

## Matanza-Riachuelo Basin Part 1: Environmental Samples

### **Identification and environmental significance of organic pollutants and heavy metal contaminants found in water and sediments collected from the Matanza-Riachuelo Basin, Argentina 1997**

Prepared by Angela Stephenson, Iryna Labunska, Ruth Stringer and David Santillo  
Greenpeace Research Laboratory, University of Exeter, UK  
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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 (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, thirty samples of water and sediment were collected from the Matanza-Riachuelo Basin, with the aim of identifying the range of organic pollutants and heavy metal contaminants present. 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, and stored in 100ml glass Duran bottles. Aqueous samples were collected in 1-litre bottles, the 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 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 clean 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. 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. 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.

### **Field Measurements**

Dissolved oxygen (O<sub>2</sub>) was determined for all water samples, at the time of sampling, using an Aqua-Merck 11/107 Reagent Kit.

pH was determined using universal indicator paper, pH range 1-14.

### **Results**

Figure 1 shows the area sampled, identifying all individual sampling sites.

Table 1 shows the groups of organic compounds reliably identified in each of the samples. With Figure 2 showing 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. PAHs and PAH derivatives (most notably naphthalene) were found in 67% of the samples, with alkylbenzenes found in 30% of the samples. Eight of the samples (25%) contained aliphatic hydrocarbons in combination with PAHs, PAH derivatives and alkylbenzenes.

53% of the samples contained organohalogen compounds. Isomers of dichlorobenzene being the most frequently found, identified in 50% of the samples.

The phenol derivative: 2,6-bis (1,1-dimethylethyl)-methyphenol, also known as BHT (butylated hydroxytoluene) was reliably identified in 13% of the samples. Other aromatics found included steroids (30% of samples), terpenoids (23% of samples), benzyl alcohols (13%), biphenyls, indene derivatives and terphenyls.

Table 2 shows the number and type of organic compounds identified in each sample of river water and sediment collected. Table 3 shows the levels of heavy metals found in the same samples. Sample type and sampling site details are also shown.

The highest numbers of organic compounds isolated were found in sediments collected from the Riachuelo, especially in the areas of Buenos Aires City and Avellaneda. The highest numbers of PAHs, alkylbenzenes and other aromatics were found in these samples. The isolation and identification of organohalogenes was more scattered, with no one district appearing to be more contaminated than another.

The highest levels of heavy metals, especially Cr, Zn, Cu and Pb, were also found in the Riachuelo sediments, collected from Buenos Aires City, Avellaneda and Lomas de Zamora. With one exception (sample AG7025), the lowest levels found are in the Rio Matanza sediments collected from the districts of Canuelas/Marcos Paz, La Matanza and Ezeiza.

Tables 4 and 5 show the Certified Reference Material and Quality Control data, accompanying the heavy metals results.

## **Discussion**

### **1. Rio Matanza**

The Rio Matanza passes through the rural districts of Canuelas, General Las Heras and Marcos Paz, in the upper part of the basin area; then through Ezeiza, Esteban Echeverria, La Matanza and Lomas de Zamora, after which it becomes the Riachuelo. Thirteen samples of sediment and four of water were collected along its path. Sediment was collected in preference to water at the majority of sampling sites, as analysis of sediment provides an excellent picture of the extent of pollution within a defined area. Water, due to fluctuations in emission and flow, follows a less well defined pattern (Bryan and Langston 1992).

Heavy metals and many persistent organic pollutants, will bind predominantly to suspended material, and finally accumulate in the sediment, thus providing a reliable history of pollution. As concentrations in sediment can exceed those of the overlying water by between three and five orders of magnitude (Schuhmacher et al. 1995, Bryan and Langston 1992), the bioavailability of even a minute fraction of the total sediment metal or organic pollutant assumes considerable importance.

Uncontaminated riverine sediments will usually contain less than 0.5 mg/kg of Cd and Hg; less than 50 mg/kg of Pb, Cr, Cu, Co, and Ni; less than 100 mg/kg of Zn; and less than 1000 mg/kg of Mn (Goncalves 1990, Salomons and Forstner 1984). Of the thirteen samples of riverine sediment collected along the Rio Matanza, all but two (AG7027 and AG7041) contained some degree of heavy metal contamination.

Regarding organic pollutants, our analysis was qualitative, identifying large numbers of organic compounds as opposed to quantitatively determining few. However the mere presence of many of the organic compounds identified, such organohalogenes and PAHs, can be indicative of anthropogenic contamination. Of the thirteen samples of riverine sediment collected, all but four (AG7001, AG7002, AG7044 and AG7046) contained some degree of organic pollutant contamination.

#### **a) Canuelas/Marcos Paz (AG7001-AG7002)**

The rural districts of Canuelas and Marcos Paz are situated in the upper Matanza-Riachuelo basin. As industrial activity in this area is minimal, the two sampling points selected were chosen as control sites, i.e. chosen to establish naturally occurring background levels of heavy metals, and the naturally occurring presence of organic compounds.

No organic compounds were reliably identified in either of these samples. With levels of Mn, Cr, Zn, Cu, Pb, Ni, Co and Hg, all typical of those found in uncontaminated sediments. Cd was present at a slightly elevated concentration of 1 mg/kg in both samples.

Generally speaking, the most often mentioned sources of Cd entering the aquatic environment are industrial effluents and sewage. As there is little industry and urbanisation in the area, these sources can effectively be eliminated. This level could be the naturally occurring background concentration of Cd, however as other sediments further downstream do not show similar levels (in fact Cd is present at non-detectable levels in the majority of the Rio Matanza samples), perhaps other sources need to be considered and investigated.

One such source could be phosphate fertilisers. Cd is found naturally in association with phosphate rock, which in turn is used to make phosphate fertilisers. These can contain up to 10 mg/kg of Cd, and thus their agricultural application can dramatically increase soil Cd concentrations (Butler and Timperley 1995). As Cd is one of the most labile metals, past and present farming activities could potentially result in the release and migration of Cd in agricultural soils, with the eventual effect that any Cd present in agricultural runoff could then be deposited in the river.

