentane:toluene, and evaporated down to a volume 2 ml under a stream of clean nitrogen. 1-bromonaphthalene was then added as a marker.

Sample Number	Sample Type	Sample Description
AG7003	Effluent	Collected from pipe discharging from the AQUISA S.A. chemical company, into the Arroyo Chacon, La Matanza
AG7004	Sediment	See AG7003
AG7012	Soil	Collected under pipe discharging from the ATANOR/CLARIANT chemical company, into the Arroyo del Rey, Lomas de Zamora
AG7013	Effluent	See AG7012
AG7016	Sediment	Collected under pipe discharging from the G.R.D. tannery, into the Riachuelo River, Avellaneda
AG7017	Effluent	See AG7016
AG7020	Effluent	Collected from pipe discharging from a chemical company into the Riachuelo River, Lanus
AG7035b	Effluent	Collected from pipe discharging close to the AMERICO GAITA and ACUBA tanneries, into the Riachuelo River, Lanus
AG7035c	Sediment	See AG7035b
AG7050	Effluent	Collected from pipe discharging from the PAPELERA TUCUMAN paper company, into the Arroyo las Tunas, Tigre
AG7051	Sediment	See AG7050
AG7052	Effluent	Collected from stream close to the Lady chemical company, finally discharging into the Riachuelo River, General Sarmiento, Buenos Aires Province
AG7053	Sediment	See AG7052
AG7054	Sediment	Collected from pipe discharging from the MERANOL chemical company, into the Riachuelo River
AG8004	Effluent	See AG7012
AG8007	Effluent	Collected from pipe discharging from the CHEMOTECNICA SINTYAL S.A. agrochemical company, into the Arroyo Alegre, Esteban Echeverria
AG8008	Sediment	See AG8007

Table 1 Descriptions of samples collected from the Matanza-Riachuelo basin area, 1997-1998

Aqueous Samples

Prior to the extraction, samples were spiked with deuterated (d8) naphthalene (an internal standard) at a concentration of 150 ug/l. 20 ml of pentane was added, and the sample agitated for 2 hours on a bottle roller to maximise contact between solvent and sample.

After separation of the phases, the solvent extract was filtered through a hydrophobic phase separator filter and collected in pre-cleaned reagent tube. The aqueous sample was acidified to pH 2 with 10% nitric acid, a second portion of 20 ml pentane was added and the extraction procedure repeated. The clean-up procedure was as for solid samples.

Chromatographic Analysis

Samples were analysed using a Hewlett Packard (HP) 5890 Series II gas chromatograph, interfaced with a HP ChemStation data system, and linked to a HP 5972 Mass Selective Detector operated in scan mode. The identification of compounds was carried out by computer matching against a HP Wiley 275 library of 270,000 mass spectra. Results are reported as a list of those compounds reliably and tentatively identified. Match qualities of 90% or greater are assumed to give reliable identifications; tentative identification refers to qualities between 51% and 90%. Analytes yielding match qualities of 50% or less are assumed to be unidentified.

2. Heavy Metal Analysis

Solid Samples

Samples were dried in an oven for 48 hours, until dry weight readings became constant. They were then crushed using a pestle and mortar until homogenous and sieved through a 2 mm mesh. 0.5 g of sample was weighed into a 120 ml Teflon microwave vessel fitted with a screw cap and pressure relief valve. To this 10 ml of deionised water was added, followed by 7.5 ml of concentrated hydrochloric acid and 2.5 ml of concentrated nitric acid. The vessels were then sealed, placed on a rotating table in a microwave oven (model MDS-2000, CEM Corp.), and allowed to digest for one hour at full power (630 W).

After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed. A Standard Reference Material, PACS-1 (trace elements in marine sediment), certified by the National Research Council, Canada, and a blank sample, were prepared with each batch of 10 samples. All were prepared in 15% v/v hydrochloric acid and 5% v/v nitric acid.

Aqueous Samples

Water samples were preserved in 5% v/v nitric acid on arrival. 50 ml was transferred to a 120 ml Teflon microwave vessel and digested using the same procedure and programming conditions described above. After cooling to ambient temperature, samples were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed. A quality control standard (internally prepared at a concentration of 8.0 mg/l) and a blank sample were prepared with each batch of ten samples. Both were prepared in 5% v/v nitric acid.

ICP-AES Analysis

Following preparation, all samples were analysed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), using a Varian Liberty-100 Sequential Spectrometer. The following metals were quantified directly: manganese (Mn), chromium (Cr), zinc (Zn), copper (Cu), lead (Pb), nickel (Ni), cobalt (Co) and cadmium (Cd). A multi-element instrument calibration standard was prepared at a concentration of 10 mg/l (matrix matched to the samples). The calibration was validated using a quality control standard, prepared from

different reagent stocks, at 8 mg/l. Samples exceeding the calibration range were diluted appropriately, in duplicate, and re-analysed. The spectrometer was re-calibrated after twenty samples to adjust for fluctuations in sensitivity.

Mercury (Hg) was determined using Cold Vapour Generation ICP-AES. Mercury (II) was reduced to mercury (0) i.e. a vapour, following reduction of the samples with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The 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). Samples exceeding this range were diluted and re-analysed. The quality control standard was again prepared from a different reagent stock at 80% of the calibration range (i.e. 80 ug/l). The spectrometer was re-calibrated after every 10 samples.

Results

Results are given in Tables 2-4

Table 2 shows the results of the heavy metals analysis. They show that significant levels of chromium, zinc, copper, lead, cobalt and mercury were found in some samples.

Sample Number	Mn (ppm)	Cr (ppm)	Zn (ppm)	Cu (ppm)	Pb (ppm)	Ni (ppm)	Co (ppm)	Cd (ppm)	Hg (ppm)
AG7003	0.02	0.01	0.12	0.01	<0.03	0.03	<0.01	<0.01	<0.002
AG7004	302	56	154	36	18	12	9	n/d	0.5
AG7012	319	27	76	26	16	12	7	n/d	0.2
AG7013	0.19	<0.01	1.07	0.04	<0.03	<0.01	<0.01	<0.01	<0.002
AG7016	125	2883	218	52	34	9	4	n/d	0.5
AG7017	0.20	7.53	0.90	0.09	<0.03	<0.01	0.07	<0.01	<0.002
AG7020	0.20	<0.01	0.04	0.02	<0.03	<0.01	<0.01	<0.01	<0.002
AG7035b	0.09	1.59	0.17	<0.01	<0.03	<0.01	<0.01	<0.01	<0.002
AG7035c	164	4918	172	66	36	9	1	n/d	0.2
AG7050	0.10	0.01	0.18	0.03	<0.03	<0.01	<0.01	<0.01	0.002
AG7051	141	128	1802	838	592	47	7	n/d	0.2
AG7052	2.52	0.04	1.99	0.22	1.32	<0.01	0.21	0.01	0.002
AG7053	585	49	3759	321	49	30	144	2	0.2
AG7054	119	73	56	97	204	29	7	1	100
AG8004	0.03	<0.01	0.28	<0.01	<0.03	<0.01	<0.01	<0.01	0.003
AG8007	0.02	<0.01	0.18	<0.01	<0.03	0.01	<0.01	<0.01	0.003
AG8008	245	284	999	161	371	64	7	n/d	4.8

Table 2 Results of heavy metals analysis, Matanza-Riachuelo Basin area Argentina 1997-1998

Chromium levels found in the effluent samples ranged from <0.01 mg/l in samples AG7013, AG7020, AG8004 and AG8007, to 7.53 mg/l in sample AG7017, discharging from the G.R.D. tannery. Sediment levels ranging from 49mg/kg in sample AG7053 to 4918 mg/kg in sample AG7035c collected close to the AMERICO GAITA and ACUBA tanneries.

Effluent levels of zinc ranged from 0.04 mg/l in sample AG7020 to 1.99 mg/l in sample AG7052 collected from the chemical company Lady. With sediment levels ranging from 56mg/kg in sample AG7054 to 3759 mg/kg in sample AG7053, collected from the same place as AG7052.

