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Behavior and Fate of Chloronitrobenzenes in a Fluvial Environment

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Studies about the environmental persistence of dangerous chemicals are often very important to evaluate both their toxic actions and bioaccumulation. Several works have been carried out on the occurence in surface waters of widespread pollutants such as PCBs, PAHs, some herbicides and insecticides. On the other hand, not much attention has been given to many industrial contaminants released into the environment from specifical industrial processes (production of polymers, pharmaceutical, etc.): because of their punctual source, these compounds, such as chloronitroderivatives (Steinwandter 1987; Rivera et al. 1986), are usually present only in restricted areas. The purpose of this study was to determine concentrations and evolution of chloronitrobenzenes (starting materials for the production of chloroanilines, nitroanilines and nitrophenols, intermediates used to manufacture dyes, pharmaceuticals, rubber chemicals, corrosion inhibitors) in a fluvial environment; the work was carried out on the Bormida River (Piedmont, North-Western Italy).

MATERIALS AND METHODS

The chloronitrobenzenes (o,m and p) determination was performed by a liquid-liquid extraction followed by a gas chromatographic analysis.

Extraction - 1 liter samples were extracted using 10 ml of cyclohexane containing 40 µg/L of 1,2,3,5 -tetrachlorobenzene as internal standard; the extracts were dried with anhydrous Sodium Sulphate and then analyzed by gas chromatography using an electron capture detector. Recoveries, measured by adding known amounts of the three isomers to not contaminated fluvial water, varied between 85 and 90%.

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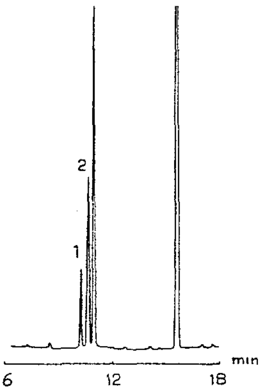

Figure 1. Chromatogram of an extract of contaminated river water: (1) m-chloronitrobenzene, (2) p-chloronitrobenzene, (3) o-chloronitrobenzene and (4) 1,2,3,5-tetrachlorobenzene (internal standard)

Gas chromatographic analysis - The gas chromatographic determination was developed using the following conditions: Hewlett Packard Gas chromatograph Mod.5880 equipped with a 63Ni electron capture detector; Column J&W DB 5, l=30 m, i.d.=0.25 mm, f.t.=0.25 micron, P=10 psi; Oven Temperature: 120^C for 18 min + post run to 200^C for 5 minutes. Injector Temperature: 250^C; ECD Temperature: 300^C; split=10 ml; injected volume: 5µL. The system calibration was obtained by injecting a solution containing the following compounds: 2-chloronitrobenzene 6.4 µg/L, 3-chloronitrobenzene 9.7 µg/L, 4-chloronitrobenzene 6.4 µg/L, 1,2,3,5-tetrachlorobenzene 10.2 µg/L in hexane.

A gas chromatogram yielded by a real sample is represented in Fig.1: following the described method, all the considered pollutants were easily detectable until 2 ng/L level.

RESULTS AND DISCUSSION

The map in Fig.2 shows the five sampling stations on the Bormida River; samples were collected 12 times between September 1989 and February 1990 at each site.

The average concentrations of o-,m- and p-isomer in water are shown in Table 1 as well as the maximum and