Studies on the bioavailability, bioaccumulation, and effects of Cd in sediments are numerous (Bryan and Langston 1992, Swartz et al. 1985, Di Toro 1990, Butler and Timperley 1995), and deleterious effects of increased Cd levels have been reported. For example, it has been suggested that a correlation between increasing levels of Cd in sediments from the Bristol Channel, in the UK, and increasing levels of Cd in limpets is responsible for the reduced ability of the limpet to utilise glucose. This is possibly due to the formation of metallothionein-like (sulphur containing) Cd-binding proteins interfering with usual enzymatic and metabolic pathways (Bryan and Langston 1992). Also, reproductive effects have been observed. The toxicity of low sediment-Cd concentration was suggested by observations showing that in San Francisco Bay, the condition of clams declined as sediment-Cd increased from about 0.1 mg/kg to 0.4mg/kg (Luoma et al. 1990).

#### **b) Ezeiza and La Matanza (AG7005, AG7040-AG7044, AG7046-AG7048)**

Three samples of water and six samples of sediment were collected from the Rio Matanza in the districts of Ezeiza and La Matanza, both situated in the centre of the Matanza-Riachuelo basin. These areas are not, in the main, heavily industrialised. However pollution could arise from the number of meat, food and beverage manufacturers, as well as a number of chemical, pharmaceutical, metallurgical and petrochemical factories. Of equal importance is the potential environmental harm caused by the release of large quantities of untreated sewage, as urbanisation increases along the river as it nears the Rio de la Plata.

#### **Organic Pollutants**

Two of the three water samples (AG7040 and AG7048) contained reliably identified organochlorine compounds and PAHs. AG7040 collected downstream of the meat processing plant "La Foresta", contained 1,2,3-trichlorobenzene, 1,3-dichlorobenzene (also known as meta-DCB, due to the positioning of the second chlorine atom), and naphthalene. AG7048,

water collected from an old section of the Rio Matanza, contained 1,4-dichlorobenzene (also known as para-DCB) and naphthalene.

As will become evident, dichlorobenzenes, predominantly p-DCB, were determined in many of the samples collected. These compounds are not naturally occurring, but are produced by chemical companies to make products for home use and other chemicals such as resins (USPHS 1997). Industrial releases contribute only a small fraction of the total environmental loading of dichlorobenzenes. It is the use and disposal of consumer products that are the major sources of environmental release (USPHS 1997). m-DCB, found in sample AG7040, is most frequently used as a fumigant. Whereas p-DCB, found in sample AG7048, is most frequently used in moth repellent products and in toilet deodoriser blocks (Merck 1989).

Due to the increased use of such consumer products in industrialised and urban areas, it has been reported that sewage sludges collected from these areas have higher dichlorobenzene concentrations than those collected from rural ones (Wang et al. 1994). This is because when released to soils and sediments, all isomers of dichlorobenzene remain moderately absorbed. As such they are useful markers of the extent of contamination from untreated sewage discharges (Chapman et al. 1996).

The fate of released dichlorobenzenes in the environment is dictated by the low solubility of these compounds in water (USPHS 1997). Therefore once discharged to surface waters or to land, dichlorobenzenes are expected to adsorb to soils and sediments. However, sorption can be reversible. Considering p-DCB specifically, it has been observed that this compound may leach from discharged raw sewage, land-applied sewage sludge and hazardous waste sites. It may be transported through groundwater, and migrate from surface water to groundwater through soil (USPHS 1997). It is expected to bioconcentrate in aquatic organisms, with examples of measured mean bioconcentration factors (which express the concentration in tissues compared to concentration in media) of 370-720 observed for rainbow trout and 1800 for guppies. There is also evidence to suggest that p-DCB has a high potential for bioaccumulation (USPHS 1997).

In terms of human and animal health, p-DCB is reported to cause headaches and dizziness, toxic effects in the liver and kidney, and increases in the rates of cancer among experimental animals (USPHS 1997, Bornatowicz et al. 1994). There is no direct evidence that p-DCB can cause cancer or birth defects or affect reproduction 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. The EPA has also determined that p-DCB is a possible human carcinogen.

Regarding 1,2,3-trichlorobenzene, less specific toxicity data or information on production and use is available. A commercial grade mixture of trichlorobenzenes, which would contain 1,2,3-trichlorobenzene, is used to combat termites, and has been found to cause irritation to eyes and mucous membranes (Merck 1989). It is worth noting that commercial applications of these chlorobenzenes do rely on their toxicity.

The Third North Sea Conference legislation lists trichlorobenzene in Annex 1A of the Hague Declaration (MINDEC 1990). Chlorobenzene and all isomers of dichlorobenzene are included in Annex 1D. Annex 1A being the priority list, and Annex 1D including compounds for which future measures and initiatives to reduce inputs must be made. The Fourth North Sea Conference in Esbjerg, Denmark, in 1995 (MINDEC 1995), agreed to continuously reduce discharges of hazardous substances such that environmental concentrations of

synthetic hazardous substances should be reduced to zero within 25 years. The 1998 Ministerial Meeting of the OSPAR Commission (Sintra Statement, OSPAR 1998a) further reinforced these objectives. Trichlorobenzene, along with chlorobenzene, and all isomers of dichlorobenzene, have been selected and included on the OSPAR 1998 List of Candidate Substances, Annex 3 of the OSPAR Strategy with regard to Hazardous Substances (OSPAR 1998b).

In addition to these organohalogen compounds, naphthalene (a PAH) was found in the same two water samples (AG7040 and AG7048). PAHs are a group of chemicals that are formed during the incomplete burning of coal, oil, gas, wood, garbage, or other organic substances, such as tobacco and charbroiled meat. Exposure can deleteriously effect human health, and individuals exposed to mixtures of PAHs, through inhalation or skin contact, for long periods of time, can develop cancer (USPHS 1997).

