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Pollution Studies in the Río Santiago Basin, Tributary of the Río de la Plata Estuary: Preliminary Risk Assessment Evaluation

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Recent developments in the field of ecotoxicological effects assessment of pollutants on aquatic systems make use of methods founded on statistical principles and requirements (Kooijman 1987; Van Straalen & Denneman 1989). Van Straalen and Kooijman methods estimate a hazardous concentration for p percent of species in a community (HCp) at a chosen protection level. Evaluations on the application of the methodology to different toxic compounds and test species using both chronic and acute toxicity data have been undertaken (Van Leeuwen 1990).

The application of the Van Straalen method to estimate the percentage of species protected at the concentration levels of several contaminants present in the Río Santiago was performed as an initial stage in the hazard assessment of the region. The area is characterized by contamination from a large petrochemical and oil refinery complex, a steel rolling mill and shipyards (Colombo et al. 1990; Catoggio 1991; Ronco et al. 1992; Porta & Ronco, 1992). The calculation of the effect of four polycyclic aromatic hydrocarbons (PAH) (Pyrene, Fluoranthene, Anthracene, Naphthalene) and phenol found in the water body was done mainly using acute toxicity data available in the literature. The assessment was performed at the condition of maximum stress by using the highest concentration level of each contaminant (Catoggio 1991; Ronco et al. 1992). Standardized acute toxicity tests with two small invertebrates and a higher plant seed were performed in a water sample. This sample was also chemically characterized. Results from the calculated assessment based on existent toxicity data for pure compounds are being compared to those from laboratory bioassays on an environmental sample.

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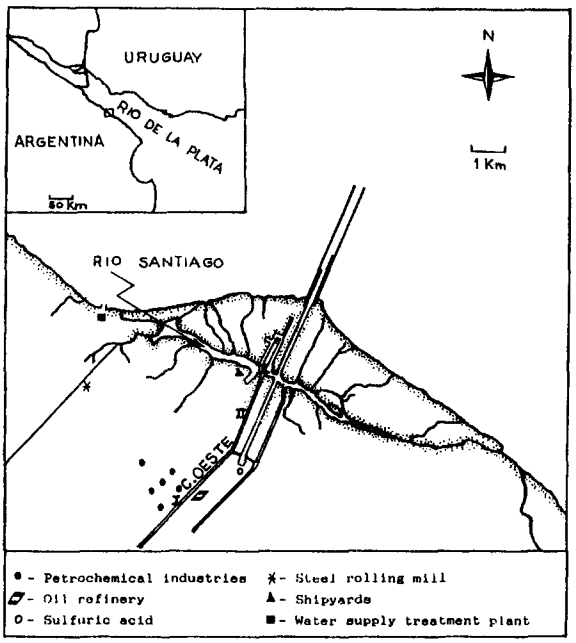

Figure 1. Study area location.

MATERIALS AND METHODS

Acute toxicity data (effective dose concentrations for a 50% reduction of a given end point) for different species were chosen from available reported data (Table 1). Species were selected taking at least 3 different organization levels of aquatic organisms.

Acute toxicity tests were carried with *Daphnia obtusa* Kurz, 1874, emend Scourfield, 1942; *Artemia salina* (Artoxkit M) and *Lactuca sativa* L. A 24h EC50 (inhibition of the mobility) with *D.obtusa* was performed according to the ISO (1989) protocol. The standardized and inter calibrated test with *A.salina*, Artoxkit M, was performed according to Vanhaecke & Persoone (1984) measuring immobility as endpoint after 48 hours of exposure (LC50). A modified lettuce seed germination test (EPA 1989) was used measuring radicle protrusion. Effect on germination was expressed as 120 h EC50. All the tests were performed with three replications and six sample dilutions. LC50 calculations were done by a log-probit curve regression and correlation computer program.

The determination of the PAH content prior solvent extraction followed by a clean up procedure in a Florisil column (Lee et al. 1982) was done by HPLC using a Beckman-Altex, model 100A, with a 4.6x250 mm

Table 1. Acute toxicity data from literature. (A) Algae, (Am) Amphibian, (An) Annelid, (B) Bacterium, (C) Crustacean, (F) Fish, (I) Insect, (P) Protozoan.

COMPOUND	TEST SPECIES	EC50 mg/l	
Anthracene	*Paramecium caudatum* (P)	0.0001	(1)
	Rana pipiens (Am)	0.025	(1)
	Musca sp. (I)	0.027	(1)
	Lepomis macrochirus (F)	0.012	(1)
Fluoranthene	*Skeletonema costatum* (A)	45	(1)
	Selenastrum capricornutum (A)	54	(1)
	Mysidopsis bahia (C)	0.4	(2)
	Neanthes arenaceodentata (An)	0.5	(1)
	Lepomis macrochirus (F)	0.4	(1)
Naphthalene	*Callinectes sapidus* (C)	2.3	(3)
	Panaeus aztecus (C)	2.5	(3)
	Cyprinodum variegatus (F)	2.4	(3)
	Pimephales promelas (F)	7.8	(4)
	Neantes arenaceodentata (An)	3.8	(3)
Pyrene	*Daphnia magna* (C)	0.0057	(1)
	Gambusia affinis (C)	0.0026	(1)
	Aedes aegypti (I)	0.035	(1)
	Pimephales promelas (F)	0.026	(1)
Phenol	*Photobacterium phosphoreum* (B)	23.5	(5)
	Spirillum volutans (B)	300	(6)
	Daphnia magna (C)	5.5	(7)
	Jordanella floridae (F)	5.1	(8)
	Lepomis macrochirus (F)	24.0	(4)

(1) Costamagna et al. 1990; (2) Suter & Rosen 1988; (3) IRPTC 1987; (4) Vitozzi & De Angelis 1991; (5) Indorato et al. 1984; (6) Dutka & Kwan 1984; (7) Obtained by the authors; (8) Holdway et al. 1991.

