

# **Identification of organic pollutants and heavy metal contaminants found in sediments and wastewaters collected from the Bahia Blanca Petrochemical Complex, Argentina 1996 and 1998**

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## **Introduction**

The petrochemical complex situated close to the bay of Bahia Blanca, in the south of Buenos Aires province, is one of the largest industrial sites in the country. The chemical processes and products generated on site (e.g. Solvay-Indupa, PBB-Dow, Polysur-Dow, YPF producing chlorine, EDC, VCM, PVC, polyethylene, polypropylene and a wide range of other petrochemicals), coupled with the close proximity of the complex to one of the most important harbours in Argentina, warrants great concern. The potential for contamination of surrounding waters through the discharge of wastewaters, runoff and the disposal of solid wastes, either intentionally or accidentally, is high.

For example the manufacture of PVC, along with chlorine, EDC and VCM, the starting products from which the PVC is made, can yield a number of toxic, persistent and bioaccumulative waste products (chlorine, EDC and VCM are also toxic in their own right). Liquid wastes generated can contain high levels of heavy metals, most notably mercury, arising from the chloralkali process use to make chlorine, along with lead, cadmium, zinc and copper, added as stabilisers, pigments etc. In addition a potentially complex and hazardous mix of organochlorines can be released. Furthermore, even if these effluents are treated, the solid residues that result can be just as contaminated, leading to problems of storage, containment and detoxification. Add to this the possible releases of long-chain aliphatic hydrocarbons, PAHs, alkylbenzenes, and other aromatics resulting from the production of petroleum derived products such as polyethylene and polypropylene, and the potential to contaminate the surrounding waters and ecosystems, is clear.

In order to investigate the extent of existing contamination, in May and July 1998, 14 samples of sediment, industrial wastewater and runoff were collected from sites in and around the complex, with the aim of identifying all organic pollutants and heavy metal contaminants present. Six of the samples were collected from a wide, open waste channel running through the middle of the site. The other eight samples were collected from a number of runoff/drainage channels running through and around the complex, close to, or leading from, the Solvay-Indupa chlorine, VCM and PVC plants (see Table 1A). This effectively continues work that began in August 1996, when nine samples from the same and similar sites were collected (see Table 1B).

## **Sampling Methodology**

All samples were 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, and stored in

100ml glass Duran bottles. 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 Laboratories, 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).

Sample Number	Sample Description
LA8041	Effluent collected from open waste channel (a.m.) running through the industrial complex
LA8042	Sediment collected from open waste channel running through industrial complex, close to the Bay
LA8044	Sediment collected from runoff/drainage channel, at point of confluence with the Bay
LA8045	Sediment collected from runoff/drainage channel, at point of confluence with the Bay (Puerto Galvan)
LA8053	Effluent collected from open waste channel (p.m.) running through the industrial complex
LA8054	Sediment collected from runoff/drainage channel running from the chlorine plant (1.63 km from site reference point)
LA8055	Effluent collected from runoff/drainage channel running from the PVC plant (1.3 km from site reference point)
LA8056	Sediment collected from a runoff/drainage channel running from the PVC plant (1.3 km from site reference point)
LA8057	Effluent collected from open waste channel (p.m.) running through the industrial complex
LA8058	Sediment collected from open waste channel running through industrial complex, upstream of LA8042
LA8059	Sediment collected from runoff/drainage channel running from the EDC/VCM plant (0.75 km from site reference point)
LA8060	Effluent collected from runoff/drainage channel running from the EDC/VCM plant (0.75 km from site reference point)
LA8061	Sediment collected from open waste channel running through industrial complex, upstream of LA8042 and LA8058
LA8062	Sediment collected from runoff/drainage channel running from the chlorine plant (1.87 km from site reference point)

*Table 1A: Descriptions of samples collected from the Bahia Blanca petrochemical complex, 1998 (site reference point: ethylene pipe crossing the main through-road)*

Sample Number	Sample Description
MI6062	Water collected from an area of dredged soils, in front of PVC, EDC, VCM and chlorine plants
MI6063	Effluent collected from runoff/drainage channel running from the PVC plant
MI6064	Sediment collected from an area of dredged soils (see MI6062)
MI6065	Soil dredged from the estuary, and stored on land, in front of the PVC, EDC, VCM and chlorine plants
MI6066	Sediment collected from runoff/drainage channel, at point of confluence with Bahia Blanca Bay
MI6067	Sediment collected from open waste channel, running through the industrial complex
MI6068	Sediment collected from runoff/drainage channel running from the chlorine plant
MI6069	Sediment collected from a runoff/drainage channel running from the EDC/VCM plant
MI6070	Sediment collected from runoff/drainage channel running through the PVC plant

*Table 1B: Descriptions of samples collected from the Bahia Blanca petrochemical complex, 1996*

## 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 105<sup>0</sup>C, and rinsed three times with low haloform pentane.

### Solid Samples

For each sample, approximately 30 g (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 20 ml pentane 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 analytical-grade nitrogen. 1-bromonaphthalene was then added as a marker.

## **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 same clean up procedure, as described above, was employed.

## **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, coupled with expert interpretation. 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 until dry weight readings became constant (approx. 48 hours). 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 the batch of 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 the batch of 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. All other instrument and laboratory quality control procedures were adhered to.

Mercury (Hg) was determined using Cold Vapour Generation ICP-AES. Hg (ii) was reduced to Hg (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 2-7.

Table 2 shows the results of the heavy metal analysis carried out in 1998. The results show that significant levels of mercury were detected in many of the sediment samples. Collected from both the open waste channel, and the runoff/drainage channels running from the chlorine, EDC/VCM and PVC plants. Concentrations ranged from 13.1 mg/kg to 57.9 mg/kg. Concentrations in effluents ranged from <2 ug/l to 18 ug/l.

Significant levels of zinc, copper and cadmium were also found in some samples. Sediment levels of zinc ranged from 49.5 mg/kg to 3729 mg/kg; copper ranged from 13.8 mg/kg to 188.2 mg/kg; chromium levels ranged from 10.2 mg/kg to 217.7 mg/kg and cadmium levels ranged from below limits of detection to 2.0 mg/kg. The results indicate little variation in the sediment levels of manganese, lead, nickel and cobalt.