Effluent levels of copper ranged from <0.01 mg/l in samples AG7035b, AG8004 and AG8007 to 0.22 mg/l in sample AG7052 (Lady), with sediment levels ranging from 36 mg/kg in sample AG7004 to 838 mg/kg in sample AG7051 collected close to the paper company PAPELERA TUCUMAN.

Effluent levels of lead ranged from <0.03 mg/l in samples AG7003, AG7013, AG7017, AG7020, AG7035b, AG7050, AG8004 and AG8007, to 1.32 mg/l in sample AG7052 (Lady). With sediment levels ranging from 18 mg/kg in sample AG7004 to 592 mg/kg in sample AG7051, collected close to the Paper Company PAPELERA TUCUMAN.

Cobalt was found in relatively high levels in samples AG7052 (0.21 mg/l) and AG7053 (144 mg/kg) both associated with the chemical company Lady. With mercury being present at anomalously high levels in sample AG7054 (100 mg/kg), collected close to the MERANOL chemical company; and at significant levels in sample AG8008 (4.8 mg/kg), collected close to the agrochemical company CHEMOTECNICA SINTYAL. Effluent sample AG7052 (Lady) also contained significant levels of manganese, with sediment sample AG7053 (Lady) containing slightly elevated levels of cadmium.

Table 3 shows the groups of organic compounds reliably identified in each of the samples. Figure 1 shows the number of samples containing compounds from each group, expressed as a percentage. The most abundantly identified organic compounds were aliphatic hydrocarbons, found in over 70% of the samples. 59% of the samples contained PAHs or PAH derivatives, with 41% of the samples containing alkylbenzenes. In addition, 53% of the samples contained other aromatic compounds such as biphenyl and indene derivatives. Six of the samples (35%) contained aliphatic hydrocarbons in combination with PAHs, PAH derivatives (most commonly naphthalene) and alkylbenzenes. When found together, these groups of compounds are often indicative of petroleum contamination (Overton 1994).

35% of the samples contained organohalogen compounds. The most frequently occurring were isomers of dichlorobenzene, monochlorobenzene, and isomers of hexachlorocyclohexane. DDT, DDD, trichlorobenzene, dichlorophenol, a chlorinated derivative of methoxybiphenyl, chlorinated alkenes and chlorinated alkanes were also identified, along with one brominated compound.

The phenol derivative 2,6-bis (1,1-dimethylethyl)4-methylphenol (also known as butylated hydroxytoluene, BHT) was reliably identified in three samples, with molecular sulphur and the organo-sulphur dibenzothiophenes, reliably identified in two of the samples.

Groups of compounds identified to better than 90%	Number of samples	Sample codes
ORGANOHALOGEN COMPOUNDS		
Hexachlorocyclohexane	2	AG7013, AG8004
DDT / DDD	1	AG8004
Trichlorobenzenes	1	AG8004
Dichlorobenzenes	3	AG7012, AG7013, AG7017
Monochlorobenzene	2	AG8007, AG8008
Dichlorophenols	1	AG8004
Chloromethoxybiphenyls	1	AG8008
Chlorinated alkenes	1	AG7013
Chlorinated alkanes	1	AG7017
Brominated compounds	1	AG7017
POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)		
Anthracene and derivatives	1	AG8008
Naphthalene and derivatives	10	AG7013, AG7017, AG7035b, AG7035c, AG7051, AG7052, AG7053, AG7054, AG8007, AG8008
Phenanthrene and derivatives	3	AG7051, AG8007, AG8008
ALKYLBENZENES	7	AG7017, AG7035c, AG7051, AG7052, AG7054, AG8007, AG8008
PHENOL DERIVATIVES	3	AG7016, AG7017, AG7053
OTHER AROMATICS		
Benzene derivatives (not already listed)	5	AG7012, AG7013, AG7017, AG7035b, AG8008
Biphenyl and alkyl derivatives	6	AG7013, AG7017, AG7035b, AG7051, AG8004, AG8008
Indene and derivatives	4	AG7017, AG7051, AG7054, AG8007
SULPHUR AND ORGANO-SULPHUR COMPOUNDS	2	AG7051, AG7054
ALIPHATIC HYDROCARBONS	12	AG7012, AG7016, AG7017, AG7020, AG7035b, AG7035c, AG7051, AG7052, AG7053, AG7054, AG8007, AG8008

Table 3 Groups of organic compounds reliably identified in samples collected from the Matanza-Riachuelo Basin area, Argentina 1997-1998

Table 4 shows the number and types of organic compounds reliably identified in each of the samples. The percentage of reliably identified compounds ranged from zero (samples AG7003, AG7004 and AG7050) to 56 (sample AG7035c) of the total number isolated compounds. It was not possible to reliably identify any compounds in two samples (AG7003 and LA7004). In these, only tentative identifications were made. In sample AG7050 only two compounds were isolated. Low numbers of reliably identified compounds occurred when there was a low organic load in the sample or in the samples with complex unresolved organic matter.

Sample Number	Number of Compounds Isolated	Reliably Identified	Number of Halogenated Compounds	Number of PAHs	Number of Alkylbenzenes	Number of other Aromatics	Number of Aliphatics
AG7003	7	0	0	0	0	0	0
AG7004	33	0	0	0	0	0	0
AG7012	23	5 (22%)	1	0	0	2	2
AG7013	23	9 (39%)	5	1	0	3	0
AG7016	48	11 (23%)	0	0	0	1	10
AG7017	101	38 (38%)	3	7	8	7	13
AG7020	20	1 (5%)	0	0	0	0	1
AG7035b	37	20 (54%)	0	8	0	2	10
AG7035c	34	19 (56%)	0	6	2	0	11
AG7050	2	0	0	0	0	0	0
AG7051	105	23 (22%)	0	11	4	6	2
AG7052	72	6 (8%)	0	2	1	0	3
AG7053	66	21 (32%)	0	4	0	1	16
AG7054	82	39 (48%)	0	8	18	1	11
AG8004	47	7 (15%)	6	0	0	1	0
AG8007	100	32 (32%)	1	12	13	3	3
AG8008	106	31 (29%)	2	16	3	5	5

Table 4 Results of organic screening analysis, Matanza-Riachuelo Basin area, Argentina 1997-1998

Discussion

1. ATANOR (and possibly CLARIANT)

Two samples of effluent were collected from a pipe discharging into the Arroyo del Rey in the district of Lomas de Zamora. The pipe is known to discharge from the Atanor S.A. chemical plant, however it may also carry waste from the nearby Clariant plant. Sample AG7013 was collected from this pipe in November 1997, during the morning hours. Sample AG8004 was collected in March 1998, at night. In addition to these effluent samples, one sample of soil, AG7012, was also collected, from under the discharge pipe, at the same time as sample AG7013.

Atanor S.A. produces a wide range of chemicals. According to the Guia de la Industria Quimica y Petroquimica (1996), these include a number of pesticides and active ingredients such as 2,4-D, 2,4-DB, diuron, endosulphan, MCPA, urea, and trifluralin. In addition they are listed as producing a wide range of phthalate esters. However as there are a number of Atanor plants within Argentina, it is not certain which chemicals are produced by which plant.

The Clariant Company manufactures pigments and colourants.

Heavy metals

Heavy metals analysis of sample AG7012 revealed detectable levels of manganese, chromium, zinc, copper, nickel, cobalt and mercury. However none of these were present at elevated levels, compared to background levels published by Salomons & Forstner (1984). Analysis of the effluent samples revealed detectable levels of manganese, zinc, copper and mercury. Of these, zinc was present at significant concentrations (1.07 mg/l).

Zinc

Zinc is most often employed in electroplating, smelting and ore processing, however it is also present in acidic mine drainage, and effluents from the chemical industry (organic synthesis, textiles, pigment and paint, fertiliser, and PVC production). Compounds of zinc can also be used as fungicides and herbicides, e.g. simple inorganic compounds such as zinc chloride, zinc sulphate and zinc phosphide, as well as more complex organic compounds such as the zinc containing fungicides metiram, mancozeb, zineb and ziram (Agrochemicals Handbook 1987, ATSDR 1997).