More than 100 different PAHs are known, however only a few have industrial / domestic applications and are manufactured specifically. Naphthalene is one of these, as it is used as a moth repellent and insecticide, although its use is decreasing due to the introduction of chlorinated compounds such as p-DCB (see above). The fate of PAHs in the environment, depend on how, and in what form, they are released. They can enter surface water through atmospheric deposition and from discharges of industrial effluents (including wood-treatment plants), municipal wastewater, and improper disposal of used motor oil. They will often be found bound to particles due to their low solubility in water. However they have been detected in groundwater, either as a result of migration directly from contaminated surface waters or through the soil (USPHS 1997).

In soils and sediments, PAHs are often degraded by microorganisms. However these metabolic processes can often be slow (Howard et al. 1991), leading to PAH accumulation in terrestrial and aquatic plants, fish, and invertebrates. Sediment-associated PAHs were seen to accumulate in bottom-dwelling invertebrates and fish (USPHS 1997). For example, Great Lakes sediments containing elevated levels of PAHs were reported to be the source of the body burdens of the compounds in bottom-dwelling invertebrates. Bioconcentration factors for fish and crustaceans were frequently in the 10-10,000 range.

Regarding the six riverine sediments collected from this section of the Rio Matanza, varying degrees of anthropogenic pollution were found. Generally speaking, far more organic compounds were identified in these samples than those identified in the three water samples.

Dichlorobenzenes were the most commonly found organohalogen compounds, found in five of the samples. p-DCB was reliably identified in samples AG7005, AG7041 and AG7047; and o-DCB (also known as 1,2-dichlorobenzene) was reliably identified in sample AG7042. o-DCB, not found in the water samples, is most commonly used as a solvent. However it too can be used as an insecticide for termites and locusts and as a fumigant. High levels of exposure can cause injury to the liver and kidneys, as well as causing CNS (central nervous system) damage (Merck 1989). As mentioned above, the presence of DCBs in environmental samples can indicate the presence of untreated sewage (Chapman et al. 1996). They can also be indicative of leachates migrating from dumpsites (Howard 1989) and industrial contamination.

As was the case with the water samples, PAHs and their derivatives were reliably identified in the sediment samples, examples including naphthalene, fluorene, derivatives of naphthalene, and derivatives of phenanthrene.

Other aromatic compounds identified in the same samples included the phenol derivative 2,6-bis (1,1-dimethylethyl)-methyl phenol (also known as butylated hydroxytoluene), identified in sample AG7042; the alkylbenzene compound 1-methyl-3-(1-methylethyl)-benzene was found in sample AG7047; and benzyl alcohol (also known as hydroxytoluene) identified in samples AG7041 and AG7047.

Butylated hydroxytoluene (BHT) is frequently employed as an antioxidant in food products and in the production of plastics, petrochemicals and some cosmetics (Merck 1989). Its use in food has been associated with certain allergic reactions (Dean et al. 1986), and there is also some evidence that BHT can act as a promoter of liver cancer, in combination with other carcinogenic substances (Williams et al. 1986). Due to its presence in many consumer products, it is frequently found in domestic sewage and sewage sludge.

Alkylbenzenes occur in the environment due to 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). As with many of the compounds identified above, due to their increased commercial use, they are also frequently found in domestic sewage and sewage sludge.

## **Heavy Metals**

Levels of heavy metals found in the water samples were not anomalously high. Heavy metals range from ng/l (parts per trillion) to ug/l (parts per million) in most unpolluted freshwater systems (National Rivers Authority, UK 1995). Based on this published data, it appears that Cu is slightly elevated in samples AG7040 and AG7043. All other metals are present at naturally occurring levels. However as mentioned previously, most of the metals present in the riverine system will be associated with the sediment.

Although essential for living organisms at very low concentrations, Cu is still one of the most toxic metals to aquatic organisms (Schuhmacher 1995, Bryan 1971). Generally speaking, but not a strictly rigid order of toxicity, Hg, Ag (silver) and Cu are considered more toxic than Cd, Zn and Pb, which in turn are considered more toxic than Cr, Ni and Co. There is considerable experimental evidence that a large number of species are sensitive to dissolved Cu in the range 1-10 ug/l. For example, it was observed that 2 ug/l Cu had significant effects of the survival of young bay scallops and clams (Nelson et al. 1988). Also, in the embryos of oysters and mussels, the 48-hour EC50 concentrations, based on the production of abnormal embryos, were about 5 ug/l (Martin et al. 1981). A similar concentration resulted in increased mortalities in populations of isopod crustaceans (Giudici and Guarino 1989). Thus the concentrations of Cu found in samples AG7043 (60 ug/l) and AG7040 (20 ug/l) collected from the Rio Matanza, could induce such deleterious reproductive and developmental effects in any aquatic biota exposed.

All other metals were found at more significant levels in the sediment samples. Generally speaking, the following concentration pattern was observed:

$$\text{Mn, Zn} > \text{Cu, Pb, Cr} > \text{Ni, Co} > \text{Cd, Hg}$$

Only one sample collected from this region (AG7041) contained levels of heavy metals associated with pristine, unpolluted sediments. Slightly elevated levels of Zn, Cu, and Pb were found in samples AG7046, and AG7047, with slightly elevated levels of Cd found in samples AG7042 and AG7044.



### **c) La Matanza and Esteban Echeverria (AG7024)**

One sample of sediment was collected from a tributary of the Rio Matanza as it flowed through the districts of La Matanza and Esteban Echeverria. Areas of these districts are highly industrialised, with a number of metal- processing operations, chemical, petrochemical and pharmaceutical plants. In addition, some areas are highly urbanised. Thus the potential to cause environmental harm, through the release of untreated industrial effluents, domestic sewage and urban runoff is considerable.

#### **Organic pollutants**

Sample AG7024 contained many different groups of organic compounds. Long chain aliphatic hydrocarbons were found, along with PAHs and dichlorobenzenes. In addition, 1-bromo-2,6-dichlorobenzene was reliably identified, along with the steroid 14.-beta.-H-Pregna, and the naturally occurring terpenoid, limonene.