Concentrations of these metals are generally low, with the exception of sample LA8060, which contained appreciable levels of manganese, zinc and copper.

Sample Number	Mn (ppm)	Cr (ppm)	Zn (ppm)	Cu (ppm)	Pb (ppm)	Ni (ppm)	Co (ppm)	Cd (ppm)	Hg (ppm)
<b>Effluents</b>									
LA8041	0.04	<0.01	0.30	0.06	0.04	<0.01	<0.01	<0.01	<0.002
LA8053	0.04	0.06	0.13	0.09	<0.03	<0.01	<0.01	<0.01	0.007
LA8055	0.13	<0.01	0.54	0.15	0.03	<0.01	<0.01	<0.01	0.007
LA8057	0.13	0.04	0.64	0.21	0.04	0.04	<0.01	<0.01	0.008
LA8060	2.13	0.06	1.85	0.64	0.03	<0.01	0.03	<0.01	0.018
<b>Sediments</b>									
LA8042	375.5	62.3	3729.4	91.7	23.5	19.1	8.3	2.0	13.1
LA8044	355.8	20.2	56.3	15.4	9.6	12.0	9.6	n/d	n/d
LA8045	525.0	10.2	49.5	13.8	16.8	6.1	6.6	n/d	n/d
LA8054	591.8	20.4	82.7	23.5	n/d	16.3	10.2	n/d	55.1
LA8056	433.7	17.3	108.7	26.0	25.0	12.5	8.7	n/d	57.9
LA8058	313.7	217.7	2887.8	188.2	19.6	26.5	5.9	2.0	54.5
LA8059	594.0	26.0	287.0	65.0	40.0	20.0	12.0	n/d	51.5
LA8061	329.0	61.0	1981.0	70.0	9.0	17.0	7.0	1.0	52.2
LA8062	220.9	11.8	145.5	56.4	64.6	12.7	4.6	1.8	22.1

Table 2: Results of heavy metals analysis, Bahia Blanca petrochemical complex (1998)

Table 3 shows the results of the heavy metal analysis carried out in 1996. Again significant levels of mercury were detected in many of the sediment samples collected from the runoff/drainage channels running from the chlorine, EDC/VCM and PVC plants. Concentrations ranged from 0.4 mg/kg to 57.8 mg/kg. However on this occasion, no mercury was detected in any of the aqueous samples.

Significant levels of zinc, copper and cadmium were also found in some samples. Sediment levels of zinc ranged from 57.7 mg/kg to 5267.0 mg/kg; copper levels ranged from 16.3 mg/kg to 569.8 mg/kg and cadmium levels ranged from below detection limits to 2.1 mg/kg. Concentrations found in the effluent were low, with only manganese and zinc present at detectable concentrations.

Sample Number	Mn (ppm)	Cr (ppm)	Zn (ppm)	Cu (ppm)	Pb (ppm)	Ni (ppm)	Co (ppm)	Cd (ppm)	Hg (ppm)
<b>Effluents</b>									
MI6062	0.27	<0.01	0.04	<0.01	<0.03	<0.01	<0.01	<0.01	<0.002
MI6063	0.34	<0.01	0.09	<0.01	<0.03	<0.01	<0.01	<0.01	<0.002
<b>Sediments</b>									
MI6064	434.3	17.6	58.3	19.4	n/d	8.3	11.1	n/d	0.7
MI6065	406.4	20.2	59.6	22.3	n/d	9.6	10.6	n/d	0.7
MI6066	717.4	19.6	60.9	16.3	8.7	9.8	n/d	n/d	0.4
MI6067	380.8	17.3	57.7	21.2	n/d	7.7	8.7	n/d	1.1
MI6068	756.3	19.8	634.4	52.1	n/d	13.5	8.3	2.1	57.8
MI6069	422.6	41.5	5267.0	569.8	35.9	34.9	9.4	n/d	5.8
MI6070	611.7	19.2	157.5	23.4	19.2	8.5	9.6	n/d	3.5

Table 3: Results of heavy metals analysis, Bahia Blanca petrochemical complex (1996)

Table 4 and Figure 1 show the groups of organic compounds identified in each of the samples collected in 1998, with match qualities greater than 90%. The most abundantly identified organic compounds were polycyclic aromatic hydrocarbons, most commonly naphthalene, and organohalogen compounds. Both found in 53% of the samples. Among the organohalogens identified were hexachlorobenzene, other chlorinated benzenes, and chlorinated ethers, alkenes and alkanes.

Aromatic compounds, such as biphenyls, indene derivatives, phthalate esters and styrene, were identified in 47% of the samples, along with straight chain and branched hydrocarbons. A third of the samples contained alkylbenzenes, in combination with aliphatic hydrocarbons, PAHs and PAH derivatives. Approximately 20% of the samples contained phenol derivatives. Table 5 and Figure 2 show the groups of organic compounds identified with the same degree of reliability, in samples collected in 1996. The most abundantly identified organic compounds were aliphatic hydrocarbons, found in nearly 90% of the samples. Organohalogen compounds were found in 44% of the samples. Examples including DDT, DDD, hexachlorobenzene, other chlorinated benzenes, chlorinated PAHs and chlorinated alkenes. PAHs, other aromatic compounds (including biphenyl and phthalate esters), alkylbenzenes and phenol derivatives were also reliably identified in these samples.