Although zinc is not regarded as being especially toxic, it is sometimes released into the environment in appreciable quantities, and can thus have deleterious effects on certain species at specific concentrations. For example, effects on fertilisation and embryonic development have been observed in species of fish and harpacticoid copepods (Ojaveer *et al.* 1980, Verriopoulos and Hardouvelis 1988).

Most of the studies relating to the human health effects of zinc concentrate on exposure via inhalation (which can cause a specific short-term disease called metal fume fever). Less is known about the long term effects of ingesting excess zinc, through food, water or dietary supplements but, although it is an essential trace element, it is recognised that ingestion of higher than recommended levels could have adverse effects on health. The recommended Dietary Allowances for zinc are 15 mg/day for men and 12 mg/day for women. If doses 10 – 15 times higher than these recommendations are taken by mouth, even for a short time, stomach cramps, nausea and vomiting may occur (ATSDR 1997). Ingesting high levels for several months may cause anaemia, damage to the pancreas, and decreased levels of high-density lipoprotein (HDL) cholesterol (ATSDR 1997).

Clearly the two most direct potential routes of exposure to humans following discharge of zinc to the river would be consumption of the water or of fish or other food derived from the river. It is not, however, possible to estimate the magnitude of the hazard that may be presented by the discharge in question in this study.

Organic Chemicals

Organic screening analysis of the two effluent samples (AG7013 and AG8004) revealed the presence of a large number of organochlorine compounds. Both samples contained isomers of hexachlorocyclohexane (HCH), and chlorinated benzenes, along with the aromatic compound, 1,1-biphenyl. In addition, sample AG8004 contained DDT, its metabolite DDD and 2,4-dichlorophenol. Sample AG7013 contained pentachloropropene.

1,2-dichlorobenzene was reliably identified in the soil sample AG7012.

Hexachlorocyclohexane (HCH)

HCH was reliably identified in both samples of effluent: as the alpha, beta and epsilon isomers in the sample AG7013 and as the gamma isomer (lindane) in the sample AG8004. HCH isomers have been detected in the Argentinean environment before. For example, they have been found in water samples from streams that discharge into the inner portion of Blanca Bay, Argentina, along its north coast (Zubillaga *et al.* 1986), in the Uruguay River, Argentina (Janiot *et al.* 1994), in the Rio de La Plata estuary (Colombo *et al.* 1995) and in Argentinean pasteurised milk (Maitre *et al.* 1994).

HCH is a well-known synthetic compound widely used as an insecticide. HCH isomers also occur as unwanted by-products of other manufacturing processes, most commonly the production of other chlorinated pesticides and chlorinated solvents (ATSDR 1997). Its main source in the environment today is from the manufacture of pesticides (Foster 1995, ATSDR 1997). HCH is a chemical that can exist in eight chemical forms (called isomers). Gamma-HCH (lindane) is the isomer most commonly used as an insecticide. Technical grade HCH, containing mixtures of alpha, beta, gamma, delta and epsilon isomers, are also manufactured, and utilised in the same way (ATSDR 1997).

The commercial applications of HCH rely on its toxicity to pest organisms. However, HCH isomers are also toxic to a wide range of other, non-target organisms, including humans. The toxicity of the isomers varies, and with respect to acute toxicity, gamma-HCH is the most toxic, followed by alpha, delta, and beta-HCH. In relation to chronic exposure, however, beta-HCH is the most toxic followed by alpha, gamma and delta-HCH. With chronic exposures, the increased toxicity of beta-HCH is probably due to its longer half-life in the body, and its accumulation in the body with time (ATSDR 1997).

Acute toxic effects may include the death of animals, birds or fish, and death or reduced growth in plants (Bunton 1996, Smith 1991). Chronic toxic effects may include shortened life-span, reproductive problems, lower fertility, and changes in behaviour. Thus any HCH introduced to the environment from industrial discharges, insecticide applications or spills, has the potential to cause significant damage.

This damage can be more non-direct and therefore more widespread than initially obvious, due to the bioaccumulation potential of these compounds, which has been widely reported (e.g. Strachan *et al.* 1994, Smith 1991, Junqueira *et al.* 1994, Larsen *et al.* 1994, Schlaud *et al.* 1995, Schoula *et al.* 1996). In humans for example, gamma-HCH concentrates in adipose (fatty) tissues. Women chronically exposed, or living in areas of intense usage, have been found to accumulate residues of different organochlorines, including alpha, beta and gamma-HCH, in their breast milk (Larsen *et al.* 1994, Schlaud *et al.* 1995, Schoula *et al.* 1996, ATSDR 1997).

Health effects associated with exposure can be summarised as follows:

In humans, blood disorders, dizziness, headaches, and changes in sex hormone levels can all result following exposure to alpha, beta and gamma HCH vapours. Humans exposed to HCH isomers via ingestion have suffered seizures and have, in some cases, died. Similar effects have been observed in animals, with animals exposed to alpha and gamma HCH, suffering seizures; and animals exposed to beta HCH becoming comatose. In addition, exposed animals have developed liver and kidney problems, with long-term exposure to alpha, beta, gamma, or technical grade HCH reported to result in liver cancer. Reduced immunity i.e. reduced ability to fight infections, and reproductive effects such as injury to the ovaries and testes, have also been observed.

The International Agency for Research on Cancer (IARC) has classified HCH as a possible human carcinogen, with the US Department of Health and Human Services determining that HCH may reasonably be anticipated to be a carcinogen (ATSDR 1997).

Dichlorodiphenyltrichloroethane (DDT) and Dichlorodiphenyldichloroethane (DDD)

DDT, and two isomers of its metabolite DDD, were reliably identified in effluent sample AG8004. DDT has been a widely used chemical to control insects on agricultural crops and

insects that carry diseases such as malaria and typhus. DDD, one of the breakdown products of DDT, has also been employed as a pesticide (ATSDR 1997). Use of both DDT and DDD is now banned in most of the world, except in cases of public health emergency. However, use of DDT still continues in a number of South American, African and Asian countries.

Both DDT and DDD are synthetically produced chemicals and are not known to occur naturally in the environment (WHO 1979). Therefore its presence in sample AG8004 is of concern. As their commercial applications and heavily restricted use suggest, DDT and DDD are extremely toxic, even at very low concentrations. They are also highly persistent and bioaccumulative. Studies on the toxicity of DDT and its primary metabolites are numerous, and major findings and conclusions of past and present research can be summarised as follows:

DDT is highly toxic to many aquatic invertebrates e.g. stoneflies, crayfish, daphnids and sea shrimp (ATSDR 1997, WHO 1979), with early developmental stages being more susceptible to the toxic effects of DDT than adults (WHO 1979). It is also highly toxic to fish, with reported 96-hour LC50s less than 10 µg/l in some species of salmon, rainbow trout, pike, bullhead, sunfish and bass. Again developmental stages are more susceptible, and it has been reported that DDT levels of 1 ng/l in Lake Michigan, were sufficient to affect the hatching of coho salmon eggs (Matsumura *et al.* 1985).

It is known that DDT and DDD can bioaccumulate significantly in fish and other aquatic species, often at very low environmental concentrations. This may lead to problems of long-term (chronic), and potentially more in-direct and widespread contamination.

Eating food containing large amounts of DDT and its metabolites over a short period of time, will most notably effect the central nervous system. People who have accidentally swallowed large amounts of DDT became excitable and suffered from tremors and seizures. Humans exposed to DDT in smaller doses over a longer period of time have developed liver problems. Animal studies have confirmed the effects of DDT on the liver, with oral exposures particularly, linked to liver cancer. In addition, more recent research has implicated DDT as a chemical capable of interfering with the endocrine (hormone) system in animals (e.g. Colborn *et al.* 1993, Guillette *et al.* 1994).

