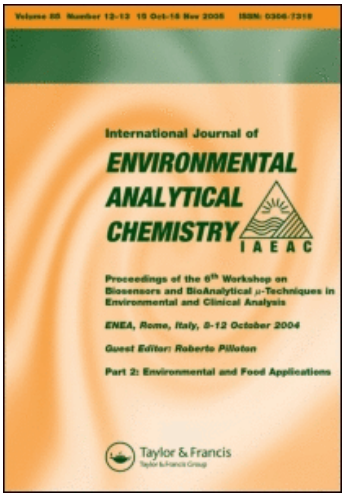

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Fate of Atrazine and Trifluralin from an Industrial Waste Dumping at the Llobregat River. Presence in Fish, Raw and Finished Water†

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Analysis carried out after fish mortality in an industrial area in the neighbourhood of the Llobregat River, water supplier for Barcelona and its area, led us to identify two herbicides (atrazine and trifluralin) in the wastewaters from an industrial sewage where, among other factories one at least, is devoted to pesticide manufacturing. The fate of these herbicides is followed in fish (dorsal muscle), raw water entering the water works plant and tap water. Analyses by GC, GC/MS/DS and mass fragmentography were routinely employed.

KEY WORDS: Organic micropollutants, atrazine, trifluralin, fish.

INTRODUCTION

The growing awareness of water pollution by a wide range of anthropogenic compounds has led to the development of several

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programs in order to devise rational procedures to permit early detection of potential dangerous compounds. The priority pollutants list issued by EPA and EEC[1,2] includes a large variety of organic compounds suspected of potential risk to public health, although this approach generally may ignore other organic compounds occasionally present due to an accidental discharge. A monitoring of organic pollutants in river water is limited in most cases to analyze chronic pollutants or other pollutants well known for their worldwide production. The analytical results and many strategies to survey organic micropollutants in tap and drinking water have been the subject of many reports.[3,4,5] Llobregat river supplies water, used as drinking water, to Barcelona (N.E. of Spain) and its area. The river system (156 km) received discharges from a wide range of industries (salt works, textile, leather, galvanic...). The water works plant is located 7 km far from the mouth of the river and receives all these discharges. The monitoring of organic pollutants in Llobregat river includes at first stage identification of the chronic pollutants and their source. The continuous monitoring carried out led us to identify more than 100 compounds commonly described in the literature.

In this context, the present work describes the fate of two herbicides—atrazine and trifluralin—first identified 40 km upstream of the water works, in a dumping of an industrial area related with pesticide and surfactants' manufacturing; in dorsal muscle of dead fish, and finally in raw water entering the water works plant and tap water.

Analyses have been limited to compounds which are amenable to gas chromatography. GC/MS has been routinely employed.

EXPERIMENTAL

Sampling

Discharge water sampler of a common pipeline of waste dumping of industrial area (see Figure 1) were collected with a Struerst automatic samples at a rate of 10 ml/min during a 34 hour period.

Organic compounds from Llobregat river raw water entering to the water works plant (30 km downstream) and finished water were collected by passing 2000 liters of water through a column of

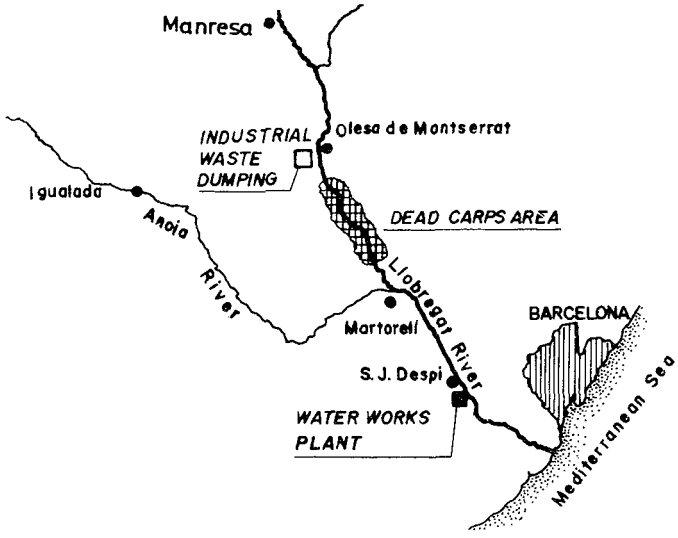

FIGURE 1 Map illustrating location of sampling sites.

granular activated carbon (115 g) Pittsbourg F-200, the same type as used in the water works plant. These samples were the average of one month of sampling.