<b>Groups of compounds identified to better than 90%</b>	<b>Number of samples</b>	<b>Sample numbers</b>
<b>ORGANOHALOGEN COMPOUNDS</b>		
Hexachlorobenzene	1	LA8057
Trichlorobenzenes	2	LA8058, LA8061
Dichlorobenzenes	4	LA8053, LA8056, LA8058, LA8061
Chlorobenzenes	1	LA8056
Chlorinated ethers	1	LA8055
Chlorinated Alkenes	7	LA8053, LA8055, LA8056, LA8057, LA8058, LA8060, LA8062
Chlorinated Alkanes	5	LA8053, LA8055, LA8056, LA8060, LA8062
<b>PHENOL DERIVATIVES</b>		
2,2-[(1-methyl-11,2-ethanediyl)bis(nitrilomethylidyne)]bis phenol	1	LA8053
Nonyl-phenol	3	LA8053, LA8055, LA8058
<b>POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)</b>		
Acenaphthene and derivatives	1	LA8058
Acenaphthylene and derivatives	2	LA8053, LA8058
Anthracene and derivatives	1	LA8058
Fluorene and derivatives	5	LA8041, LA8053, LA8057, LA8058, LA8061
Naphthalene and derivatives	8	LA8041, LA8042, LA8053, LA8056, LA8057, LA8058, LA8059, LA8061
Phenanthrene and derivatives	5	LA8041, LA8042, LA8057, LA8058, LA8061
<b>ALKYL BENZENES</b>	5	LA8053, LA8057, LA8058, LA8061, LA8062
<b>OTHER AROMATICS</b>		
Benzaldehyde	1	LA8044
Benzene	4	LA8053, LA8057, LA8058, LA8061
Biphenyls and alkyl derivatives	5	LA8041, LA8053, LA8057, LA8058, LA8061
Indene and derivatives	4	LA8053, LA8057, LA8058, LA8061
Phthalate esters	3	LA8057, LA8058, LA8061
Styrene	4	LA8053, LA8057, LA8058, LA8062
<b>TERPENOIDS</b>	1	LA8053
<b>ALIPHATIC HYDROCARBONS AND DERIVATIVES (both straight and chain)</b>	7	LA8041, LA8053, LA8057, LA8058, LA8060, LA8061, LA8062

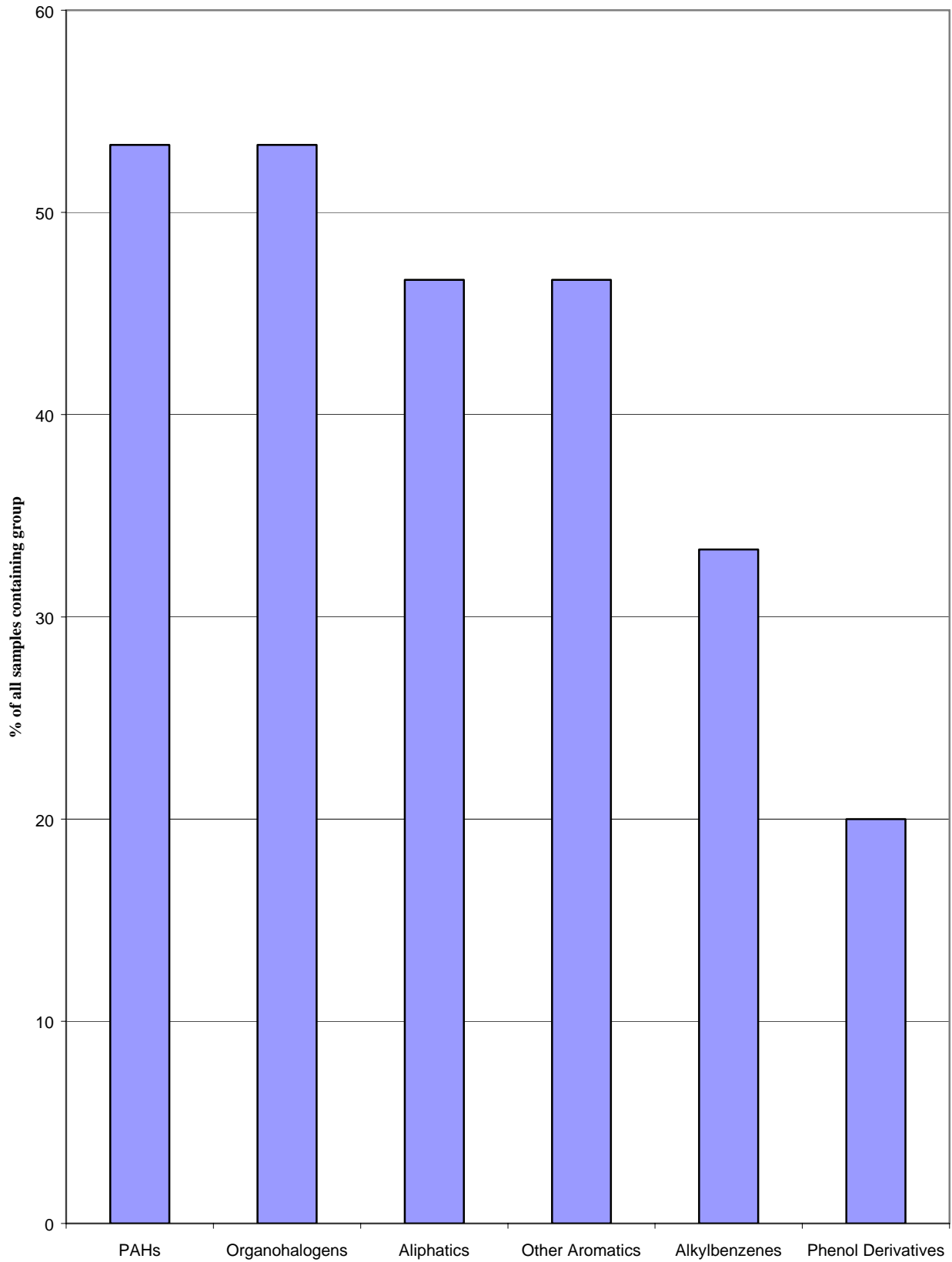
*Table 4 Groups of organic compounds reliably identified in samples collected from the Bahia Blanca petrochemical complex (1998)*



<b>Groups of compounds identified to better than 90%</b>	<b>Number of samples</b>	<b>Sample numbers</b>
<b>ORGANOHALOGEN COMPOUNDS</b>		
DDT	1	MI6065
DDD	1	MI6065
Hexachlorobenzene	1	MI6069
Pentachlorobenzene	2	MI6069, MI6070
Trichlorobenzenes	3	MI6063, MI6069, MI6070
Dichlorobenzenes	2	MI6063, MI6070
Chlorobenzenes	1	MI6070
Chlorinated PAHs	1	MI6070
Chlorinated Alkenes	2	MI6063, MI6070
<b>PHENOL DERIVATIVES</b>		
Phenol, 2,6-bis(1,1-dimethylethyl)4-methyl	1	MI6070
<b>POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)</b>		
Fluorene and derivatives	1	MI6070
Naphthalene and derivatives	3	MI6063, MI6069, MI6070
Phenanthrene and derivatives	1	MI6069
<b>ALKYL BENZENES</b>		
	2	MI6069, MI6070
<b>OTHER AROMATICS</b>		
Aromatic organo-nitrogen compounds	1	MI6070
Benzene derivatives (not listed above)	1	MI6068
Biphenyls and alkyl derivatives	1	MI6069
Phthalate esters	1	MI6070
<b>STEROIDS</b>		
	2	MI6068, MI6069
<b>ALIPHATIC HYDROCARBONS AND DERIVATIVES (both straight and chain)</b>		
	8	MI6062, MI6064, MI6065, MI6066, MI6067, MI6068, MI6069, MI6070