The Department of Health and Human Services has determined that DDT may reasonably be anticipated to be a human carcinogen. The International Agency for Research on Cancer (IARC) has determined that DDT, DDE and DDD are possibly carcinogenic in humans, and the EPA has determined that DDT, DDE and DDD are probable human carcinogens (ATSDR 1997).

On account of its acute and chronic toxicity, and its persistence in the environment, DDT is one of the twelve priority POPs (persistent organic pollutants), intended for global action by the UN Environment Programme (UNEP) Governing Council. It is intended that DDT will be phased out worldwide under a convention currently being drawn up (UNEP 1995, 1997).

2,4-Dichlorophenol (2,4-DCP)

2,4-DCP was reliably identified in effluent sample AG8004. It is widely used in the manufacture of a number of industrial and agricultural products such as pesticides, germicides, soil sterilants, seed disinfectants and antiseptics. It is also a key intermediate in the synthesis of the herbicide (2,4-dichlorophenoxy) acetic acid (2,4-D) (Budavari *et al.* 1989). 2,4-D and the related compound 4-(2,4-dichlorophenoxy) butanoic acid (2,4-DB) are

both produced commercially by Atanor S.A. (Guia de la Industria Quimica y Petroquimica 1996).

Industrial wastes containing phenolic compounds are highly toxic and pose a direct threat to human and aquatic life (Veningerova *et al.* 1994). They are compounds with a wide spectrum of toxic effects including teratogenic (Zhao *et al.* 1995) and carcinogenic actions (Nagyova and Ginter 1995, Mehmood *et al.* 1997). They are also relatively persistent in the environment (Narasimhan *et al.* 1992, Zhao *et al.* 1995).

2,4-Dichlorophenol is rapidly absorbed through the skin, either as a pure chemical or dissolved in water, where it can then enter the blood stream (ATSDR 1991). Although a single dose may have a relatively short biological half-life in humans (2-3 days), long term or repeated exposure to significant doses may lead to permanent damage to the skin, eyes, liver and kidney. In addition, this compound is a suspected animal carcinogen, and a probable or possible human carcinogen (ATSDR 1991).

Chlorinated Benzenes

1,2-Dichlorobenzene (o-DCB) was reliably identified in samples AG7012 (soil) and AG7013 (effluent). It is most commonly used as a solvent for waxes, tars, oils and resins; and as an insecticide to combat termites and locusts. It can also be used as a fumigant, a degreasing agent and as a chemical intermediate in organic synthesis (Budavari *et al.* 1989).

Dichlorobenzenes are potent liver and, to a lesser extent, kidney toxins (Valentovic *et al.* 1993). Exposure to higher concentrations can result in central nervous system (CNS) depression. The toxicity of DCBs depends on their precise isomeric forms, with 1,2-dichlorobenzene (o-DCB) generally reported as more toxic in laboratory studies than the 1,3-(m-DCB) and 1,4- (p-DCB) substituted isomers. According to the U.S. EPA, o-DCB is toxic to animals, birds and fish, and can cause death or induce a low growth rate in plants (US EPA 1988). Along with other isomers of dichlorobenzene, o-DCB is persistent in the environment, and has the potential to bioaccumulate (IUCLID 1996).

1,3,5-Trichlorobenzene was reliably identified in sample AG8004. Little specific toxicity data or information on production and use is available, however trichlorobenzenes are expected to induce similar toxic effects in aquatic and terrestrial organisms to those seen in organisms exposed to dichlorobenzenes. As with dichlorobenzenes, they tend to persist in the environment, and have a strong tendency to bioaccumulate (IUCLID 1996). A commercial grade mixture of trichlorobenzenes, which would contain 1,3,5-trichlorobenzene, is used to combat termites, and has been found to cause irritation to eyes and mucous membranes (Budavari *et al.* 1989).

1,1,2,3,3-Pentachloro-1-propene

1,1,2,3,3-Pentachloro-1-propene was reliably identified in effluent sample AG7013. Although little specific toxicity data or information on production and use is available, it has been identified as mutagenic in the Salmonella-microsome-test (Ames assay). A test often used to assess the genotoxic potential of environmental samples (Matsuda *et al.* 1991). It has also been detected in many effluents associated with industrial chlorination processes (Rosenberg *et al.* 1991).

1,1-Biphenyl

Relatively little is also known about the chronic toxicity of 1,1-biphenyl, although animal studies have linked exposure with increased respiratory rate, loss of appetite and weight, and muscular weakness. Workers involved in impregnating paper with biphenyl (it has been used as a pesticide) complained of headaches, diffuse pain, nausea and numbness and aching in the limbs (Edwards *et al.* 1991).

2. CHEMOTECNICA SINTYAL S.A.

Two samples, one effluent (AG8007) and one sediment (AG8008), were collected from a pipe discharging into the Arroyo Alegre, in the district of Lomas de Zamora. The pipe belonged to the chemical company Chemotecnica Sintyal S.A., who, according to the Guia de la Industria Quimica y Petroquimica (1996), produce the pesticides dichlorvos and lindane (gamma-HCH), as well as many other halogenated and non-halogenated compounds.

Heavy metals

Heavy metals analysis of sample AG8007 revealed detectable levels of manganese, zinc and nickel, albeit at low concentrations. However sample AG8008 contained significant levels of chromium (284 mg/kg), zinc (999 mg/kg), copper (161 mg/kg), lead (371 mg/kg), and mercury (4.8 mg/kg). The uses, toxicological properties and environmental significance of zinc have been discussed above, however it should be stressed that a sediment concentration of 999 mg/kg is nearly 10 times higher than levels usually associated with clean sediments (Salomons and Forsner 1984).

The uses, toxicological properties and environmental significance of these other heavy metals can be summarised as follows:

Chromium

Background concentrations of chromium in sediment range from less than 50 to 100 mg/kg (Salomons and Forstner 1984). Examples of published background values include levels ranging from 1 mg/kg to 94 mg/kg in the Yangtze River (Licheng and Kezhun 1992); levels ranging from 1 mg/kg to 25 mg/kg in the tropical lakes of Zimbabwe (Berg *et al.* 1995); levels ranging from 5 mg/kg to 100 mg/kg in Tinto and Odiel Rivers in Spain (Nelson and Lamothe 1993); and levels less than 15 mg/kg in the Ave River basin in Portugal (Goncalves 1990) and the Ebro River in Spain.

A level of 284 mg/kg was found in this sample.

Elevations above the background range are nearly always due to anthropogenic discharges, with two industrial sectors responsible for the majority of releases: metallurgical and chemical (e.g. tanning agents, pigments, catalysts).

Information on the effects of elevated environmental levels on aquatic biota, fish, deposit feeding and wading birds is limited; and how sediment-bound chromium reaches animal and plant tissues is uncertain, although it is recognised that the speciation of chromium determines its bioavailability. Chromium (VI) will be accumulated more readily than chromium (III), as it has been shown to cross biological membranes more readily (Bryan and Langston 1992). Whereas chromium (III) is a trace nutrient at low concentrations, chromium (VI) is non-essential and toxic. Its compounds have been classified as carcinogenic by the International Agency of Research on Cancer (ATSDR 1997).

Most of the chromium associated with aquatic sediment will be in the trivalent form, and although not as environmentally mobile as chromium (VI), accumulation and movement up the food chain have been experimentally studied (Aislabie and Loutit 1986, Bremer and Loutit 1986). Accumulation of chromium in cockles, polychaetes and mud snails has been shown to occur following exposure to chromium (III) contaminated sediments.

For freshwater fish and shellfish, the uptake of metals through their food may be quite substantial (Heath 1987, Dallinger *et al.* 1987), and metals taken up by plants can be an important route to make metals in the sediments bioavailable to herbivore species (Berg *et al.* 1995). Chromium levels in edible oysters, mussels, clams and molluscs have been reported to range from <0.1 mg/kg to 6.8 mg/kg (Bryne and DeLeon 1986, Ramelow *et al.* 1989). Fish and shellfish collected from ocean dump sites off New York City, Delaware Bay, and New Haven, Connecticut, contained <0.3 mg/kg to 2.7 mg/kg (ATSDR 1997).