The environmental sources and significance of PAHs, and dichlorobenzenes have been discussed above. Sources and significance of the other compounds reliably identified are as follows:

Long chain aliphatic hydrocarbons are difficult to source in the environment, as they can occur both naturally and as a result of anthropogenic activity. However, in many of our samples they were found together with PAHs and alkylbenzenes, and this combination is often indicative of anthropogenic petroleum-based pollution (Overton 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. They can be found, albeit at low concentrations, in sewage (Connell 1974). However levels released in these wastes can be significant due to the large volumes involved.

1-bromo-2,6-dichlorobenzene is classified as an organohalogen. Although no specific toxicity data is available for this compound, and no information on its uses could be found, it is not found naturally occurring, and retailing manufacturers do class it as an irritant, especially to the eyes, skin and respiratory system (Fisher 1996).

14.-beta.-H-Pregna belongs to the steroid group. It is a short chain sterane isomer, often found in petroleum (Requejo et al. 1997).

#### **Heavy Metals**

Elevated levels of Zn (269 mg/kg), Cu (82 mg/kg) and Pb (92 mg/kg) were determined in sample AG7024.

##### **(i) Zinc**

Background levels of Zn in sediment are usually quoted as being less than 100 mg/kg (Goncalves et al. 1990, Bryan and Langston. 1992, Licheng and Kezhun 1992, USPHS 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).

Environmental releases of Zn from anthropogenic sources far exceed the releases from natural sources (USPHS 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 production), and discharges of untreated domestic sewage. It is often forgotten that the latter can be a significant source of heavy metals, with Zn being the most abundant heavy metal present, occurring at concentrations of approximately 250 ppm (Lester 1988).

Evidence for the bioavailability of Zn in sediments comes from research on plants and deposit feeding invertebrates. Schuhmacher (1995), found that Zn in molluscs and algae collected from the Ebro River reflected sediment concentrations. Although Zn actively bioaccumulates in aquatic systems, biota appears to represent a relatively minor sink compared to sediments. Steady-state zinc bioconcentration factors (BCFs) for 12 aquatic species range from 4 to 24,000 (EPA 1987). Crustaceans and fish can accumulate zinc from both water and food. A BCF of 1,000 was reported for both aquatic plants and fish, and a value of 10,000 was reported for aquatic invertebrates (Fishbein 1981). The order of enrichment of zinc in different aquatic organisms was as follows (zinc concentrations in mg/g dry weight appear in parentheses): fish (25), shrimp (50), mussel (60), periphyton (260), zooplankton (330), oyster (3,300) (Ramelow et al. 1989). The high enrichment in oysters may be due to their ingestion of particulate matter containing higher concentrations of zinc than does ambient water. Other investigators have also indicated that organisms associated with sediments have higher zinc concentrations than organisms living in the aqueous layer (Biddinger and Gloss 1984).

A study investigating levels of heavy metals in biota from the Rio de la Plata, which provides the freshwater supply for Buenos Aires (Verrengia-Guerrero and Kesten 1993) showed the accumulation of Zn in fish and benthic organisms associated with polluted sediments. Sediment levels were quoted as ranging from 43 to 133 mg/kg. Examples of associated biotic concentrations include levels ranging from 80 to 109 mg/kg in fish, 340 to 450 mg/kg in the pancreatic tissues of snails.

Although Zn 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). However, most field and experimental examples of Zn toxicity refer to concentrations often far exceeding those found in this study.

Although most of the studies relating to the human health effects of Zn 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 Zn are 15 mg/day for men and 12 mg/kg 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 (USPHS 1997). Ingesting high levels for several months may cause anaemia, damage to the pancreas, and decreased levels of high-density lipoprotein (HDL) cholesterol (USPHS 1997).

## (ii) Copper

Background levels of Cu in sediment are quoted as ranging 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). Examples of concentrations associated with contaminated sites include levels ranging from <100 mg/kg to 6500 mg/kg found in lake sediments of the Kola Peninsula in Russia, areas situated at varying distances from two heavy metal smelters (Dauvalter 1994); levels ranging from <100 mg/kg to 3000 mg/kg in river sediments collected from the Tinto and Odiel rivers, in Spain, associated with past and present mining activities (Nelson and Lamothe 1993); levels ranging from <100 mg/kg to 1800 mg/kg in the Avoca River, Southeast Ireland, another river polluted by discharges of acid mine drainage (Herr and Gray 1997); and levels exceeding 2000 mg/kg in Restronguet Creek, Southwest England. This branch of the Fal Estuary also receives acidic drainage from past and present mining activity, via the Carnon River (Bryan and Langston 1992). In Argentina, Cu levels have been reported as ranging from 10 mg/kg to 50 mg/kg in the Rio de la Plata, Buenos Aires (Verrengia-Guerrero and Kesten 1993). 82 mg/kg of Cu were found in this sample of sediment collected from the Rio Matanza.

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; agricultural runoff (Cu compounds are used as nutritional supplements in fertilisers and animal feed, fungicides and other agricultural chemicals) and domestic sewage effluents.

As mentioned previously, Cu is toxic to aquatic species, even at very low (part per billion) levels. A very significant relationship between Cu levels in aquatic biota and the levels found in sediments has been demonstrated, with clear relationships 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.

Copper residues in muscle of 268 fish specimens were analysed over a 5- year period in several surface water systems in eastern Tennessee (Blevins and Pancorbo 1986). The mean residue levels in the muscle of different species of fish from nine stations ranged from 0.12-0.86 ppm (wet weight). Maximum levels ranged from 0.14-2.2 ppm.