*Table 5 Groups of organic compounds reliably identified in samples collected from the Bahia Blanca petrochemical complex (1996)*

**Fig 1 Occurrence (in %) of groups of organic compounds found in samples collected from the Bahia Blanca Petrochemical Complex, Argentina 1998**



**Fig 2 Occurrence (in %) of groups of organic compounds found in samples collected from the Bahia Blanca Petrochemical Complex, Argentina 1996**

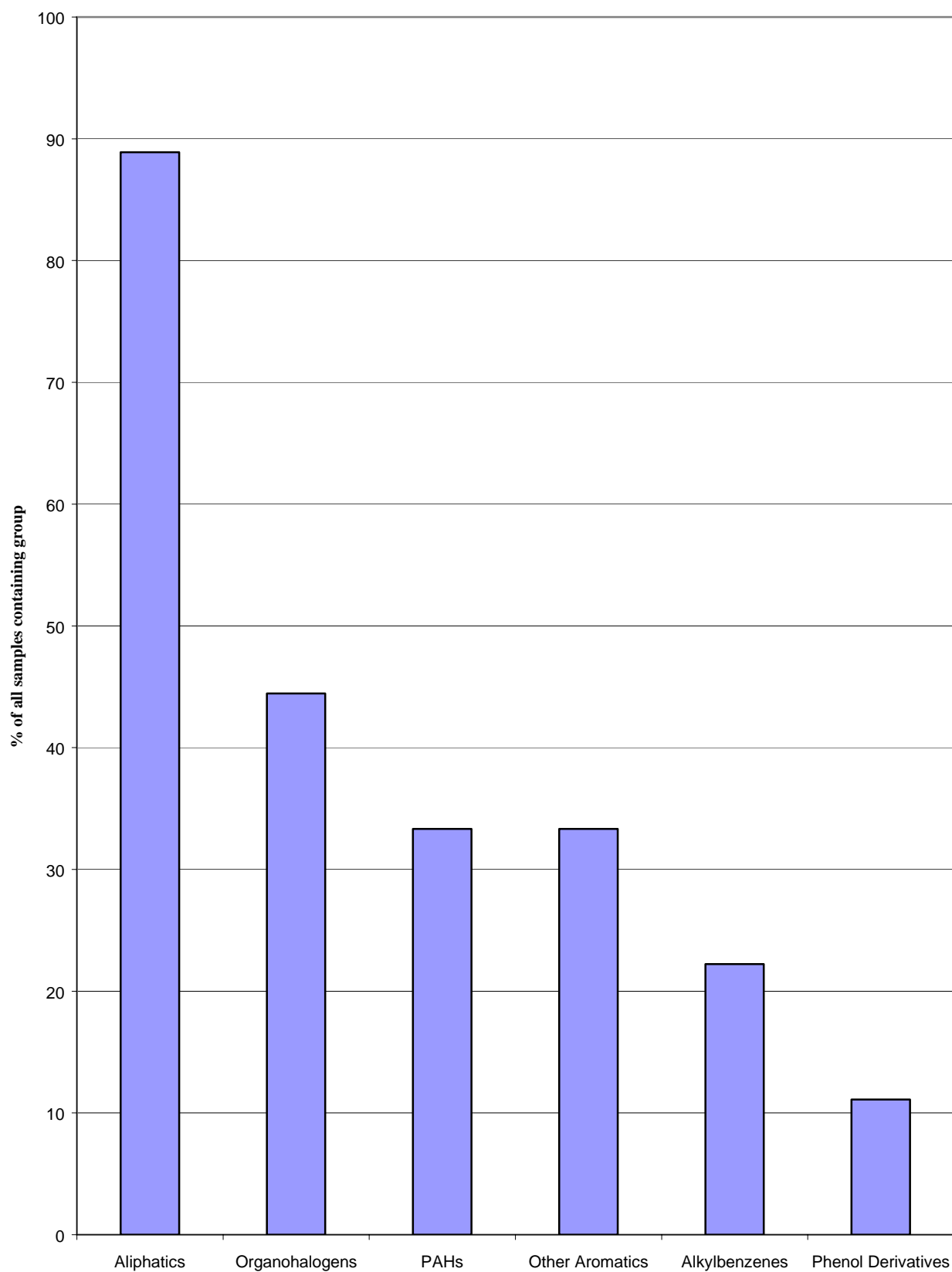


Table 6 shows the number and type of organic compounds identified with a high degree of reliability in each of the samples collected in 1998. Proportions of identified compounds ranged from 54% of the total isolated in sample LA8053, to 7% of the total number isolated in samples LA8044 and LA8059.

Sample Number	Number of Compounds Isolated	Reliably Identified	Number of Halogenated Compounds	Number of PAHs	Number of Alkyl Benzenes	Number of other Aromatics
LA8041	17	6 (35%)	0	4	0	1
LA8042	5	2 (40%)	0	2	0	0
LA8044	14	1 (7%)	0	0	0	1
LA8045	10	0	0	0	0	0
LA8053	52	28 (54%)	3	6	10	6
LA8054	15	0	0	0	0	0
LA8055	25	8 (32%)	5	1	0	1
LA8056	25	6 (25%)	5	1	0	0
LA8057	65	23 (35%)	2	5	5	8
LA8058	89	40 (45%)	4	16	9	10
LA8059	14	1 (7%)	0	1	0	0
LA8060	26	3 (12%)	2	0	0	0
LA8061	152	55 (36%)	5	17	17	7
LA8062	30	10 (33%)	7	0	1	1

*Table 6 Results of organic screening analysis, Bahia Blanca petrochemical complex (1998)*

Table 7 shows the number and type of organic compounds identified in each of the samples collected in 1996. Numbers of identified compounds ranged from 24% of the total number isolated in sample MI6069, to 7% of the total number isolated in sample MI6063.