An average daily intake of 50-200 ug/day of chromium (III) is recommended for adults (ATSDR 1997), chromium (III) being an essential nutrient, required for normal energy metabolism. However the consumption of contaminated fish, other foodstuffs and drinking water could increase the daily intake levels far beyond those recommended. Ingesting small amounts of chromium (both III and VI forms) has not been reported to cause harm, however ingesting higher than recommended levels over long periods of time can result in adverse health effects including gastro-intestinal irritation, stomach ulcers, kidney and liver damage (ATSDR 1997).

Dermal exposure to both chromium (III) and chromium (VI) can result in severe redness and swelling of the skin (ATSDR 1997). Whereas breathing in high levels of chromium (far less likely in this case) can cause irritation of the nasal and respiratory membranes. These effects have primarily occurred in factory workers who make or use chromium (VI) for several months to many years. Long term occupational exposure to chromium (VI) is believed to be primarily responsible for the increased lung cancer rates (ATSDR 1997).

Copper

Background levels of copper in sediment range from less than 10 mg/kg to 75 mg/kg (Salomons and Forstner 1984, Byran and Langston 1992, Licheng and Kezhun 1992, Goncalves *et al.* 1990). 161 mg/kg was detected in this sample.

Again, as is the case with most heavy metals, elevations above background are nearly always due to anthropogenic discharges. The most important discharges arising from mining, smelting and metal plating operations; chemical discharges, agricultural runoff (copper compounds are used as nutritional supplements in fertilisers and animal feed, fungicides and other agricultural chemicals), and domestic sewage effluents.

The presence of elevated levels of copper in the environment warrants concern, as copper is toxic to aquatic species at very low (part per billion) concentrations. Furthermore a very significant relationship between copper levels in aquatic biota and the levels found in sediments, has been demonstrated. Clear relationships have been found between animal and sediment concentrations from as little as 10 mg/kg to more than 2000 mg/kg (Bryan and Langston 1991). The bioconcentration factor (BCF) of copper in fish obtained in field studies is 10-100. The BCF is higher in molluscs, especially oysters, where it may reach 30,000 (Perwack *et al.* 1980). This may be due to the fact that they are filter feeders, and copper concentrations are higher in particulates than in water.

Like zinc, copper is necessary for good health. However very large single or daily intakes of copper, or prolonged exposure to lower levels can have adverse effects on human health. Consumption of food or drinking water containing elevated levels of copper can result in vomiting, diarrhoea, stomach cramps and nausea (ATSDR 1997).

Lead

Concentrations of lead found in uncontaminated sediments range from <10 mg/kg to 50 mg/kg (Salomons and Forstner 1984, Bryan and Langston 1992, Licheng and Kezhun 1992, Goncalves *et al.* 1992). 371 mg/kg was detected in this sample.

Anthropogenic inputs of lead could arise from primary and secondary metal smelting and processing. Less direct, yet significant sources, arise from urban runoff, chemical and domestic sewage discharges, and automotive emissions (although these are declining).

Even though lead is not considered to be one of the most environmentally mobile metals, often heavily bound to suspended particulate and sediment material (Berg *et al.* 1995, Hapke 1991), there is appreciable evidence showing that sediment lead is available to deposit-feeding species (Bryan and Langston 1992).

High bioconcentration factors (BCFs) were determined in studies using oysters (6,600 for *Crassostrea virginica*), freshwater algae (92,000 for *Senenastrium capricornutum*) and rainbow trout (726 for *Salmon gairdneri*) (Eisler 1988). Lead is toxic to all aquatic biota and organisms higher up the food chain may experience lead poisoning as a result of eating lead-contaminated food.

As well as occurring in its inorganic state, there is some evidence that even in the absence of organolead inputs, inorganic lead may be alkylated, chemically or biologically, to produce mono-, di-, and trialkyl lead compounds (Radojevic and Harrison 1987). The chemical speciation of the lead will often dictate its toxicity. Organolead compounds are more toxic than inorganic forms and have been shown to bioconcentrate in aquatic organisms (Eisler 1988).

Unlike some heavy metals, lead is not required by animals (including humans) or plants for normal growth and development. It has no known nutritional or biochemical function and if present in sufficient quantities will inhibit animal and plant growth, development and health (Nriagu 1988).

In terms of human health the effects of lead are the same irrespective of whether it is inhaled or ingested (ATSDR 1997). Lead can cause irreversible central nervous system damage and decreased intelligence at extremely low doses (Needleman *et al.* 1990, ATSDR 1997). At higher levels of exposure anaemia may result, along with severe kidney damage (ATSDR 1997). Children are especially susceptible to lead poisoning because they absorb and retain more lead in proportion to their weight than adults (ATSDR 1997).

Mercury

Mercury concentrations associated with clean sediments are extremely low, with levels ranging from 0.03 mg/kg to 0.5 mg/kg (Bryan and Langston 1992, Salomons and Forstner 1984, Licheng and Kezhun 1992). 4.8 mg/kg was detected in this sample.

Elevated levels in aquatic systems are primarily due to anthropogenic discharges of inorganic mercury. Sediments associated with gold mining sites and chlor-alkali discharges, the two major sources of anthropogenic mercury in the environment, can contain levels ranging from 0.6 to over 150 mg/kg (Bryan and Langston 1992, Reuther 1994, Nriagu 1992, Maserti and Ferrara 1991). On a smaller scale, mercury and mercury compounds can also be used in organic synthesis, as pesticides, and as antiseptic, antibacterial and disinfectant agents. However, due to the high toxicity of mercury and its compounds, many of these uses are now banned (ATSDR 1997).

Mercury is a non-essential trace metal, having no biochemical or nutritional function. Biological mechanisms for its removal are poor, and mercury is the only metal known to biomagnify i.e. progressively accumulate through the food chain (WHO 1989, ICME 1995). It is extremely toxic to both animals and plants at low concentrations. Therefore any elevation above baseline levels could have a deleterious effect on any exposed biota (ATSDR 1997).

Since the poisoning incident that devastated the Japanese town of Minamata, the implementation of widespread regulations on mercury disposal has greatly reduced the threat of similar incidents. However the retention of mercury by sediments may delay the elimination of contamination for many years. For example, concentrations as high as 100 mg/kg were still present in sediments at certain sites in Minamata Bay, ten years after discharges ceased (Bryan and Langston 1992, Tsubaki and Irukayama 1977). This is important because mercury accumulation from sediments may be a dominant pathway for uptake in aquatic organisms and accounts for relatively high concentrations in deposit-feeders both in freshwater and estuarine systems (Bryan and Langston 1992, Kiorboe *et al.* 1983). Also it is known that inorganic mercury can be methylated by microorganisms within the sediment, and it is widely accepted that organic forms of mercury are even more toxic than the inorganic forms (ATSDR 1997).

The most common form of mercury is methylmercury (MeHg), and although there is evidence which links levels of total mercury in the environment with those in higher predators such as fish, concern centers on methylmercury accumulation. Methylmercury exhibits high lipid solubility. It is able to cross cell membranes easily, and therefore quickly enters the aquatic food chain. It also has a long biological half-life, and due to increased longevity of top predators in association with these other properties, it provides one of the rare examples of metal biomagnification in food chains. For example, methylmercury concentrations in carnivorous fish at the top of freshwater and salt-water food chains (e.g., pike, tuna and swordfish) are biomagnified in the order of 10,000-1,000,000 times the concentrations found in ambient waters (Callahan *et al.* 1979, EPA 1980 & 1984, ATSDR 1997).