The dead carps (*cyprinus carpio*) were collected in the area near the waste dumping (2 km downstream).

Extraction procedure

Samples obtained from wastewaters of the industrial area were fractionated in acidic and base + neutral fractions according to EPA method 625.[6] Llobregat river raw water and finished water organic extracts were disadsorbed from granular activated carbon with dichloromethane by soxhlet extraction (48 h). The total extract was concentrated to ca. 2 ml with a rotary evaporator (Büchi, Switzerland), followed by evaporation using a gentle stream of nitrogen. The residue was redissolved with diethylether and fractionated in acids and bases + neutrals. The acidic fractions were analyzed as methylesters via derivatization with BF_3/MeOH. The bases + neutrals fractions contained high amounts of elemental sulphur that was

removed by passing the extract through a minicolumn of activated copper.

Liver and dorsal muscle of carps were analyzed according to the method of Hladka and Kovac.[7] The sample is homogenized in a mixer, dehydrated and extracted with a mixture of benzene/methanol (2:1). The extract is cleaned by passing through a column of silica gel, eluted with benzene/methanol and evaporated. The residue redissolved in petroleum ether and partitioned with acetonitrile. The acetonitrile layer is diluted with water and extracted with chloroform. The extract is evaporated to an appropriate volume for GC/MS analysis.

Analytical instrumentation

Gas chromatographic analyses were carried out on Konik-2000 equipped with ^{63}Ni electron capture detector (Tracor 560) and flame ionization detector respectively, DB-5 and DB-1 fused silica capillary columns (S.G.E. Australia) were employed. Hydrogen was the carrier gas with a back pressure of a 1.0 bar. Temperature program was from 70°C to 300°C (10 min) at 6°C/min. Splitless injections were carried out for 45 sec. Organic compounds were identified by mass spectral matching techniques from the GC/MS data. A MS-9 VG updated mass spectrometer with a VG 11/250 data system was used for mass spectrometric measurements. GC/MS analyses were carried out with a DB-1 fused silica capillary column coupled directly to the ion source. Helium was the carrier gas with a back pressure of 0.8 bar. Temperature program was from 70°C (3 min) to 275°C (25 min) at 2°C/min. For the EI mode, the conditions were as follows: ionization energy 70 eV, mass range 40–500, scan time 4 sec and 1000 of resolving power.

RESULTS AND DISCUSSIONS

The main identified compounds in the waste dumping of the industrial area (Figure 1) are: 2-chloro-N-ethyl-N′-(1-methylethyl)-1,3,5-triazine-2,4-diamine (atrazine), 2,6-dinitro-N,N-dipropyl-4-trifluromethylaniline (trifluralin), long chain alcohols (C-10, C-12, and C-14), dodecylbenzenes, nonylphenols and nonylphenolmono-

ethoxylates (see Figure 2). These products are related with surfactants' industry while atrazine and trifluralin are herbicides. Atrazine is one of the *s*-triazine group of herbicides which are currently being used world-wide and their environmental presence and toxicological effects are well documented in the literature.[8,9]

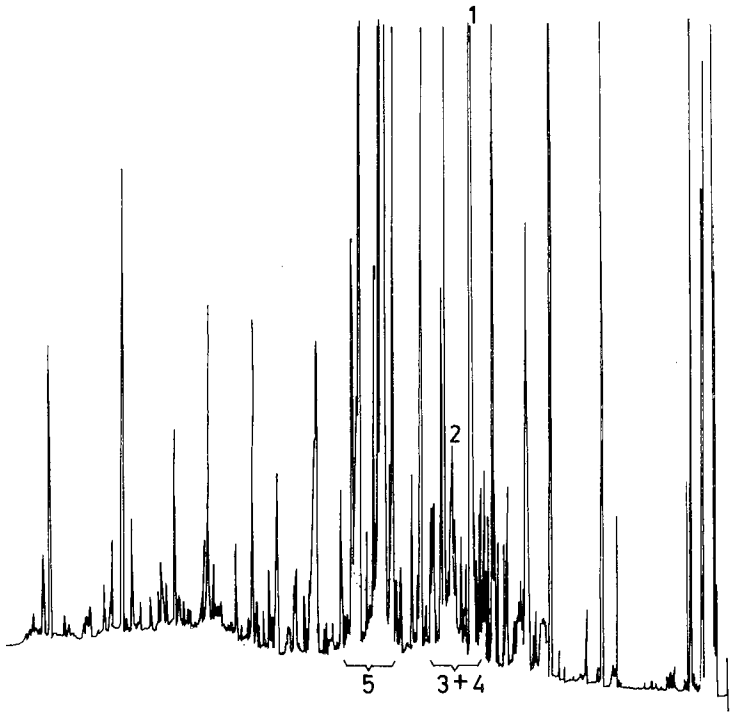

FIGURE 2 Gas chromatogram of a wastewater extract of industrial area. 1 Trifluralin, 2 atrazine and isomers, 3+4 dodecylbenzenes and nonylphenols, 5 nonylphenols monoethoxylates. Conditions of analysis are described in the text.