Sample Number	Number of Compounds Isolated	Reliably Identified	Number of Halogenated Compounds	Number of PAHs	Number of Alkyl Benzenes	Number of other Aromatics
MI6062	94	10 (11%)	0	0	0	0
MI6063	55	4 (7%)	3	1	0	0
MI6064	78	6 (8%)	0	0	0	0
MI6065	85	7 (8%)	2	0	0	0
MI6066	77	12 (16%)	0	0	0	0
MI6067	66	2 (3%)	0	0	0	0
MI6068	155	9 (6%)	0	0	0	2
MI6069	133	32 (24%)	3	9	3	1
MI6070	170	32 (19%)	6	3	2	3

*Table 7 Results of organic screening analysis, Bahia Blanca petrochemical complex (1996)*

## Discussion

### 1. Open waste channel

Seven samples were collected from the open waste channel running through the centre of the Bahia Blanca petrochemical complex. Six were collected in 1998 (LA8041, LA8042, LA8053, LA8058, LA8059 and LA8061), one in 1996 (MI6067). The channel runs past many of the companies on site, and appears to carry communal waste from the complex out into bay. The results obtained from these samples highlight the presence of many organic pollutants and heavy metal contaminants, some of which are extremely toxic, environmentally persistent, and bioaccumulative.

Three samples of effluent were collected from the channel, one during the morning hours, and two at night. Sample LA8041, collected in the morning, contained fluorene, phenanthrene, and naphthalene derivatives, all classed as polycyclic aromatic hydrocarbons (PAHs), as well as the aromatic compound, 1,1-biphenyl. Detectable levels of manganese, zinc, copper and lead were also found, albeit at low (parts per billion) concentrations.

*PAHs are a group of compounds formed during the incomplete combustion of coal, oil, gas, wood, garbage or other organic substances. Once 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. In terms of human health, prolonged exposure to PAHs can have a deleterious effect, 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).*

*Less is known about 1,1-biphenyl, however 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 herbicide) complained of headaches, diffuse pain, nausea and numbness and aching in the limbs (Edwards et al. 1991).*

Samples LA8053 and LA8057, collected at night, contained a wider range of compounds, including a number of organochlorines, PAHs, benzene, alkylbenzenes, and other aromatics (biphenyl, indene, di (2-ethylhexyl) phthalate (DEHP), phenol derivatives and styrene). In addition, detectable levels of mercury, manganese, chromium, zinc, copper, lead and nickel were also found.

Of great significance is the identification of five organochlorine compounds. Hexachlorobenzene (HCB) and tetrachloroethene were identified in sample LA8057. While chloroform, tetrachloroethene (perchloroethylene) and 1,3-dichlorobenzene were identified in sample LA8053.

*HCB has been used as a fungicide and as an intermediate in organic synthesis, especially of chlorinated chemicals. In addition it is often formed as a by-product of the synthesis of chloro-organics (Johnston et al. 1994, Budavari et al. 1989). It is highly toxic, persistent and bioaccumulative. Animal studies show that oral exposure can damage the liver, the immune system, the kidneys and the skin, with exposure to very high concentrations resulting in cancers of the liver and thyroid (ATSDR 1998). The International Agency for Research on Cancer (IARC) has listed HCB as a confirmed animal carcinogen. In terms of environmental persistence, half-lives for HCB in soils and aerobic aquatic systems have been estimated as*

between 2.7 and 5.7 years. In anaerobic sediments this could be as long as 10-23 years (Howard et al. 1991). On account of its acute and chronic toxicity, and its persistence in the environment, HCB 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 HCB will be phased out worldwide under a convention currently being drawn up (UNEP 1995, 1997).

1,3-dichlorobenzene is most commonly used as a fumigant (Budavari et al. 1989), however it is possible that it is present at this site as a by-product of the PVC manufacturing process, rather than through dedicated manufacturing processes. All isomers of dichlorobenzene have been shown to be toxic in animal studies, with the liver, and to a lesser extent, the kidney, being the organs most affected. They are persistent in the environment, and have the potential to bioaccumulate (IUCLID 1996).

Tetrachloroethene is used extensively as a solvent, most commonly in dry-cleaning and metal-degreasing operations. It is also used as a starting material in the production of other synthetic chemicals. Furthermore it is frequently found in PVC industry wastes (Johnston et al. 1994), and can be manufactured from these wastes on a large scale (see e.g. ICI 1994). Due to its volatility, the most common exposure comes from inhalation. Human exposure to high concentrations can cause dizziness, headaches, sleepiness, confusion, nausea, and possibly unconsciousness and death if exposed to high concentrations in a closed, poorly ventilated area. As expected, these symptoms occur almost entirely in the working environment. However the long-term effects to humans exposed to lower level have not yet been fully identified (ATSDR 1997). Based on animal data, the U.S. Department of Health and Human services has determined that tetrachloroethene may reasonably be anticipated to be a carcinogen. In addition, the International Agency for Research on Cancer (IARC) has determined that tetrachloroethene is possibly carcinogenic to humans (ATSDR 1997).

Chloroform (trichloromethane), when intentionally used, is most commonly employed as a solvent. However it is often found as an unintentional by-product of the PVC production process (Johnston et al. 1994). In humans exposed to highly contaminated air or water, chloroform can affect the central nervous system, the liver and the kidneys. If smaller amounts are consumed over a long period of time, liver and kidney damage may still result (ATSDR 1997). Furthermore, studies in which humans were exposed to chloroform-contaminated drinking water showed a possible link between the chloroform in chlorinated drinking water and the occurrence of cancer of the colon and bladder. Based on these studies, the U.S. Department of Health and Human Services has determined that chloroform may reasonably be anticipated to be a carcinogen. The International Agency for Research on Cancer (IARC) has determined that chloroform is possibly carcinogenic to humans. Whilst the EPA has determined that chloroform is a probable human carcinogen.