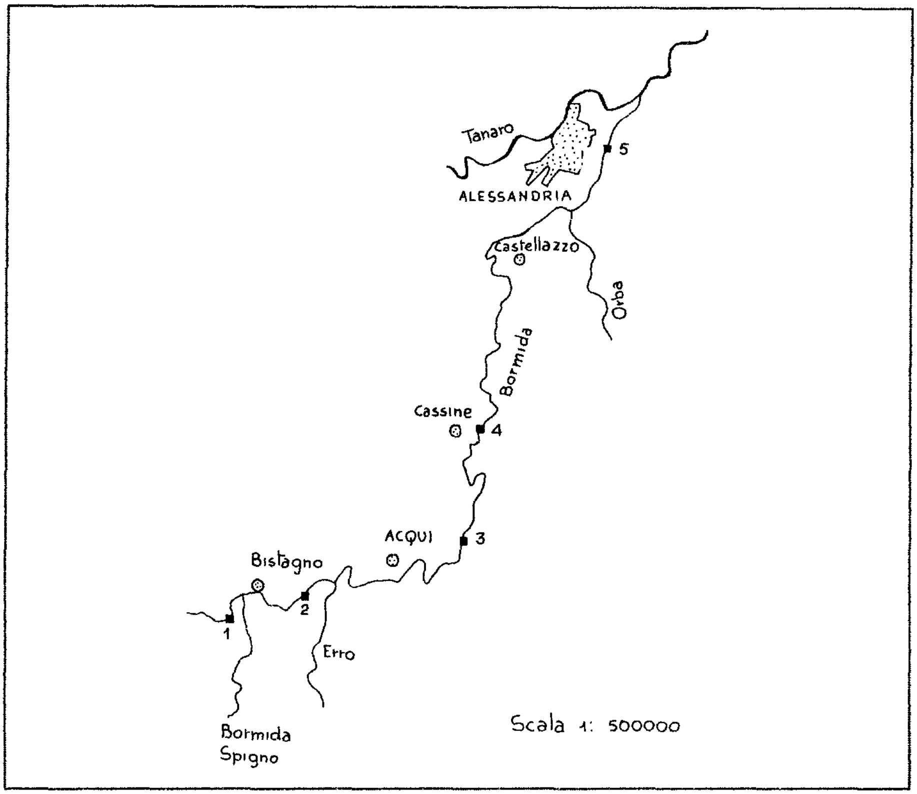

Figure 2. Study area and samplig sites (Alessandria District, Piedmont, North - Western Italy)

Table 1 - Chloronitrobenzenes levels in the Bormida River (µg/L), September 1989 - February 1990

Samplig Site	N		o-	m-	p-
Bistagno	1	min	0.10	0.05	0.02
		max	0.84	0.19	0.37
		ave	0.48	0.12	0.19
Terzo	2	min	0.06	0.008	0.02
		max	0.27	0.054	0.17
		ave	0.25	0.030	0.07
Strevi	3	min	0.08	0.02	0.02
		max	0.19	0.04	0.09
		ave	0.14	0.03	0.06
Cassine	4	min	0.09	0.02	0.04
		max	0.35	0.06	0.10
		ave	0.17	0.04	0.07
Alessandria	5	min	0.02	0.002	0.002
		max	0.17	0.02	0.05
		ave	0.03	0.01	0.01

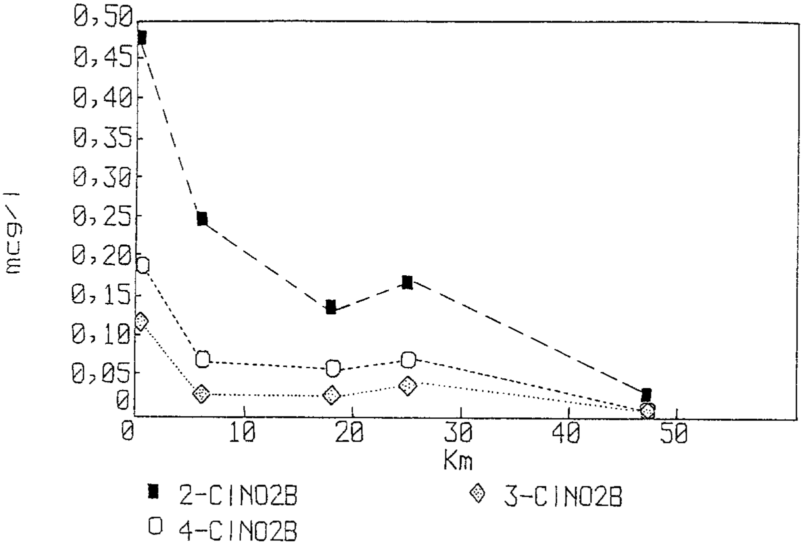

Figure 3. Horizontal profiles of the concentrations of chloronitrobenzenes in the Bormida River.