Quantitative results of atrazine and trifluralin showed relatively high contents (4 ppm and 2 ppm, average for 34 hour period). These data were based on GC peak areas measured from chromatograms of the extracts before any cleanup procedures were applied. Recoveries of atrazine and trifluralin were calculated in distilled water with 75 and 99% respectively ($n=3$, relative standard deviation 5.4 and

3.8%). Other errors in quantitation might result from GC resolution due to high background interferences (Figure 2).

Qualitative analyses of liver and dorsal muscle of dead carps led us to identify trifluralin as well as nonylphenols and nonylphenol monoethoxylates in the dorsal muscle. Trifluralin has been identified by mass fragmentography of its more relevant peaks (m/z 264 and 306) (see Figure 3). Neither atrazine (m/z 200 and 215), nor hydroxyatrazine or their metabolites[10,11] have been identified in liver and dorsal muscle although mass fragmentography method has been employed. The main identified compounds are summarized in Table I.

Both herbicides have also been identified in the extracts of raw water entering the water works, located 30 km downstream of waste dumping, as well as in finished water, by mass fragmentography. (see Figures 4 and 5).

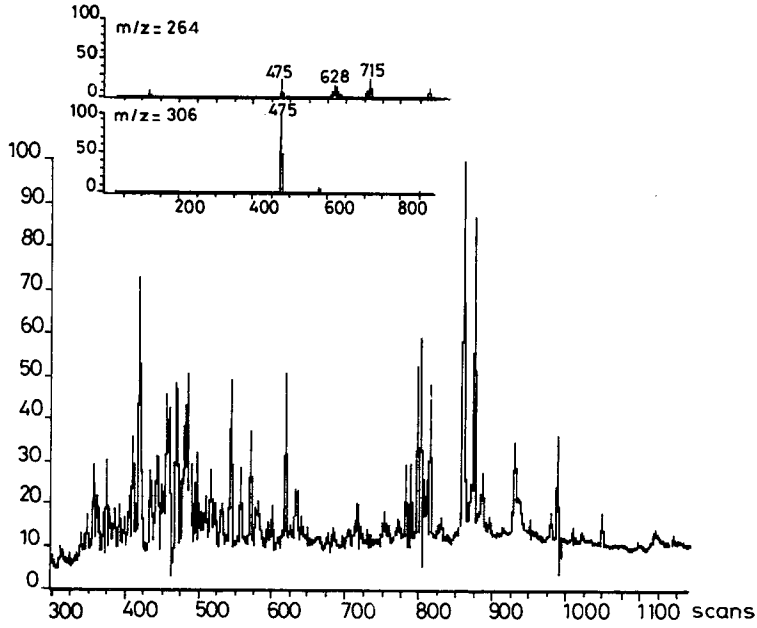

FIGURE 3 Total ion chromatogram from GC/MS analysis of a dorsal muscle extract of dead carps and top: mass fragmentogram of trifluralin (m/z: 264, 306). Conditions of analysis are described in the text.

TABLE I

Main identified compounds in the extracts of the dead carps.

Dorsal muscle	Liver
Tetrachloroethene	Alkylbenzenes
Xylenes	Long chain alcohols (C10–14)
1-Cyclohexyl-3-methyl-benzene	Hexadecanoic acid
3,3′,4,4′-Tetramethyl-1,1′-biphenyl	3-Cholest-7-en-3-ol
Trifluralin	
2-Hydroxy-l-(hydroxymethyl)ethyl hexadecanoic acid	
Nonylphenol monoethoxylates	