Other environmentally significant compounds identified in these samples included benzene, a large number of alkylbenzenes and PAHs, di(2-ethylhexyl)phthalate (DEHP), nonylphenol, styrene, biphenyl, and a number of straight chain and branched aliphatic hydrocarbons. PAHs and biphenyl have been discussed above. Regarding the other contaminants identified, their uses, toxicological properties and environmental significance can be summarised as follows:

*Benzene is found in the environment due to both human activities and natural processes. It was first discovered and isolated from coal tar. However today it is mostly produced from petroleum sources. Various industries use benzene to make other chemicals, such as styrene (for Styrofoam® and other plastics), cumene (for various resins), and cyclohexane (for nylon and synthetic fibers). It is also used for the manufacturing of some types of rubbers, lubricants, dyes, detergents, drugs, and pesticides (ATSDR 1997). In terms of toxicity, acute exposure, either from inhalation, ingestion, or skin absorption, can cause irritation to mucous membranes. It can also cause restlessness, convulsions and depression. Death may follow from respiratory failure. Chronic exposure to lower levels can cause bone marrow suppression, which can, albeit rarely, lead to leukemia. Because of this benzene is listed as a known carcinogen (ATSDR 1997).*

*Alkylbenzenes occur in the environment largely as a result of their presence in crude oil and petroleum products. They are also produced following 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).*

*Phthalate esters e.g. DEHP, are moderately persistent in the environment. They are used as additives in a wide range of product categories, including toys, household products, medical equipment and packaging. 90% is used in the production of soft PVC products. DEHP remains one of the most abundantly used (Menzert et al. 1986), although longer chain isomeric mixtures (e.g. DINP) are increasingly in use. DEHP can exert a number of chronic toxic effects following longer exposures and may be an important reproductive poison, (Life Systems, Inc. 1993). More recently, concern has been raised about the ability of DEHP and some other phthalates to interact with hormone receptors in animals (Jobling et al. 1995).*

*Alkylphenols, such as nonylphenol, are widely found in surface waters and aquatic sediments. Nonylphenol itself is used in the preparation of lubricating oil additives, resins and plasticisers. It is also a product of the microbial breakdown of alkylphenol polyethoxylates (APEs), widely used in industrial detergents, paints, herbicides and cosmetics (Jobling et al. 1996). Because of their lipid solubility and persistence, alkylphenols are bioaccumulative (Jobling and Sumpter 1993). In addition, it has been demonstrated that nonylphenol, along with some of the other biodegradation products of APEs, are capable of disrupting the endocrine system of animals, including fish and mammals (Jobling and Sumpter 1993). In fish, effects on testicular growth and vitellogenin synthesis (a process normally dependent on endogenous estrogens) have been observed (Jobling et al. 1996).*

*Styrene is used extensively in the manufacture of numerous polymers and copolymers, including polystyrene, acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN), styrene-butadiene latex, and styrene-butadiene rubber. Several cohort studies have suggested that workers exposed to styrene in the chemical industry suffer increased mortality from lymphatic and hematopoietic cancer (Kolstad et al. 1994). However, this finding has not been consistently reproduced in studies of reinforced plastics manufacturers, whose exposures to styrene are generally higher. Other studies showed that relatively low levels of styrene (250 to 500 ppm) can cause extensive mortality and hepatotoxicity for mice, while rats and humans*

*exhibit only nasal and eye irritations at exposure concentrations well above 500 ppm (Sumner et al. 1994).*

*Aliphatic hydrocarbons are naturally present in the complex mixture that makes up petroleum, and can therefore be released into the environment through natural seeps, non-point source urban runoffs, and by large quantities of accidentally released oil. When present in combination with PAHs and alkylbenzenes, they are often indicative of petroleum contamination (Overton 1994)*

As mentioned above, in addition to these effluent samples, four samples of sediment were collected along the waste channel, downstream of the industrial complex (LA8042, LA8058, LA8061 and MI6067). The collection of sediment was deemed appropriate as its analysis provides a reliable history of pollution within a given area (Bryan and Langston 1992). Most metals and many persistent organic pollutants will bind predominantly to suspended material before finally accumulating in the sediment.

These samples contained large numbers of organic compounds, including organohalogenes (isomers of dichloro- and trichlorobenzene and tetrachloroethene), PAHs (most notably naphthalene), alkylbenzenes, DEHP, nonylphenol and styrene. In addition, anomalously high levels of mercury (1.1mg/kg to 54.5 mg/kg) and zinc (57.7 mg/kg to 3729 mg/kg) were also found. With the exception of trichlorobenzene, mercury and zinc, all of these compounds and groups of compounds have been discussed above. The uses, toxicity and environmental significance of these others can be summarised as follows:

*1,2,4-trichlorobenzene was identified in samples LA8058 and LA8061. 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 are persistent in the environment, and have a high tendency to bioaccumulate (IUCLID 1996). Commercial grade mixtures of trichlorobenzenes, which would contain 1,2,4-trichlorobenzene, is used to combat termites. Exposure causes irritation to eyes and mucous membranes (Budavari et al. 1989).*

*Hg 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). 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 Hg 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).*

*Mercury levels ranged from 1.1 mg/kg in sample MI6067 (1996) to 54.5 mg/kg in sample LA8058 (1998). Using the 0.5 mg/kg as the background figure, mercury levels these samples are between 2 and 100 times higher than those normally associated with uncontaminated sediments, and due to the toxic, persistent and bioaccumulative properties of mercury and its compounds, these levels warrant serious concern.*



*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 even at low concentrations. Therefore any elevation above baseline levels could have a deleterious effect on any biota exposed (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. Thus 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). The importance of this is the fact that 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 MeHg accumulation. MeHg 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, MeHg 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 10,000-1000,000 times the concentrations found in ambient waters (Callahan et al. 1979, EPA 1980, 1984, ATSDR 1997).*

*The significance of this is that biomagnification of MeHg 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 (i.e. maintained equilibrium between mercury entering the body and leaving for it. 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, therefore excessive exposure to metallic, inorganic or organic mercury can permanently damage these organs (ATSDR 1997).*

*Background sediment levels of zinc are usually quoted as being less than 100 mg/kg (Goncalves et al. 1990, Bryan and Langston. 1992, Licheng and Kezhun 1992, ATSDR 1997). Examples of levels associated with contaminated sites, such as those receiving acidic mine drainage and other manufacturing / metal processing effluents and domestic sewage, include*

650 mg/kg to 1187 mg/kg found in Avoca River in Ireland (Herr and Gray 1997); <100 mg/kg to 1320 mg/kg found in the Kola Lake Peninsula, Russia (Dauvalter 1994); 200 mg/kg to 5000 mg/kg found in the Tinto and Odiel River and Estuary system, Spain (Nelson and Lamothe 1993); and levels up to 3000 mg/kg found in Restongneut Creek in the Southwest of England (Bryan and Langston 1992).