Mean and median copper concentrations of 127 samples of edible fish from Chesapeake Bay and its tributaries were 1.66 and 0.36 ppm in 1978, and 1.85 and 0.61 ppm in 1979 (Eisenberg and Topping 1986). Copper levels were increased in the livers and to a lesser degree, the gonads, compared with the flesh. The copper content of muscle tissue of several species of fish collected from metal - contaminated lakes near Sudbury, Ontario, ranged from 0.5 - 1.4 ppm (Bradley and Morris 1986). The copper concentration in the livers, ranged from 5-185 ppm. Thus the liver tissue is a good indicator of copper availability and bioaccumulation in these fish.

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

### (iii) Lead

Concentrations of Pb 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). Concentrations associated with contaminated sites include levels of up to 2700 mg/kg found in the Gannel estuary in the Southwest of England, which is still contaminated from past Pb mining activities (Bryan and Langston 1991). Levels ranging from 1000 mg/kg to 2000 mg/kg have been found in the Tinto River in Spain, with levels ranging from 200 mg/kg to 2000 mg/kg found in the Odiel River. Both rivers receive anthropogenic inputs resulting from mining operations. Other anthropogenic inputs of Pb could arise from primary and secondary metal smelting and processing. With less direct, yet significant sources, arising from urban runoff, domestic sewage discharges, and automotive emissions (although declining).

In Argentina, levels ranging from 30 mg/kg to 70 mg/kg were found in the Rio de la Plata, Buenos Aires (Verrengia-Guerrero, and Kesten 1993). 92 mg/kg were found in this sample collected from the Rio Matanza.

Even though Pb 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 Pb is available to deposit-feeding species (Bryan and Langston 1992). In aquatic organisms, lead concentrations are usually highest in benthic organisms and algae, and lowest in upper trophic level predators (e.g., carnivorous fish).

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*). Although most median BCF values for aquatic biota are significantly lower: 42 for fish, 536 for oysters, 500 for insects, 725 for algae, and 2,570 for mussels (Eisler 1988). Lead is toxic to all aquatic biota and organisms higher on 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 Pb may be alkylated, chemically or biologically, to produce mono-, di-, and trialkyl Pb compounds (Radojevic and Harrison 1987). The chemical speciation of the Pb will often dictate the toxicity. Organolead compounds are more toxic than inorganic forms and have been shown to bioconcentrate in aquatic organisms. Tetraalkyl lead compounds are more toxic than trialkyl lead compounds, and ethyl forms are more toxic than methyl forms (Eisler 1988).

Unlike some heavy metals, Pb is not required in trace amounts 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 Pb are the same irrespective of whether it is inhaled or ingested (USPHS 1997). Pb can cause irreversible central nervous system damage and decreased intelligence at extremely low doses (Needleman et al. 1990, USPHS 1997). At higher levels of exposure anaemia may result, along with severe kidney damage (USPHS 1997). Children are especially susceptible to Pb poisoning because they absorb and retain more Pb in proportion to their weight than adults (USPHS 1997).

To conclude, this sample contained a mixture of organic compounds and heavy metal contaminants associated with a wide range of industrial, urban and domestic activities.

#### **d) La Matanza and Lomas de Zamora (AG7025-AG7027, AG7029-AG7030)**

Four samples of river sediment, and one of water, were collected from sections and tributaries of the Rio Matanza as it flowed through the districts of La Matanza and Lomas de Zamora. Again, areas of these districts are highly industrialised, with a number of metal processing operations, chemical, petrochemical and pharmaceutical plants, paper and textile mills. In addition, some areas are highly urbanised. Thus the potential to cause environmental harm, through the release of untreated industrial effluents, domestic sewage and urban runoff is again considerable.

#### **Organic Pollutants**

Many different groups of organic compounds were reliably identified in these samples. Long chain aliphatic hydrocarbons were found in all but one sample (AG7025). PAHs (most commonly naphthalene, phenanthrene, and derivatives) were found in four of the five samples (AG7025, AG7026, AG7029 and AG7030). Other aromatic compounds including phenol derivatives (AG7027), steroids (AG7029), naturally occurring terpenoids such as limonene (AG7030) and alkylbenzenes (AG7030), were found in three of the five samples. Dichlorobenzenes were identified in two of the samples (AG7027 and AG7030).

The environmental sources and significance of PAHs, phenol derivatives, alkylbenzenes, aliphatic hydrocarbons, steroids and dichlorobenzenes have been discussed above.

To conclude, all of the samples collected from this section of the Rio Matanza, contained a diverse mixture of organic compounds associated with a wide range of industrial, urban and domestic activities.

#### **Heavy Metals**

Analysis of the water sample (AG7030) found detectable levels of Mn, Zn, Cu and Ni. Of these, Zn appears to be present at concentrations above those usually associated with clean, freshwater systems (Salomons and Forstner 1984, Bryan and Langston 1992). More significant results were obtained from the sediment analysis. Only sample AG7027, collected from a stream running into the Santa Catalina / Arroyo del Rey, contained levels of heavy metals usually associated with uncontaminated sediment. Of the other four, the following observations were made:

- Sample AG7025, collected approximately 200 metres downstream of the confluence with the Camino de Cintura, contained elevated levels of Cr, Zn, Cu, Pb and Hg.
- Sample AG7026, collected prior to the confluence between the Matanza River and the Santa Catalina Stream, contained elevated levels of Cr, Zn, Cu and Pb.
- Sample AG7029, collected from the Rio Matanza rectification, downstream of the Santa Catalina / Arroyo del Rey confluence, contained elevated levels of Zn, Cu, Pb, Cd and Hg.

The environmental significance and toxicological properties of Zn, Cu and Pb have been discussed above, the significance of increased environmental levels of Cr, Hg and Cd, are discussed here.

#### (i) Chromium

Background concentrations of Cr 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.

Elevations above this background range are nearly always due to anthropogenic discharges, with three industrial sectors responsible for the majority of releases: metallurgical, chemical and refractory. In the metallurgical industry Cr is used in the production of stainless steel, alloy cast irons and non-ferrous alloys. In the chemical industry it is used primarily in leather tanning, in the production of pigments, metal finishing and wood treatment. Smaller amounts are used in water treatment, textiles and as catalysts. Based on data obtained from the Argentine Secretary of Natural Resources and Sustainable Development (1997), tannery waste seems to be one of the most likely sources of Cr in the Matanza-Riachuelo Basin.