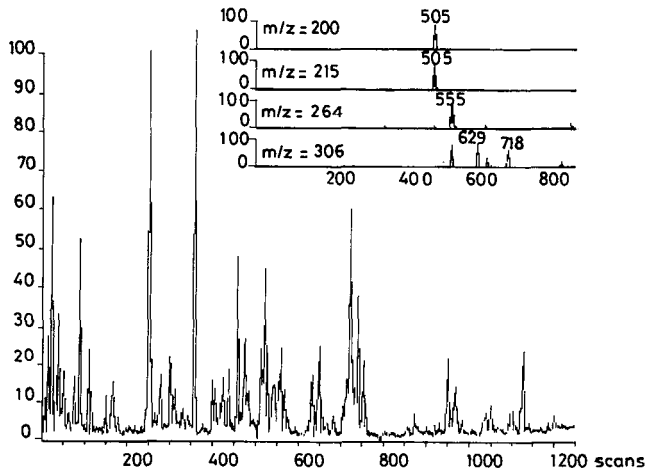

FIGURE 4 Total ion chromatogram from GC analysis of a Llobregat river raw water extract entering the water works plant, and top: mass fragmentogram of trifluralin (m/z: 264, 306) and atrazin (m/z: 200 and 215).

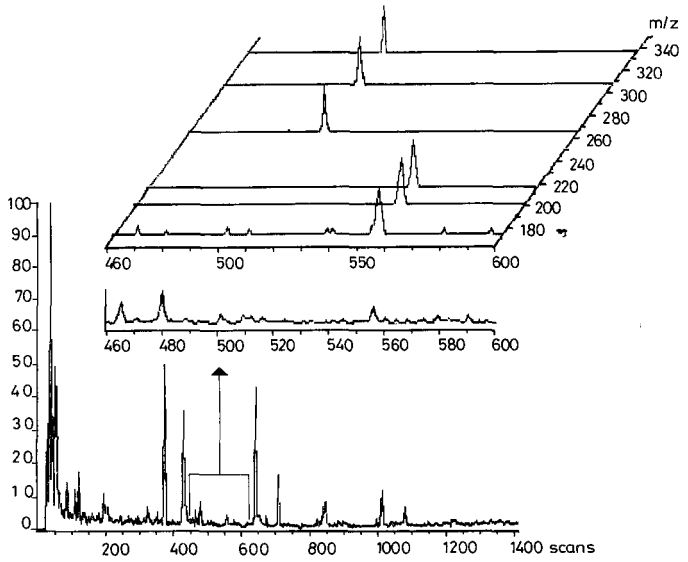

FIGURE 5 Total ion chromatogram from GC analysis of a finished water extract of the water works plant, and top: mass fragmentogram of trifluralin (m/z: 264, 306, 335) and atrazine (m/z: 173, 200, 215).

Semiquantitative analyses has given a 1–20 ppb range for both compounds. The lack of toxicological data, persistence and fate on many industrial chemicals, makes it difficult to assess their relative importance to environmental concerns.

CONCLUSIONS

The analysis by GC/MS/DS and mass fragmentography of extractable compounds in the waste dumping effluent from an industrial area dealing with surfactants and pesticide manufacturing, as well as that of raw, drinking water and dead carps indicated the presence of two herbicides (atrazine and trifluralin) and other miscellaneous compounds.

Although these two herbicides had not been previously detected in the continuous monitoring of Llobregat river's water, their identification 40 km far from the source of pollution, and besides one of

them (trifluralin) was also found in the dorsal muscle of carps, led us to think of it as the cause for fish death. However, the degree of pollution suffered by Llobregat river and extreme changes in flow regime, makes it difficult to assess the exact cause of fish mortality.

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References

1. L. H. Keith and W. A. Telliard, *Environ. Sci. Technol.* **134,** 416 (1979).
2. Liste I de la directive 76/464/CEE du Conseil.
3. J. C. Peterson, G. Guiochon, C. Democrate and M. Dutang, *Intern. J. Anal. Chem.* **14,** 23 (1983).
4. R. A. Moore and F. W. Karasek, *Intern. J. Anal. Chem.* **17,** 203 (1984).
5. L. S. Sheldon and R. A. Hites, *Environ. Sci. Technol.* **13,** 574 (1979).
6. U.S. Environment Protection Agency, *Federal Register* **44,** 69464:575 (December 3, 1979).
7. A. Hladka and J. Kovac, *Fresenius Z. Anal. Chem.* **265,** 339 (1973).
8. *Analysis of Organic Micropollutants in Water (COST 64b bis)*, CEC Directorate-General for Science, Research and Development, Environment Research Programme (Fourth edition, 1984).
9. R. Bathe and K. Sachsse, *Proc. Eur. Soc. Toxicol.* **16,** 113 (1975).
10. N. M. Vermeulen, Z. Apostolides, D. J. Potgieter, P. C. Nel and S. H. Smit, *J. Chromatogr.* **240,** 247 (1982).
11. S. Safe and O. Hutzinger, *Mass Spectrometry of Pesticides and Pollutants* (CRC Press, 1973), pp. 169, 204.