Levels ranging from 58 mg/kg to 3729 mg/kg were detected in these samples, levels up to 300 times higher than those quoted as being typical of uncontaminated sediments.

*Environmental releases of zinc from anthropogenic sources far exceed the releases from natural sources (ATSDR 1997). Such anthropogenic releases include those resulting from electroplating, smelting and ore processing, as well as acid mine drainage, effluents from chemical processes (textiles, pigment and paint, fertiliser, and PVC production).*

*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).*

*Although 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 too much zinc, through food, water or dietary supplements. It is an essential trace element, but ingestion of higher than recommended levels can 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).*

## 2. Runoff / drainage channels

In addition to the open waste channel running through the centre of the complex, a network of open runoff and drainage channels were observed running through and around the site. Some leading directly from the chlorine, EDC/VCM and PVC plants, others running around the plant finally discharging into the bay. In 1998 eight samples were collected from these channels. Six samples of sediment, along with two samples of effluent mixed with runoff and/or rainwater. In 1996 five samples were collected from similar channels, four samples of sediment and one of effluent.

In 1998, two samples of sediment were collected from channels running from the Solvay-Indupa chlorine plant (LA8054 and LA8062). With sample MI6068, collected in 1996, taken from the same channel as LA8054. Sample LA8054 did not contain any reliably identified organic compounds, and sample MI6068, collected in 1996, containing only straight chain and cyclic hydrocarbons and a number of steroid compounds. However, levels of mercury in

these samples were exceptionally high, with over 50 mg/kg of mercury detected in both samples.

Sample LA8062, collected from a different channel, contained isomers of hexa- and pentachlorobutadiene, hexachloroethane, tetrachloroethene, trichloroethene, tetrachloromethane and chloroform. Mercury levels were again high, with 22 mg/kg detected in this sample. In addition, elevated levels of zinc were found. Most of these contaminants have been discussed above. The uses, toxicological properties and environmental significance of the others can be summarised as follows:

*Whereas little information is available regarding the toxicity of pentachlorobutadiene, hexachlorobutadiene (HCBD) has been well characterised. It is likely that, as with the chlorinated phenols and benzenes, toxicity may increase with increasing degree of chlorination, HCBD being the most toxic. Increased chlorination is also likely to mean increased environmental persistence (ATSDR 1997).*

*HCBD is a fairly common contaminant produced as a by-product in a number of industrial processes involving chlorine chemistry, particularly the production of ethylene dichloride (EDC) a precursor of PVC, and the secondary oxychlorination of EDC wastes in the manufacture of solvents (Johnston et al. 1994). It is also reported as a contaminant in technical formulations of pentachlorophenol, once used widely as a wood preservative (Goodrichmahoney et al. 1993). Although its use in many countries is now restricted. Furthermore, it is often considered to be useful indicator for the presence of chlorinated dioxins and furans (Costner et al. 1995).*

*In terms of toxicity, HCBD is a potent kidney toxin in laboratory animals (Werner et al. 1995), often showing greater toxicity in males than females for equivalent doses (Birner et al. 1995). It is a known animal carcinogen and a suspected carcinogen in humans (listed by the USEPA). If ingested, HCBD concentrates in the kidney, interferes with fundamental processes of cell respiration and can, as a result of conjugation with other compounds in the body, react with DNA, resulting in cell death or the development of tumours (ATSDR 1997). Short and long term exposure to very low doses via food, induced kidney and liver damage in laboratory animals, with juveniles more at risk than adults.*

*Little information regarding the toxicological properties of hexachloroethane is available. It is most widely used as an industrial solvent, and in sufficient concentrations can be irritating to the skin and mucous membranes (Budavari et al. 1989). As with the other organochlorine contaminants found in this study, it can be produced as a byproduct of PVC manufacturing (Johnston et al. 1994).*

*Trichloroethene, also widely produced as a by-product of PVC manufacturing (Johnston et al. 1994), is most commonly used as a degreasing solvent. In the past it was used as an anesthetic for surgery. Hence, as expected, people exposed to large amounts of trichloroethene can become dizzy or sleepy and may become unconscious. Death may occur from inhalation of large amounts. Animals that were exposed to moderate levels of trichloroethene had enlarged livers, and high-level exposure caused liver and kidney damage.*

*However, it is not known whether these changes would occur in humans although research continues (ATSDR 1997).*

*Tetrachloromethane (carbon tetrachloride), again often produced as a by-product of PVC manufacturing (Johnston et al. 1994) is most commonly used as a solvent for oils, fats, varnishes, rubber, waxes and resins; and is the starting product in the manufacture of many organic compounds. It is highly toxic, and acute exposure, via inhalation, ingestion or skin absorption can cause nausea, vomiting, diarrhoea, headaches, renal damage and liver failure. Chronic exposure to lower concentrations over a longer period of time can result in permanent liver damage, along with kidney failure and visual impairments. Repeated skin contact can cause dermatitis (Merck 1989). The U.S. Department of Health and Human Services (DHHS) has determined that carbon tetrachloride may reasonably be anticipated to be a carcinogen. The International Agency for Research on Cancer (IARC) has determined that carbon tetrachloride is possibly carcinogenic to humans, and the EPA has determined that carbon tetrachloride is a probable human carcinogen (ATSDR 1997).*

Three samples were taken from a similar channel running from the Solvay-Indupa EDC/VCM plant. LA8060 (effluent) and LA8059 (sediment) were collected in 1998; MI6069 (sediment) collected in 1996. Sample LA8060 contained 1,2-dichloroethane and tetrachloroethene. In addition, significant levels of manganese, zinc, copper and mercury were found. No organic compounds were reliably identified in the sediment sample collected from the same site. However again, mercury levels were anomalously high. Sample MI6069 collected in 1996 from a slightly different place, did contain a large number of compounds, most importantly hexachlorobenzene, pentachlorobenzene, trichlorobenzene, PAHs and PAH derivatives, alkylbenzenes, steroids and aliphatic hydrocarbons. Mercury, zinc and copper were also present at significant levels. Most of these contaminants have been discussed above. The uses, toxicological properties and environmental significance of the others can be summarised as follows:

*Dichloroethane is also known as ethylene dichloride (EDC). The largest individual use of dichloroethane is as an intermediate in the manufacture of other products, particularly vinyl chloride (ATSDR 1997), and it is the manufacture of EDC for PVC production generates large quantities of dioxins (ICI 1994, Stringer et al. 1995). Reliable information on how dichloroethane affects the health of humans is scarce. Brief exposure to dichloroethane in the air at very high levels has caused death in animals, and it is likely that exposure to similar levels would cause death in humans. Some studies in animals have shown that dichloroethane can cause kidney disease after long-term, high-level exposure in the air. Also, delayed growth was observed in the offspring of animals who breathed high concentrations of dichloroethane during pregnancy. However, there is no information as yet to indicate that these effects do occur in humans (ATSDR 1997).*

*Exposure to dichloroethane has so far not been associated with cancer in humans. One epidemiological study revealed a relationship between cancer incidence and exposure to environmental pollutants in groundwater, including dichloroethane; however, subjects were probably exposed to numerous other chemicals at the same time. Cancer studies in animals have shown that dermal exposure to dichloroethane can lead to the development of lung*

*tumors. Further studies showed that inhalation of dichloroethane may also cause cancer in animals.*

*In view of the cancer findings in animals, the possibility of dichloroethane exposure causing cancer in humans cannot be ruled out. The Department of Health and Human Services (DHHS) has determined that dichloroethane may reasonably be anticipated to be a carcinogen. The International Agency for Research on Cancer (IARC) has determined that dichloroethane is possibly carcinogenic to humans. Whilst the EPA has determined that dichloroethane is a probable human carcinogen (ATSDR 1997).*

In addition to these samples, four samples were collected from a channel running from the Solvay-Indupa PVC plant. LA8055 (effluent/rainwater) and LA8056 (sediment) collected in 1998; MI6063 (effluent/rainwater) and MI6070 (sediment) collected in 1996. All were highly complex and highly chlorinated. Sample LA8055 contained chloroform, 1,2-dichloroethane, trichloroethene, tetrachloroethene and 2-chloroethylether, along with nonylphenol and naphthalene. Whilst sample LA8056 contained 1,1-dichloroethane, trichloropropene, dichlorobutene, chlorobenzene, 1,4-dichlorobenzene and naphthalene. In addition, 58 mg/kg of mercury was found. Sample MI6063 contained 1,3-dichlorobenzene, 1,4-dichlorobutene, 1,2,4-trichlorobenzene and a derivative of naphthalene. Whilst the corresponding sediment sample, MI6070, contained isomers of dichloro- and trichlorobenzene, dichlorobutene, pentachlorobenzene, chlorinated naphthalene, butylated hydroxytoluene, and a large number of straight chain and branched hydrocarbons. In addition, mercury levels 10 times higher than those usually associated with clean sediments were found.

### 3. Other samples

A number of other samples were collected from channels located away from the main industrial complex (1998 and 1996). In addition, samples collected from an area containing dredged material from the bay were also taken. Samples LA8044, LA8045 and MI6066 contained mainly straight chain aliphatic hydrocarbons, as did samples collected from the swampy area containing dredged materials (MI6062 and MI6064). However a sample of dredged estuarine sediment (MI6065, collected in 1996) now stored on land within the complex, contained dichlorodiphenyltrichloroethane (DDT) and its metabolite, dichlorodiphenyldichloroethane (DDD).

*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 in a number of South American, African and Asian countries continues.*

*Both DDT and DDD are synthetically produced chemicals and are not known to occur naturally in the environment (WHO 1979). 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 ug/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 (ATSDR 1997). Thus leading to problems of long-term (chronic), and potentially more in-direct and widespread contamination. If terrestrial organisms, including humans, thus consume contaminated food and / drinking water deleterious health effects can result.*

*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. They have also suggested that short-term exposure to DDT in food may have a harmful effect on reproduction.*

*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).*

## **Conclusion**

Our results have highlighted the presence of anomalously high levels of mercury and zinc, and a potentially hazardous mix of organochlorines and other organic pollutants. As discussed, many of these compounds are highly toxic and have the potential to bioaccumulate through the food chain. In addition, many are highly persistent, and therefore even if discharges ceased in the very near future, retention by sediments (as illustrated), plant, animal and human tissues, will delay the elimination of these contaminants for many years.

Of great concern are the levels of mercury found in many of the samples, levels 100 times higher than those usually associated with clean sediments. Of equal concern is the presence of DDT, DDD, HCB, HCBd, other chlorinated benzenes and butadienes, chlorinated alkenes and alkanes. Contamination further complicated by the presence of a wide range of PAHs and PAH derivatives, DEHP, nonylphenol, styrene, benzene, alkylbenzenes and a large number of straight chain and branched aliphatic hydrocarbons. Whilst some of these compounds are (or

have been) manufactured commercially, many are not. Instead they are produced unintentionally and frequently in the wastes or discharges of the PVC manufacturing industry (Costner *et al.* 1995, Johnston *et al.* 1994, Stringer *et al.* 1995). It is therefore reasonable to assume that the organic contamination found here, coupled with the anomalously high levels of Hg (greater in 1998 than 1996), derive wholly or partly from PVC manufacture, with intentional manufacture or historical use, other potential, though less probable sources.

To conclude, the immediate clean-up this petrochemical site is essential, and although this will not be achieved quickly, continued reliance on short-term solutions such as wastewater treatment and the dredging of harbor and estuarine sediments, both of which are currently in practice, must be avoided. The mere shift of chemicals from one environmental medium to another is not the answer. In stead pollution prevention not control must be the way forward. Clean production processes based on renewable resources and minimal waste generation need to be employed, and ultimately the industries themselves, the processes they employ and the products they generate need to be assessed. If the relevant industrial and governmental bodies do not address this current situation, then the threat of widespread environmental contamination to this much utilised and important coastal region of Argentina cannot be removed.

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