Supelco column containing Ultrasphere (5μm), with a Hitachi Vis-UV spectrophotometer as detector and a Hewlett Packard HP 3396A combined computing integrator and plotter.

A direct photometric method (APHA 1985) was used for determination of steam-distillable phenolic compounds, measuring absorbance at 500 nm in the presence of 4-aminoantipyrine and potassium ferricyanide.

The Van Straalen method (Van Straalen & Denneman 1989) was used to estimate the risk associated with the concentration level of each contaminant in the

Table 2. Percentage of species protected as calculated with the Van Straalen and Denneman extrapolation procedure at maximum concentration of toxicants in (I) EFFLUENT DUMPING SITE in CANAL OESTE (sampling campaign 1987-89); (II)down stream in the CANAL OESTE (sampling campaign 1987-89) and, in the RIO SANTIAGO (sampling campaign 1985-86) using acute toxicity from literature.

COMPOUND	CONCENTRATION mg/l			$\overline{EC}50$ mg/l	T	HC5 mg/l	% SPECIES PROTECTED		
	I	II	III				I	II	III
Antrhracene	0.08	0.018	0.007	0.0053	2240	$2.4x10^{-6}$	26.2	47.4	47.4
Fluoranthene	1.1	0.024	0.13	2.9	1230	0.0023	59.8	87.9	78.2
Naphtalene	0.07	0.22	0.01	3.3	4	0.81	100	100	100
Pyrene	0.3	0.6	0.02	0.011	35	$3.0x10^{-4}$	6.0	32.6	37.5
Phenol	53	15	40	21.8	91	0.24	35.8	55.9	40.1

Table 3. Percentage of species protected as calculated with the Van Straalen and Denneman extrapolation procedure at the concentration levels of the toxicants in Canal Oeste (II sampling point, April 1992).

COMPOUND	CONCENTRATION mg/l	% SPECIES PROTECTED
Anthracene	0.018	38.6
Fluoranthene	0.01	91.2
Naphthalene	0.2	99.7
Pyrene	0.66	3.2
Phenol	15	55.9

locations indicated in Figure 1. Calculations included the percentage of species protected at the different contaminant concentrations in the environment. The fraction of water life not protected by the HCp was arbitrarily chosen at 0.05 (HC5) as recommended by Van Leeuwen (1990). Four or five test species per toxicant were used in this calculations. Similar calculations were done using experimental results from acute toxicity determinations to a whole water sample.

RESULTS AND DISCUSSION.

The estimation of the risk associated with the concentration levels of anthracene, fluoranthene, naphthalene, pyrene and phenol in the industries dumping sites and down stream the Canal Oeste and the run off to the Río Santiago basin shows a high impact on the aquatic life of this water bodies. Although chronic test data is recommended for the Van Straalen and Denneman extrapolation procedure, the scope of this work only limits to the initial stage in the regional hazard assessment. Risks related to industrial spills in the area evaluated with acute toxicity data can be a helpful tool complementary with the water quality parameters characterization.

Table 2 shows the calculated percentage of species protected for the maximum concentration levels of the contaminants in the three different locations seen in figure 1. T is an application factor which is already included in the calculation of the HC_5.

Even though the very low solubility of PAHs, their

content in the water compartment in the study area associated with the suspended matter, added to the soluble fraction, can reach levels over this limit. Percentages of species protected could be as low as 6% in the industrial dumping sites, partly recovering down stream to 32% in the Canal and 37 % in Río Santiago. This is only considering the effects of single contaminants.

The results of the acute toxicity to three species in laboratory assays to whole water from the II sampling point show LC/EC50 values (expressed as % v/v) of 12.7 to *D.obtusa*, 40.0 to *A.salina* and 56,0 to *L.sativa*. Using these experimental LC/EC50 values in the Van Straalen and Denneman extrapolation procedure to calculate the hazard concentration, it is found that only dilutions of this water of 2.7% or larger would protect 95% of the species (HC5=2.7%; T=11.3). Making the inverse calculation for zero dilution (100% sample water) 19.1 % of the species will be protected.

The estimated percentages of species protected at the concentration levels of anthracene, fluoranthene, naphthalene, pyrene and phenol in the same water sample (Table 3) reach a minimum of 3.2% for a level of pyrene of 0.66 ppm.

Although the estimated percentage of species protected with experimental results is larger than the minimum value obtained from Table 2, this could be due to interactions between the toxicants and other components present in the water as for example dissolved and particulate matter.

These results support field observations in the area. Biota are almost absent within the course of the Canal Oeste and in the sector of Río Santiago where this canal flows into.

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