Cr was present at a level of 337 mg/kg in sample AG7025, with levels ranging from 28 to 79 mg/kg found in the other samples. Examples of published data collected from polluted sites receiving mining, metallurgical, and tannery waste, include UK values ranging from 200 mg/kg to 800 mg/kg, determined in the Loughor Estuary, South Wales, a site of tinplate production (Bryan and Langston 1992); and values ranging from 70 mg/kg to 3000 mg/kg in rivers receiving tannery and electroplating waste in the Guipuzcoa region of Spain (Sola et al. 1991). The level of Cr found in sample AG7025 falls within this range, between 3 and 6 times greater than background concentrations depending on which data set is used for comparison.

Information on the effects of such levels on aquatic biota, fish, deposit feeding and wading birds is limited. How sediment-bound Cr reaches animal and plant tissues is uncertain, although it is recognised that the speciation of Cr determines its bioavailability. Cr (VI) will be accumulated more readily than Cr (III), as it has been shown to cross biological membranes more readily (Bryan and Langston 1992). Whereas Cr (III) is a trace nutrient at low concentrations, Cr (VI) is non-essential and toxic. Its compounds being classified as carcinogenic by the International Agency of Research on Cancer (USPHS 1997). Most of the Cr associated with aquatic sediment will be in the trivalent form, and although not as environmentally mobile as Cr (VI), accumulation and movement up the food chain have been experimentally studied (Aislabie and Loutit 1986, Bremer and Loutit 1986). Accumulation of Cr in cockles, polychaetes and mud snails has been shown to occur following exposure to Cr contaminated sediments. The sediments became contaminated due to tannery waste (trivalent Cr) discharges in Sawyer's Bay, New Zealand (Aislabie and Loutit 1986). Whether the tissue concentrations reported were sufficient to produce deleterious effects is not known.

For fresh water fish and shell fish, 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). Cr 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 (USPHS 1997). An average daily intake of 50-200 ug/day of Cr (III) is recommended for adults (USPHS 1997), Cr (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 Cr (both +3 and +6 forms) will generally not 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 (USPHS 1997).

Dermal exposure to both Cr (III) and Cr (VI) can result in severe redness and swelling of the skin (USPHS 1997). Whereas breathing in high levels of Cr (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 Cr (VI) for several months to many years. Long term occupational exposure to Cr (VI) is believed to be primarily responsible for the increased lung cancer rates (USPHS 1997).

#### (ii) Cadmium

Background levels of Cd in sediments are extremely low, with values less than 0.2 mg/kg, most commonly quoted (Bryan and Langston 1992, Salomons and Forstner 1984, Licheng and Kezhun 1992, Goncalves et al. 1990). Levels of 10 mg/kg have been associated with contaminated sites in the UK (Bryan and Langston 1992), with levels in Spain, i.e. the River Tinto and Odiel basin, cited as ranging from 0.1 mg/kg to 30 mg/kg (Nelson and Lamothe 1993). In Argentina, levels ranging from <0.01 mg/kg to 0.08 mg/kg were found in sediments collected from the Rio de la Plata, Buenos Aires (Verrengia-Guerrero and Kesten 1993).

Levels of Cd found in this section of the Matanza ranged from <1 mg/kg, found in samples AG7026 and AG7027, to 2.0 mg/kg found in sample AG7025. The most often mentioned sources of Cd 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 by human activities such as mining and smelting operations, fuel combustion, disposal of metal-containing products, and application of phosphate fertiliser or sewage sludges (Elinder 1985).

Cd has no biological function, and is highly toxic to both animals and plants. The low concentrations of Cd usually encountered in the environment do not cause acute toxicity, however elevations above background concentrations can have deleterious effects on plant and animal health (Bryan and Langston 1992, Alloway 1990). There is evidence to show that Cd 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). It is known to be one of the more mobile, and hence bioavailable, trace metals (Jensen and Bro-Rasmussen 1990).

High tissue Cd concentrations are often associated with the presence of metallothionein (sulphur-binding) proteins. The induction of these proteins in response to Cd 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. These include observed correlations between increased levels of Cd found in limpets and a reduced ability to utilise glucose (Shore et al. 1975). Reductions in reproduction rates and thus population numbers in copepods and isopods (Giudici and

Guarino 1989). The toxicity of low sediment-Cd concentrations was also suggested by observations showing that in San Francisco Bay, the condition of certain species of clam declined as Cd concentrations rose from 0.1 to 0.4 mg/kg (Luoma et al. 1990).

As mentioned above, Cd has no biochemical or nutritional function. It is highly toxic even at low concentrations, persistent in the environment, and has the potential to bioaccumulate. Along with Hg, Cd is considered to be one of the most toxic metals, and as such much legislation exists to control and monitor Cd discharged to the environment. Examples of European Environmental legislation include directives 75/437/EEC regulating pollution from land based sources; 76/464/EEC Dangerous substance Discharge; and 83/513/EEC on limit values and quality objectives for Cd discharges).

Regarding potential human exposure, food, water and cigarette smoke will be the largest sources of Cd for members of the general population. Eating food or drinking water with very high Cd levels can severely irritate the stomach, leading to vomiting and diarrhoea (USPHS 1997). Eating lower levels of Cd over a long period of time can lead to a build up of Cd in the kidneys. This Cd 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 Cd 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 Cd and Cd compounds may reasonably be anticipated to be carcinogens (USPHS 1997).