The significance of this is that biomagnification of methylmercury in aquatic food chains is considered the most important source of non-occupational human exposure to the element (EPA 1984, ATSDR 1997), and as mercury is highly toxic and persistent, anomalous environmental levels warrant concern. Mercury has no beneficial effects in humans, and there is no known homeostasis for it (i.e. there is no way to maintain equilibrium between mercury entering and leaving the body). Any long-term exposure may therefore be expected to progressively cause severe disruptions in the normal functioning of any accumulating organ (Nriagu 1988). Accumulating organs include the kidneys, liver and central nervous system, and exposure to high levels of metallic, inorganic or organic mercury can permanently damage these organs (ATSDR 1997).

Organic Chemicals

Organic screening analysis of these samples revealed the presence of a large number of PAHs, PAH derivatives (most notably naphthalene and phenanthrene), alkylbenzenes and aliphatic hydrocarbons. These, when found together, are often indicative of petroleum contamination (Overton 1994). In addition, effluent sample AG8007 contained a number of indene derivatives, also associated with petroleum contamination (Budavari *et al.* 1989) and chlorobenzene. Sediment sample AG8008 contained a number of biphenyl derivatives, including 2-chloro-5-methoxy-1,1-biphenyl. 1-Chloro-3-methyl-benzene and xylene were also identified.

Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are a group of compounds found in coal and oil. They can also be produced as products of incomplete combustion of numerous different fuels. More than 100 different PAHs are known, however only a few have industrial or domestic applications. Naphthalene is one of these, as it is used as a moth repellent and insecticide.

Once PAHs are released into the aquatic environment, degradation by microorganisms is often slow, leading to their accumulation in exposed sediments, soils, aquatic and terrestrial plants, fish and invertebrates. PAHs can have a deleterious effect on human health, and individuals exposed to mixtures of PAHs, through inhalation or skin contact, for long periods of time, have been shown to develop cancer (ATSDR 1997).

PAHs are prevalent pollutants in the aquatic environment that can cause a wide range of toxic effects. PAHs and alkylbenzenes are considered to be the most toxic components of crude oil (Overton, 1994). The toxicity of certain PAHs to aquatic organisms can be greatly increased upon exposure of the organisms to ultraviolet (UV) radiation present in sunlight (Monson *et al.* 1995; Ankley *et al.* 1995; Arfsten *et al.* 1996; McConkey *et al.* 1997). It was found that toxicity to aquatic plants was clearly a function of both PAH dose and light intensity (Ankley *et al.* 1995; Huang *et al.* 1997).

Alkylbenzenes

Alkylbenzenes are single-ring aromatic compounds containing one or more aliphatic side chains. While there are theoretically thousands of alkylbenzenes, those which are the major products of commerce are those to which humans are most likely to be exposed. These include toluene (methylbenzene), ethylbenzene, cumene (isopropylbenzene), and three xylenes (1,2-, 1,3-, and 1,4-dimethylbenzene).

Alkylbenzenes occur in the environment due to their presence in crude oil and petroleum products. They are also produced by the degradation of linear alkylbenzene sulphonate (LAS) detergents. The alkylbenzenes are highly resistant to degradation and may accumulate and reside in sediments for long periods of time (Preston and Raymundo 1993). Alkylbenzenes are useful sewage markers (Chaloux *et al.* 1995) and due to their stability in sediments, they are very useful in tracing the transport of contaminants from their point sources. Monoaromatic (benzene derivatives) and polyaromatic hydrocarbons (PAHs) are considered to be the most toxic components of crude oil (Overton 1994).

The acute toxic effect of inhaled alkylbenzenes is central nervous system (CNS) depression (Klaassen *et al.* 1996). Acute toxicity does not vary very much between compounds within the group. In animal models, relatively similar concentrations of inhaled alkylbenzene

vapours were found to be lethal. Impaired reaction times and impaired speech are the two most commonly noted CNS effects in humans (Klaassen *et al.* 1996). All alkylbenzenes mentioned above are irritating to the eyes and mucous membranes, can cause irritation and burning of the skin, and all are narcotics at high concentrations. Benzene itself is a known carcinogen (Fourth Annual Report on Carcinogens 1985). Chronic exposure can lead to bone marrow depression, which in a few cases, can progress to leukemia (Budavari *et al.* 1989).

Xylene was reliably identified in sediment sample AG8008. It is found naturally and is usually obtained from coal tar. It is most frequently employed as a solvent, and as a starting product in the manufacture of a wide range of organic chemicals, such as benzoic acid, phthalic anhydride, isophthalic and terephthalic acids as well as their dimethyl esters used in the manufacture of polyester fibers. It is narcotic in high concentrations and although its chronic toxicity is less than benzene, it is not well- defined (Budavari *et al.* 1989).

Chlorobenzene

Chlorobenzene was reliably identified in sediment sample AG8007. It is most frequently used as a solvent, but is also employed as an intermediate in the synthesis of other halogenated organics (ATSDR 1997). Animal studies have shown that exposure to high concentrations can cause damage to the brain, liver and kidney. Unconsciousness, tremors and restlessness have been observed, as well severe injury to the liver and kidneys. Studies in animals have also shown that chlorobenzene can produce liver nodules, providing some, but not clear, evidence of a cancer risk (ATSDR 1997).

2-Chloro-5-methoxy-1,1-biphenyl

No specific information can be found regarding the uses and toxicity of this compound, reliably identified in sediment sample AG8008. However the fact that it is chlorinated, and related to the aromatic compound 1,1-biphenyl, known to be toxic, suggests that this compound may also be environmentally harmful and possibly persistent. It is also quite usual for a complex mixture of chlorinated compounds to be present in effluents associated with industrial chlorination processes (Johnston *et al.* 1994, Rosenberg *et al.* 1991).

3. G.R.D. and AMERICO GAITA / ACUBA (tanneries)

Two samples, one effluent (AG7017) and one sediment (AG7016) were collected from a pipe belonging to the G.R.D. tannery, discharging into the Riachuelo river in the district of Avellaneda. In addition two samples were collected close to the Americo Gaita / ACUBA tanneries in Lanus. One was collected from a pipe discharging into the Riachuelo River (AG7035b), and another, a sample of sediment, was collected close to the discharge (AG7035c).

Heavy metals

All of these samples contained anomalously high levels of chromium. Sample AG7017 contained 7.53 mg/l of chromium, with sample AG7016 containing 2.88 g/kg (almost 0.3% of this sediment was chromium). Sample AG7035b contained 1.59 mg/l of chromium with sample AG7035c, containing 4.92 g/kg (almost 0.5%). As mentioned previously, levels of chromium associated with clean sediments are usually less than 50 mg/kg, thus sample AG7016 contained levels nearly 60 times greater than background concentrations, with sample AG7035c containing levels nearly 100 times greater than background concentrations.

Furthermore, this severe chromium contamination can be linked directly to the tannery wastes discharged.

Chromium Tanning

When an animal is killed and skinned, bacterial degradation starts immediately. The process of tanning preserves the hide, stabilising the collagen proteins of which it is composed. Thus preventing chemical, thermal and biological degradation. The most common tanning agents are chromium salts, because they are cheap, and chromium tanned leather is of a light colour (blue), which can therefore be dyed easily, is strong, durable, and resistant to cracking from flexing (UNEP 1991).

However, chromium is a controversial chemical on account of the persistence and potential toxicity of some of its chemical forms. Depending on its chemical state it has various levels of impact on humans, aquatic life and terrestrial plants, with some ability to move between media (UNEP 1991). Chromium can occur in oxidation states ranging from II to VI, however only the trivalent (III) and hexavalent (VI) forms are of biological importance. The trivalent is the more common form and is considered an essential trace nutrient, but like any trace element, toxic effects can result following exposure to elevated concentrations (ATSDR 1997). Hexavalent chromium is, on the other hand, non-essential and toxic at low concentrations, and the International Agency of Research on Cancer (IARC) classifies chromium (VI) compounds as carcinogenic (ATSDR 1997).

The known harmful effects of chromium in humans have all been attributed to the hexavalent form. Trivalent chromium compounds are considerably less toxic and are neither irritating nor corrosive. There is also insufficient evidence regarding their carcinogenicity. Nevertheless, nearly all industrial workers (including tannery workers) are exposed to both forms (UNEP 1991).

