



## Organic pollutants and heavy metals found in sediments and water samples associated with the petrochemical complex in La Plata district, Argentina, 2000

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## **1 INTRODUCTION**

YPF oil distillery is located between two residential districts Ensenada and Berisso of the La Plata, Argentina. Companies PETROKEN (polypropylene) and IPAKO (polyethylene) are also operating on this site. Wastewaters from all companies are discharged into two large channels (East Channel and West Channel). West and East channels are linked together on the south surrounding petrochemical complex and each channel discharges into the Rio Santiago on the north from the complex. Rio Santiago itself discharges into the Rio de la Plata. Flow direction in the channels is changing depending upon tidal regime. Greenpeace previously visited this site in 1998 when samples of sediments and water from both channels were collected. Analysis of these samples showed widespread contamination by a range of organic pollutants and heavy metals. Details of this survey and toxicological profiles for key compounds are given in the following report:

Stephenson, A. & Labunska, I. (1998) Identification of organic pollutants and heavy metal contamination in samples collected from a petrochemical complex located in the district of La Plata, Argentina, 1998. Greenpeace Research Laboratories Technical Note 17/98, December 1998: 13 pp.

## **2 SAMPLING PROGRAM**

In June 2000, Greenpeace re-visited this site and collected six samples around YPF petrochemical complex. The samples included three sediments and three water samples from the West and East Channels surrounding complex.

### **2.1 General Sampling Procedures**

All samples were collected and stored in pre-cleaned glass bottles that had been rinsed thoroughly with nitric acid and analytical grade pentane in order to remove all heavy metals and organic residues. Sediment and solid waste samples were collected in 100ml bottles, and the water samples were collected in 1-litre bottles. All sediment, solid waste and water samples were immediately sealed and cooled upon collection. The samples were returned to the Greenpeace Research Laboratories for analysis.

### **2.2 Sample Descriptions**

Descriptions of the samples are presented in Table 1. In most cases the locations of the sampling points during sampling tour in 2000 were the same as in previous study in 1998. The only exclusion was for the samples AM0015 and AM0016, which were collected about 0.5km further to the south than the samples LA8046 and LA8057.



Sample Code 2000	Sample Code 1998	Sample Type	Sample Description
<b>West Channel</b>			
AM0015	LA8046*	Sediment	Collected from the WEST channel, 300 metres upstream of the Rio Santiago
AM0016	LA8047*	Channel water	Collected from the WEST channel, 300 metres upstream of the Rio Santiago
AM0017	LA8051	Sediment	Collected from the WEST channel, within the petrochemical complex, downstream of PETROKEN and IPAKO, opposite YPF.
AM0018	LA8050	Channel water	Collected from the WEST channel, within the petrochemical complex, downstream of PETROKEN and IPAKO, opposite YPF.
<b>East Channel</b>			
AM0019	LA8049	Sediment	Collected from the EAST channel, within the petrochemical complex
AM0020	LA8048	Channel water	Collected from the EAST channel, within the petrochemical complex

*Table 1. Description of samples collected in June 2000 and in May 1998. \* - Samples from 1998 which were collected about 0.5km further to the south than corresponding samples collected in 2000.*

### 3 RESULTS AND DISCUSSION

The results of the organic screen analysis and heavy metals analysis of the sediment and water samples are presented in Table 2, including a breakdown of the groups of organic compounds reliably identified in the samples.

Large amount of organic compounds has been isolated from all three sediment samples: AM0015 and AM0017 from West channel and AM0019 from East channel. The majority of organic compounds reliably identified in these samples were represented by polycyclic aromatic hydrocarbons (PAHs) including naphthalene, anthracene, phenanthrene, pyrene, fluorene, benz[a]anthracene, chrysene, benz[a]pyrene and also alkylated derivatives of those PAHs. PAHs are group of compounds present in the oil (Overton 1994). Once PAHs are released into the aquatic environment, degradation by micro-organisms is often slow, leading to their accumulation in exposed sediments, soils, aquatic and terrestrial plants, fish and invertebrates (ATSDR 1997). Aliphatic hydrocarbons, alkylated benzenes, dibenzothiophenes and biphenyl, which were additionally detected in these sediment samples, are also indicative compounds for oil contamination.

Similar organic compounds, but less number of them, were also detected in the previous study (Stephenson & Labunska 1998), except of sediment sample LA8049 collected from the East channel where no organic compounds have been reliably identified. It might