### (iii) Mercury

Hg concentrations associated with clean sediments are extremely low, with levels ranging from 0.03 mg/kg to 0.2 mg/kg (Bryan and Langston 1992, Salomons and Forstner 1984, Licheng and Kezhun 1992). Elevated Hg concentrations in freshwater systems, are primarily due to anthropogenic discharges of inorganic Hg. Sediments associated with gold mining sites and chlor-alkali discharges, the two major sources of anthropogenic Hg in the environment, contain levels ranging from 0.6 to over 150 mg/kg (Bryan and Langston 1992, Reuther 1994, Nriagu 1992, Maserti and Ferrara 1991). Levels found in this section of the Matanza contained levels ranging from none detectable (AG7026) to 8.7 mg/kg (AG7025). This level of Hg is anomalously high, between 40 and 300 times higher than background, depending on which data set is used for comparison.

Like Cd, Hg is a non-essential trace metal, having no biochemical or nutritional function. Biological mechanisms for its removal are poor, and thus Hg 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 animal and plants at low concentrations. Therefore any elevation above baseline levels could have a deleterious effect on any exposed biota (USPHS 1997). Similarly, environmental legislation exists in abundance to control and monitor Hg discharges (e.g. 75/437/EEC; 82/176/EEC; 84/156/EEC; 85/613/EEC; 78/319/EEC). Since "Minimata", the implementation of widespread regulations on Hg disposal has greatly reduced the threat of similar incidents. However the retention of Hg by benthic 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 Minimata Bay ten years after discharges ceased (Bryan and Langston 1991, Tsubaki and Irukayama 1977).

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). The most



important factors affecting the toxicity of Hg to aquatic species are the concentration and chemical speciation of the Hg present. Other factors include the developmental stage of the organisms exposed, and physical-chemical parameters of the ecological system, such as pH, temperature, salinity, water hardness, oxygen levels etc.

Although there is evidence which links levels of total Hg in the environment with those in higher predators such as fish, concern centres on methylmercury (MeHg) accumulation. Inorganic mercury can be methylated by micro-organisms indigenous to soils, sediments, fresh water, and salt water, the process being mediated by various microbial populations under both aerobic and anaerobic conditions (USPHS 1997). It is widely acknowledged that organic forms of Hg are even more toxic than inorganic forms.

The most common organic form of mercury is MeHg. It exhibits high lipid solubility, easily crossing cell membranes, and thus quickly enters the aquatic food chain. It also has a high biological half-life, and due to increased longevity of top predators in association with these other properties observed, it provides one of the rare examples of metal biomagnification in food chains. For example, MeHg concentrations in carnivorous fish at the tops of freshwater and salt water food chains (e.g., pike, tuna, and swordfish) are biomagnified on the order of 10,000 to 100,000 times the concentrations found in ambient waters (Callahan et al. 1979, EPA 1980, 1984, USPHS 1997).

Bioaccumulation of methylmercury in aquatic food chains is of interest because it is generally the most important source of non-occupational human exposure to the compound (EPA 1984, USPHS 1997). As mentioned, Hg is a highly toxic, bioaccumulative, and persistent metal. It has no beneficial effects in humans, and there is no known homeostasis 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). Such accumulating organs include the kidneys, liver and central nervous system. Exposure to high enough levels of metallic, inorganic or organic Hg can permanently damage these organs (USPHS 1997).

Thus to conclude, the levels of heavy metals found in these sediments do reflect the fact that untreated industrial and domestic wastes are being discharged to the Rio Matanza.

## **2. Riachuelo**

Thirteen samples were collected along the length of the Riachuelo, as it passed through the districts of Lomas de Zamora, Buenos Aires, Lanus and Avellaneda..

### **a) Lomas de Zamora and Buenos Aires (AG7011, AG7031- AG7032, AG7035, AG7035A)**

Five samples were collected from the Riachuelo as it passed between the districts of Lomas de Zamora and Buenos Aires, four of sediment and one of water. Again, this area of the basin is highly industrialised in parts, and densely urban. This is reflected in the presence of certain groups of organic pollutants, and the levels of heavy metals found.

Again, many groups of organic compounds, associated with sewage and industrial discharges were reliably identified in these samples: dichlorobenzenes, PAHs and derivatives, steroids, terpenoids and terphenyls, alkylbenzenes, and aliphatic hydrocarbons.

Heavy metal analysis found that all five samples of sediment contained elevated levels of Cr, Zn, Cu, Pb, Cd and Hg. Cr levels determined were anomalously high, and in one sample (AG7011), levels over forty times greater than published background concentrations were found (Bryan and Langston 1992, Solomons and Forstner 1984, Licheng and Kezhun 1992, Goncalves et al. 1990). Sample AG7011 was taken close to a urban runoff / storm water discharge pipe, and based on the level of Cr found in the nearby sediment, it is probable that this channel is also being used to carry and discharge tannery waste.

#### **b) Lanus and Buenos Aires (AG7009-AG7010)**

Two samples of river sediment were collected from the Riachuelo as it passed through the districts of Lanus and Buenos Aires. Here the Riachuelo receives wastewaters discharged from the chemical, petrochemical, pharmaceutical, metallurgical, food, beverage, leather, textiles, and paper industries of the area. Domestic sewage and urban runoff are also discharged.

The chemical composition of the sediments collected and analysed from this part of the Riachuelo, reflect the large volumes and diverse chemistry of the industrial and domestic wastes discharged.

Organic screening analysis isolated large numbers of compounds: dichlorobenzenes, monochloroalkanes, PAHs, alkylbenzenes, steroids, long chain aliphatic hydrocarbons, and benzyl alcohols.

Cr, Zn, Cu, Pb, Cd and Hg were all present at concentrations significantly above those associated with unpolluted sediments.

#### **c) Avellaneda and Buenos Aires (AG7006, AG7008, AG7036-AG7039)**

Six samples were collected from this section of the river, one of river water and five of sediment. Again the area is highly industrialised, with chemicals, petrochemicals, pharmaceutical, beverage, food, leather, metal, paper and textiles, all being processed or manufactured.