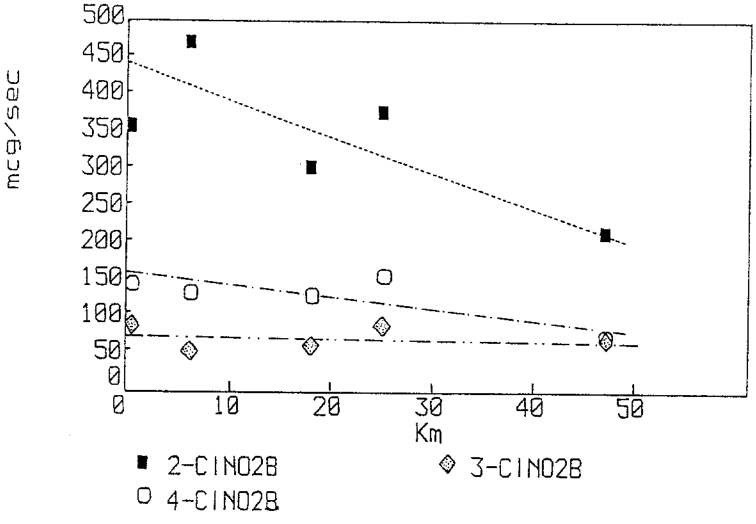

Figure 4. Absolute amounts of chloronitrobenzenes carried by the Bormida River at each sampling site.

the minimun level detected in the river.
The same average concentrations of chloronitrobenzenes are represented in Fig.3 versus the kilometric distance from the first sampling site, localized just above the

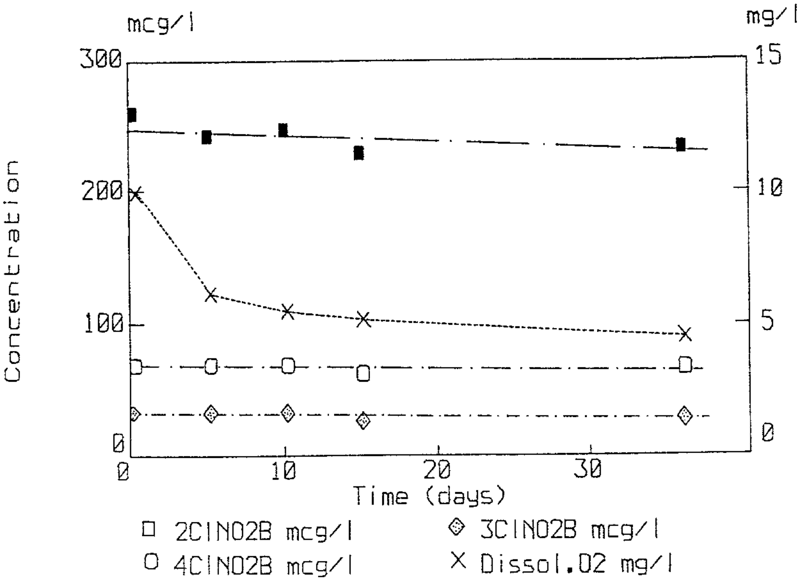

Figure 5. Variations of dissolved oxygen and chloronitrobenzenes concentrations versus incubation time (storage at 20^C in the dark).

confluence with the Spigno River, near the southern Alessandria District border.
The concentrations clearly fall as the river flows toward its estuary: however the knowledge of the biodegradation of the considered pollutants limited to these data is not satisfying by the fact that three important rivers (Spigno, Erro and Orba) add their waters to Bormida, making an important dilution of the contaminants (chloronitrobenzenes were never detected in the tributaries of the main river).
Therefore a complete study of the system can only be obtained taking into consideration the flows of the Bormida River observed at each sampling site during the autumn 1989 and the winter 1990; the average data were easily available since measurements were taken monthly by the Regional Environmental Department (Assessorato Regionale all'Ambiente) and by the Hydrodata Society (Torino, Italy).

In Fig.4 the absolute amounts of chloronitrobenzenes carried by the river (as µg/s), calculated from average flows and concentrations, are reported versus the kilometric distance from the first sampling site: the total quantity of m- and p-isomers appears about constant while the o-isomer presents a slow disappearance: only at the last station, after 50 km flowing, its absolute amount is reduced to about 50% of the initial average value.

The resistance of these compounds to biodegradation was pointed out measuring variations of dissolved oxygen and chloronitrobenzenes concentrations in 5 real samples, simultaneously collected at the site N.1 and stored at 20^C in the dark (to avoid photosyntesis interference): while the mean values for O2 clearly failed during the incubation because of microorganisms activity, the presence of the three aromatic derivatives did not show any appreciable variation (see Fig. 5).

Finally, the present results indicate that chloronitrobenzenes are quite environmental resistant compounds: however further studies are necessary to elucidate slow disappearance of o-isomer from the Bormida River water since its behaviour may be due to adsorption on particulate matter and sediments rather than biodegradation that was not observed in the described laboratory test.

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