Sample number	AM0015	AM0016	AM0017	AM0018	AM0019	AM0020
Sample Type	Sediment	Channel water	Sediment	Channel water	Sediment	Channel water
Sample description	West channel North from YPF	West channel North from YPF	West channel inside the complex	West channel inside the complex	East channel inside the complex	East channel inside the complex
<b>Metals</b>	mg/kg dw	ug/L	mg/kg dw	ug/L	mg/kg dw	ug/L
Cadmium (Cd)	<2	<20	<2	<20	<2	<20
Chromium (Cr)	61	<20	32	<20	26	<20
Cobalt (Co)	115	<20	90	<20	7	<20
Copper (Cu)	92	<20	97	<20	143	<20
Lead (Pb)	38	<30	54	33	236	<30
Manganese (Mn)	548	89	514	733	389	<10
Mercury (Hg)	0.69	<1	1.45	4.3	1.91	<1
Nickel (Ni)	39	<20	51	<20	18	<20
Zinc (Zn)	309	<10	254	<10	626	<10
No. of organic compounds isolated	127	13	102	42	161	6
No. of organic compounds reliably identified	41(32%)	1(8%)	20(20%)	24(57%)	27(17%)	3(50%)
<b>ORGANOHALOGEN COMPOUNDS</b>						
.beta.-HCH						*
Benzene, 1,4-dichloro-		*				*
<b>PAHs</b>						
Naphthalene and/or its derivatives	✓ (11)		✓ (6)	✓ (2)	✓ (9)	
Anthracene and/or its derivatives	✓ (2)		✓ (3)		✓ (3)	
Phenanthrene and/or its derivatives	✓ (6)		✓ (4)		✓ (5)	
Pyrene and/or its derivatives	✓ (3)			✓		
9H-Fluorene and/or its derivatives	✓		✓		✓	
Benz[a]anthracene and/or its derivatives	✓ (3)					
Benz[a]pyrene and/or its derivatives	✓					
Chrysene and/or its derivatives	✓					
<b>ORGANOSULPHUR COMPOUNDS</b>						
Dibenzothiophene derivatives	✓					
Benzene, (methylthio)-				✓		
Toluene, (methylthio)-				✓ (2)		
<b>PHENOLIC COMPOUNDS</b>						
BHT						✓
<b>OTHER AROMATIC COMPOUNDS</b>						
Alkylated benzenes	✓ (2)			✓ (5)	✓	
Indene and/or its derivatives	✓ (2)		✓		✓ (2)	
Biphenyl and/or its derivatives	✓					
<b>ALIPHATIC HYDROCARBONS</b>						
Linear	✓ (4)		✓ (5)	✓ (13)	✓ (5)	
Cyclic	✓ (3)				✓ (2)	

Table 2. Organic chemicals and heavy metals identified in samples associated with the YPF petrochemical complex, La Plata, Argentina, 2000. For the groups of organic compounds reliably; ✓ (#) signifies compounds identified using general GC/MS screening method, with the number of compound given in parentheses for groups with more than one compound; \* signifies compounds detected only at trace levels using a selective ion monitoring (SIM) method. Metal concentrations are given in mg/kg dry weight for solid samples and ug/l for liquid samples.



indicate either contamination input from the West channel as these two channels are connected, or direct discharge from the companies of the petrochemical complex.

Levels of heavy metals found in the sediment samples AM0015, AM0017 and AM0019 were generally similar to the corresponding samples LA8046, LA8051 and LA8049 collected in 1998. In the sample AM0015 the levels of zinc, mercury and copper were lightly elevated in comparison with the background levels found in clean sediments, in sample AM0017 levels of zinc and mercury were elevated, and in sample AM0019 copper, lead, mercury and zinc were also above background levels. The only significant difference in the results of both studies was the levels of mercury, which were about 5 times less in the sediment samples from the West Channel AM0015 and AM0017 (current study) than in the samples LA8046 and LA8051 (previous study).

Not many organic compounds have been isolated from the channel water samples AM0016, AM0018 (West channel) and AM0020 (East channel) in comparison to the sediment samples. It might be due to a limited solubility of the oil components in the water. However, water sample AM0018 from the West channel contained PAHs (naphthalene and pyrene derivatives), organosulphur compounds (methylthiobenzene and methylthiotoluene), alkylated benzenes and aliphatic hydrocarbons. All of these compounds are components of oil. Additionally, two organochlorine compounds were detected at trace levels only: 1,4-dichlorobenzene (samples AM0016 and AM0020) and beta isomer of hexachlorocyclohexane (sample AM0020).

1,4-dichlorobenzene is very common environmental pollutant mainly due to its use in room deodorants and sanitary deodorant blocks (ATSDR 1997). 1,4-dichlorobenzene is a highly volatile substance that sublimates at room temperature and most of its environmental releases are to the atmosphere. However, this compound may be sorbed to the soil or sediment and adsorption to soil particles may inhibit volatilization by an order of magnitude compared to volatilization from water (ATSDR 1997). Therefore, it is unclear what application caused the presence of 1,4-dichlorobenzene in the samples AM0016 and AM0020 because West and East channels are open and there is a possibility of the 1,4-dichlorobenzene being air transported with soil particles from other locations.

The presence of trace amounts of beta-HCH at this location might be due to the use of technical HCH as an insecticide in the past since HCH may persist for many years in the environment (Martijn *et al* 1993) and beta-isomer is the most persistent among other isomers (ATSDR 1997).

Levels of heavy metals that were determined in the water samples AM0016, AM0018 and AM0020 were generally low. However, concentration of manganese found in the sample AM0018 (West channel) was about 11 times of background concentration for freshwaters (Bowen, 1966) and about 3 times higher than previously detected in the sample LA8050 collected in 1998. Mercury was also detected in the sample AM0018 at levels significantly higher than published background levels (ATSDR 1997), however



these background levels are very low (<0.005ppb). Mercury wasn't detected in any water samples in the previous study.

#### **4 CONCLUSIONS**

The study of water samples and corresponding sediments from the West and East Channels surrounding YPF petrochemical complex showed that the area is still contaminated by the petroleum products. Several heavy metals (copper, lead, mercury and zinc) have been detected in the sediment samples above background levels. Manganese and mercury levels that were found in the water sample AM0018 from the West Channel were much higher than the background levels for the freshwaters.

#### **5 REFERENCES**

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