A wide variety of alternative tanning materials, which have a lower acute toxicity than chromium are available, including aluminium, titanium and zirconium salts, and vegetable tannins. It is the lack of familiarity with such alternatives, and the fact that they do not necessarily produce exactly the same leather product, that has inhibited their widespread adoption to date (ATSDR 1997, UNEP 1991).

Organic Chemicals

Organic screening analysis of these samples revealed the presence of a large number of PAHs, PAH derivatives, long chain aliphatic hydrocarbons, alkylbenzenes, and indene derivatives, all indicators of petroleum contamination (Overton 1994). In addition, the phenol derivative 2,6-bis (1,1-dimethylethyl)-4-methylphenol (BHT) was reliably identified in sediment sample AG7016 and effluent sample AG7017. Both effluent samples AG7017 and AG7035b contained 1,1-biphenyl. 1,4-dichlorobenzene, 1-bromohexadecane and 1-chlorooctadecane were reliably identified in effluent sample AG7017.

1,1'-Biphenyl

The main users of 1,1'-biphenyl, also called diphenyl, are thought to be textile mills that use biphenyl in mixtures that dissolve dyes (US EPA, 1994). The occurrence of this compound in the effluents from the tanneries might be of the same origin. In the past, companies have also used biphenyl as a heat transfer agent, as a starting material to make polychlorinated biphenyls, and as a fungicide for oranges (applied inside shipping containers or wrappers)

(Edwards *et al.* 1991; Budavari *et al.*1989). Biphenyl is toxic to experimental animals, causing CNS depression, paralysis and convulsions (Budavari *et al.*1989). Biphenyl has high acute toxicity and low chronic toxicity to aquatic life (US EPA 1994).

Butylated hydroxytoluene (BHT)

BHT is frequently employed as an antioxidant in food products and in the production of plastics, petrochemicals and some cosmetics (Budavari *et al.* 1989). It is also manufactured as an anti-skinning agent in paints, varnishes and other surface finishes. Its use in food has been associated with certain allergic reactions (Klaassen *et al.* 1996), and there is also some evidence that BHT can act as a promoter of liver cancer, in combination with other carcinogenic substances (Klaassen *et al.* 1996). Due to its presence in many consumer products, it is frequently found in domestic sewage and sewage sludge.

Additionally, BHT is one of the main degradation products of the herbicide terbutol (2,6-di-tert-butyl-4-methylphenyl N-methylcarbamate) (Suzuki *et al.*1996).

1,4-Dichlorobenzene (p-DCB)

p-DCB is most frequently used in moth repellent products and in toilet deodoriser blocks (Budavari *et al.* 1989). p-DCB is a potent liver and, to a lesser extent, kidney toxin (Valentovic *et al.* 1993), with exposure to higher concentrations resulting in central nervous system (CNS) depression. p-DCB is also reported to cause increases in the rates of cancer among experimental animals (ATSDR 1997, Bornatowicz *et al.* 1994). There is no direct evidence that p-DCB can cause cancer in humans. However, the Department of Health and Human Services (DHHS) in the United States has determined that p-DCB may reasonably be anticipated to be a carcinogen. The International Agency for research on Cancer (IARC) has determined that p-DCB is possibly carcinogenic to humans, with the EPA determining that p-DCB is a possible human carcinogen (ATSDR 1997).

1-Bromohexadecane and 1-Chlorooctadecane

No specific data on the uses and toxicological properties of 1-bromohexadecane and 1-chloro-octadecane is available.

4. LADY (chemical)

Samples AG7052 (effluent) and AG7053 (sediment) were collected from the chemical company Lady. They were collected from a stream running from the chemical plant, finally discharging into the Riachuelo river in the district of General Sarmiento, Buenos Aires Province.

Heavy metals

Heavy metals analysis revealed high concentrations of manganese, zinc, lead and cadmium in sample AG7052. The associated sediment sample, AG7053, contained high levels of zinc and cobalt, and elevated levels of copper and cadmium. The toxicological properties and environmental significance of zinc, lead and copper have been discussed above. The properties and significance of cadmium, cobalt and manganese can be summarised as follows:

Cadmium

Background levels of cadmium in the environment are extremely low. Water concentrations of ng/l are usual (parts per trillion), and sediment levels are usually less than 0.2 mg/kg (Bryan and Langston 1992, Salomons and Forstner 1984, Licheng and Kezhun 1992, Goncalves *et al.* 1990). 2.0 mg/kg of cadmium was found in sample AG7052, resulting from cadmium containing discharges being released by the chemical company Lady (10 ug/l).

The most frequently cited sources of cadmium entering the aquatic environment are industrial effluents and sewage (Butler and Timperley 1995). Small amounts of cadmium enter the environment from the natural weathering of minerals, but most is released through human activities (Elinder 1985).

Cadmium has no biological function and is highly toxic to both animals and plants. The low concentrations of cadmium usually encountered in the environment do not cause acute toxicity, but elevations above background concentrations can have deleterious effects on plant and animal health (Bryan and Langston 1992, Alloway 1990). It is known to be one of the more mobile, and hence bioavailable, trace metals (Jensen and Bro-Rasmussen 1990). There is evidence to show that cadmium can be absorbed from surface sediments, suspended particular matter and water (Bryan and Langston 1992, Bryan and Humberstone 1973, Ray *et al.* 1980, Schwartz *et al.* 1985).

High tissue cadmium concentrations are often associated with the presence of metallothionein (sulphur-binding) proteins. The induction of these proteins in response to cadmium is well established and is thought to afford protection against the toxic effects of the metal, at least until the system becomes saturated (Bryan and Langston 1992). However deleterious effects have been reported, including correlations between increased levels of cadmium found in limpets and a reduced ability to utilise glucose (Shore *et al.* 1975). Reproduction rates and thus population numbers in copepods and isopods can also be reduced (Giudici and Guarino 1989). The toxicity of low sediment cadmium concentrations was also suggested by observations showing that in San Francisco Bay, the condition of certain species of clam declined as cadmium concentrations rose from 0.1 to 0.4 mg/kg (Luoma *et al.* 1990).

Regarding potential human exposure, food, water and cigarette smoke will be the largest sources of cadmium for members of the general population. Eating food or drinking water with very high cadmium levels can severely irritate the stomach, leading to vomiting and diarrhoea (ATSDR 1997). Eating lower levels of cadmium over a long period of time can lead to a build up of cadmium in the kidneys. This cadmium build-up causes kidney damage, and also leads to the weakening of bone (Nriagu 1988). Studies concerned with the effects of eating and drinking high levels of cadmium are not strong enough to show that such exposure can lead to an increased rate of cancer. However the U.S. Department of Health and Human Services and the U.S. Environment Protection Agency have both determined that cadmium and cadmium compounds may reasonably be anticipated to be carcinogens (ATSDR 1997).

Cobalt

The important synthetic sources of cobalt in the environment are the byproducts of burning of coal and oil; exhaust from cars, trucks, and aircraft; and industrial processes that use the metal or its compounds. The main industrial use of cobalt is in the manufacture of alloys, including superalloys (alloys that maintain their strength at high temperatures), however cobalt compounds are also widely used as paints, pigments and catalysts (ATSDR 1997).

In terms of environmental exposure, cobalt has both beneficial and harmful effects on human health. It is beneficial as it is incorporated in the vitamin B12 molecule, essential for growth

and its anti-anaemic properties. Cobalt is also essential for the growth and development of certain animals, such as cows and sheep. However when too much cobalt is taken into the body, harmful health effects can occur.

Animal studies have shown that short-term exposure of high levels of cobalt in the air can result in lung damage and possibly death, with longer-term exposure to lower concentrations causing the same effects. Short-term exposure to high levels in food and drinking water caused damage and changes to the blood, liver, kidneys and heart, with longer-term exposure to lower levels causing the same damage and changes, as well as affecting reproduction and behaviour (ATSDR 1997).