Thus, as expected, organic screen analysis of the sediments isolated large numbers of compounds: dichlorobenzenes, PAHs, alkylbenzenes, steroids, terpenoids, indenenes, and cyclic and long chain aliphatic hydrocarbons. Whereas heavy metal analysis found high levels of Cr, Zn, Cu, Pb, Cd and Hg. 2380 mg/kg of Cr was determined in sample AG7036, nearly fifty times greater than published background levels (Bryan and Langston 1992, Solomons and Forstner 1984, Licheng and Kezhun 1992, Goncalves et al. 1992). It is highly likely therefore, that this section of the Riachuelo is exposed to large quantities of tannery waste.

The water sample (AG7037) also contained compounds of interest and concern. Two isomers of dichlorobenzene were reliably identified, as were naphthalene, one of its alkyl derivatives and the terpenoid, limonene. Elevated levels of Cr, Zn and Cu were found with Cr again present at environmentally detrimental concentrations. 70 ug/l was determined in this sample, 70 times higher than levels usually found in fresh waters (Bryan and Langston 1992)

To conclude, these samples, along with many of the other collected from the Riachuelo, are amongst the most polluted found. Levels of heavy metals and the presence of a diverse mix of organic pollutants are indicative of significant anthropogenic contamination. Contamination capable of having a direct deleterious effect on the aquatic ecosystems

exposed, as well as having the indirect consequence of effecting terrestrial animal and human health through the consumption of contaminated food, water supplies and recreational waters.

Furthermore once contaminated aquatic sediment poses a particularly pernicious form of pollution, acting as a long-term reservoir that can introduce toxins to the environment far from the original source and long after discharge activity has shut down. Polluted aquatic sediments can cause environmental damage by releasing toxins to surrounding waters, directly contaminating aquatic plants and animals living within and ingesting the sediments, and by introducing toxins into the food chain, which are then transferred up the trophic ladder to higher organisms, including humans (Marcus 1991).

### **Dissolved Oxygen, Hydrogen Sulphide and pH**

The deterioration of water quality in the lower parts of the Rio Matanza and the whole of the Riachuelo was strikingly obvious, with sediments becoming increasingly black and anoxic as more industrial facilities and domestic sewage outfalls were observed. In addition, increased quantities of hydrogen sulphide gas were seen bubbling through the sediments and water, readily detectable due to its characteristic “rotten egg” odour. Its presence is an indication that oxygen levels are low, possibly non-existent, and potentially unable to sustain marine life. Indeed dissolved oxygen was only detectable in the upper part of the Rio Matanza. Beyond sampling point AG7024 (2 mg/l of oxygen), no dissolved oxygen was detected.

There could be several possible sources of hydrogen sulphide. Hydrogen sulphide can be present, and continually produced, in sulphur containing waters under anaerobic (no oxygen) conditions. The discharge of oxygen depleting substances in both sewage (nutrients and biodegradable wastes) and industrial wastes will lead to an increased production of hydrogen sulphide. It is also the product of a bacterial reaction in the presence of sulphate.  $H_2S$  is produced by a variety of bacteria including species of salmonella. The detection of  $H_2S$  in water can be indicative of their presence (Gawthorne et al. 1996). Other sources include industrial effluents, of particular importance are discharges from petrochemical industries and tanneries (Chirila et al. 1994, Sekaran, et al. 1996).

Hydrogen sulphide is poisonous to aerobic organisms (Heller et al. 1995) and it is extremely hazardous to humans (Merck 1989). In high concentrations it plays a major role in accidental deaths in the wastewater treatment and oilfield industries. Collapse, coma, and death from respiratory failure may result in a few seconds, after only one or two inspirations. In sufficiently high concentrations hydrogen sulphide will dull the sense of smell, preventing an unwary worker from detecting its presence. Low concentrations of hydrogen sulphide produce irritation in conjunctiva and mucous membranes. The reaction of hydrogen sulphide with fluids in the nose and lungs forms sulphuric acid.

Finally, a pH range of between 6 and 7 was measured in the upper part of the Rio Matanza (control sampling sites AG7001-AG7002). pH 8, slightly alkaline, was measured in all other river samples further downstream, with the exception of AG7030 (pH 6).

### **Conclusion**

Of the thirty samples collected as part of this study, two thirds contained some degree of heavy metal or organic pollutant contamination. As expected, the highest levels of pollution were associated with the more industrial and residential areas.

As discussed above, many of the heavy metals and organic compounds identified are toxic at very low concentrations and have the potential to bioaccumulate through the food chain. Many of the compounds found are also highly persistent, and therefore even if discharges ceased in the very near future, retention by sediments, soils, animal and human tissues, would delay the elimination of this contamination for many years. Thus the continued discharge of anthropogenic wastes into the basin can only lead to more extensive and environmentally harmful contamination.

It is widely known that discharges of toxic, persistent and bioaccumulative pollutants in the environment are currently being addressed at several international conventions, and that an abundance of environmental legislation exists regarding attainable discharge limits and environmental quality standards. However due to the increasing global burden of persistent organic pollutants and certain heavy metal contaminants, legislation is changing. Most recently, the Fourth International Conference on the North Sea (MINDEC 1995), the 1998 Ministerial Meeting of the OSPAR Commission (Sintra Statement, OSPAR 1998a,b), and the proposed UNEP POPs Treaty (UNEP 1995, 1997), all set out aims to continuously reduce discharges of hazardous substances and indeed to phase out the most hazardous. To achieve this, and to avoid the mere shift of chemicals from one environmental medium to another, pollution prevention, and not control must be the way forward.

For this to apply to the Matanza-Riachuelo Basin, and indeed to all other contaminated Argentine coastal and inland waters-courses, long-term solution based on clean production alternatives, renewable resources and minimal waste generation need to be employed. In the shorter term clean-up of the basin is essential, and industry, along with the bodies accountable for sewage treatment and water quality, must take full financial and legal responsibility for whatever this may entail.

Clean up of the Matanza-Riachuelo basin will not happen over night, however ultimately, the industries themselves, the processes they employ and the products they generate need to be assessed. In addition to this, secondary, if not tertiary, sewage treatment must be implemented, and domestic and industrial wastes must not be conveniently mixed and discharged through the same channels. 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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