Human exposure to high airborne levels can have serious effects on the lungs, including wheezing, asthma and pneumonia. Allergies resulting in asthma and skin rashes can also occur. Ingestion of high levels of cobalt can cause vomiting and nausea.

Cobalt has not been found to cause cancer in humans or in animals, following exposure in the air or in the food or water. However cobalt has been shown to cause cancer when placed directly into the muscle or under the skin. Based on the animal data available, the International Agency for Research on Cancer (IARC) has determined that cobalt is possibly carcinogenic to humans (ATSDR 1997).

Manganese

Like cobalt, manganese is an essential trace element. However exposure to high levels can cause serious illness.

The main use of manganese is in the production of steel (carbon, stainless, high-temperature), along with the manufacture of cast iron and superalloys. The most important compounds of manganese are manganese dioxide, manganese chloride, manganese sulphate and potassium permanganate. Manganese dioxide is commonly used in the production of dry-cell batteries, matches, fireworks, porcelain and glass-bonding materials, and as the starting material for production of other manganese compounds. Manganese chloride often used as a precursor for other manganese compounds, as well as being used as a catalyst in the chlorination of organic compounds. Manganese sulphate is used in glazes and varnishes, in ceramics, fertilisers, as a fungicide and as a nutritional supplement; and potassium permanganate is used as an oxidizing agent, a disinfectant, an anti-algal agent, a cleaning agent and as a preservative for fresh flowers and fruits. Also of importance is the organo-manganese compound MMT, which is used as an antiknock additive in unleaded gasoline.

Workers chronically exposed to high levels of manganese in the air have suffered both mental and emotional disturbances (ATSDR 1997), along with increased slowness and clumsiness of body movements. This combination of symptoms is a disease called manganism. The symptoms can be reduced by medical treatment, but due to the high levels of manganese accumulated in the brain, any brain injury is often permanent.

It is not certain whether eating or drinking elevated levels of manganese can cause manganism or not. In one report, humans exposed to contaminated drinking water, developed symptoms similar to those seen in manganese miners or steel workers, but it is not certain if the effects were caused by the manganese alone. Another report found that people who drank water with above average levels of manganese seemed to have a slightly higher frequency of symptoms such as weakness, stiff muscles, and trembling of the hands. However, these

symptoms are not specific for manganese, and might have been caused by other factors (ATSDR 1997).

Studies in animals have shown that very high levels of manganese in food or water can cause changes in the brain, suggesting that high levels might cause brain injury. In addition, animal studies have indicated that manganese may also be a reproductive toxicant, especially to males, injuring the testes and causing impotence.

Organic Chemicals

Organic screening analysis of samples AG7052 and AG7053 highlighted the presence of PAH derivatives (most notably naphthalene), long chain and cyclic aliphatic hydrocarbons, alkylbenzenes, and BHT. The occurrence of these compounds and their toxicity are discussed above.

Terpenes were reliably identified in both samples from this site: terpinolene and terpinene in the sample AG7052 and limonene in the sample AG7053. These compounds are of natural origin, they are responsible for the flavor of different essential plant oils. For example, limonene and valencene are flavoring components of fruits such as orange (Johnson *et al.* 1996). Terpenes are commonly used compounds in fragrances (Cooper *et al.* 1992).

5. MANN (chemical)

Sediment sample AG7054 was collected from a pipe belonging to the chemical company Meranol, discharging waste into the Canal Dock Sud, which meets with the Riachuelo River in the district of Avellaneda.

Heavy metals

100 mg/kg of mercury was detected in this sample. This level was 200 times greater than that usually associated with uncontaminated sediments (Salomons and Forstner 1984). In addition, elevated levels of lead (204 mg/kg) were also found. The uses, toxicological properties and environmental significance of elevated levels of these metals have been discussed above.

Organic Chemicals

Organic screening analysis of this sample identified a large number of alkylbenzenes, PAHs, PAH derivatives (most notably naphthalene) and long chain aliphatic hydrocarbons, all indicators of petroleum contamination (Overton 1994). In addition, one indene derivative was reliably identified, along with molecular sulphur. The occurrence of these compounds and their toxicity are discussed above.

6. PAPELERA TUCUMAN (paper)

Two samples, one effluent (AG7050) and one sediment (AG7051) were collected from a waste stream running in front of the Papelera Tucuman paper factory. The waste stream finally discharges into the Arroyo las Tunas, in the district of Tigre, Buenos Aires province.

Heavy metals analysis of effluent sample AG7050 found detectable levels of manganese, chromium, zinc, copper and mercury, albeit at low concentrations. No organic compounds were reliably identified.

Sediment sample AG7051, however, contained significant levels of chromium, zinc, copper and lead, along with a large number of organic compounds. These included dibenzothiophenes, biphenyl derivatives, indene derivatives, alkylbenzenes, PAH derivatives (naphthalene and phenanthrene) and long chain aliphatic hydrocarbons. With the exception of the dibenzothiophenes, the uses, toxicological properties and environmental significance of most of these heavy metal contaminants and organic pollutants have been discussed above.

Dibenzothiophenes

1-Ethyl-dibenzothiophene and 2-ethyl-dibenzothiophene were reliably identified in this sample. Dibenzothiophenes and its alkylated derivatives are components of crude oil (Wang and Fingas 1995). Several representative from this class of organic compounds including benzothiophene, benzothiophene sulphone, benzothiophene-2,3-dione, 3-, and 5-methylbenzothiophenes, 3-, and 5-methylbenzothiophene sulphones, 5- and 7-methylbenzothiophene-2,3-diones, dibenzothiophene, dibenzothiophene sulphoxide, and dibenzothiophene sulphone have been found to be toxic by the Microtox and *Daphnia magna* bioassays (Seymour *et al.* 1997).

7. AQUISA S.A. (chemical)

Two samples, one effluent (AG7003) and one sediment (AG7004) were collected from a waste stream running from the Aquisa S.A. chemical plant. The stream discharges into the Arroyo Chacon, in the district of La Matanza.

Neither sample contained reliably identified organic compounds, however heavy metals were found in both. Heavy metals analysis of effluent sample AG7003 found detectable concentrations of manganese, chromium, zinc, copper and nickel, albeit at low concentrations. The corresponding sediment sample contained manganese, chromium, zinc, copper, lead, nickel, cobalt and mercury, with zinc present at slightly elevated concentrations. The toxicological properties and environmental significance of these heavy metal contaminants have been discussed above.

8. MANN (chemical)

One sample of industrial effluent (AG7020) was collected from a pipe discharging into the Riachuelo River in the district of Lanus. The pipe runs close to the chemical company Mann, although it is not certain whether the company is discharging into this pipe.

Heavy metals analysis found detectable levels of manganese, zinc and copper, whilst the organic screening analysis of this sample reliably identified one long chain aliphatic hydrocarbon. The toxicological properties and environmental significance of these heavy metal contaminants have been discussed above.

Conclusion

Our analysis has highlighted the presence of a wide range of anthropogenically derived chemicals. Most of the samples collected contained some degree of contamination, with only three of the samples (AG7003, AG7004 and AG7020), containing no organic pollutants or elevated levels of heavy metals. As discussed above, and highlighted in the Environmental Samples Report, many of these heavy metals and organic compounds are toxic at very low concentrations and have the potential to bioaccumulate. Many of the compounds found are also highly persistent, and therefore even if discharges ceased in the very near future,

retention by sediments and soils (as shown), animal and human tissues, would delay the elimination of this contamination for many years.

The continued discharge of industrial wastes, which are acting as significant sources of toxic and persistent chemicals in the basin, must be addressed. Moreover, it is essential that industry, along with the bodies accountable for sewage treatment and water quality, take full financial and legal responsibility for preserving the environment of this region.

Ultimately, the industries themselves, the processes they employ and the products they generate need to be assessed. Long-term solutions based on clean production alternatives, renewable resources and pollution prevention need to be employed. If the current situation is not addressed, and clean production practices are not forthcoming, more widespread decay of the Matanza-Riachuelo basin cannot be avoided.

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