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A Strategy for Source Identification of Organic Pollutants in River Water

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Sources of organic pollution in the Oise river, France have been identified using a "mutual search" strategy. This consisted of searching the characterized discharges for compounds found in the river water and, conversely, searching river water extracts for compounds found in the discharges. The "matches" were facilitated by comparisons of retention indices on two capillary gas chromatographic columns of widely differing polarity, response factors of selective detectors, and mass spectra. These assignments were verified by the geographical correlation of the selected pollutant's point of appearance in the river with the location of the suspected source.

KEY WORDS: Pollution sources, source identification, dual detection, GC/MS.

INTRODUCTION

The Oise river in France supplies water ultimately used for drinking water for the region north of Paris. The river system (Figure 1) receives discharges from 26 different industries within a span of 110 km, varying in flow rates from 125 to 80,000 m³/d. Descriptions of many of these effluents, which vary in content from food processing to dyestuff waste, are found in Table I. The water company involved, the Compagnie

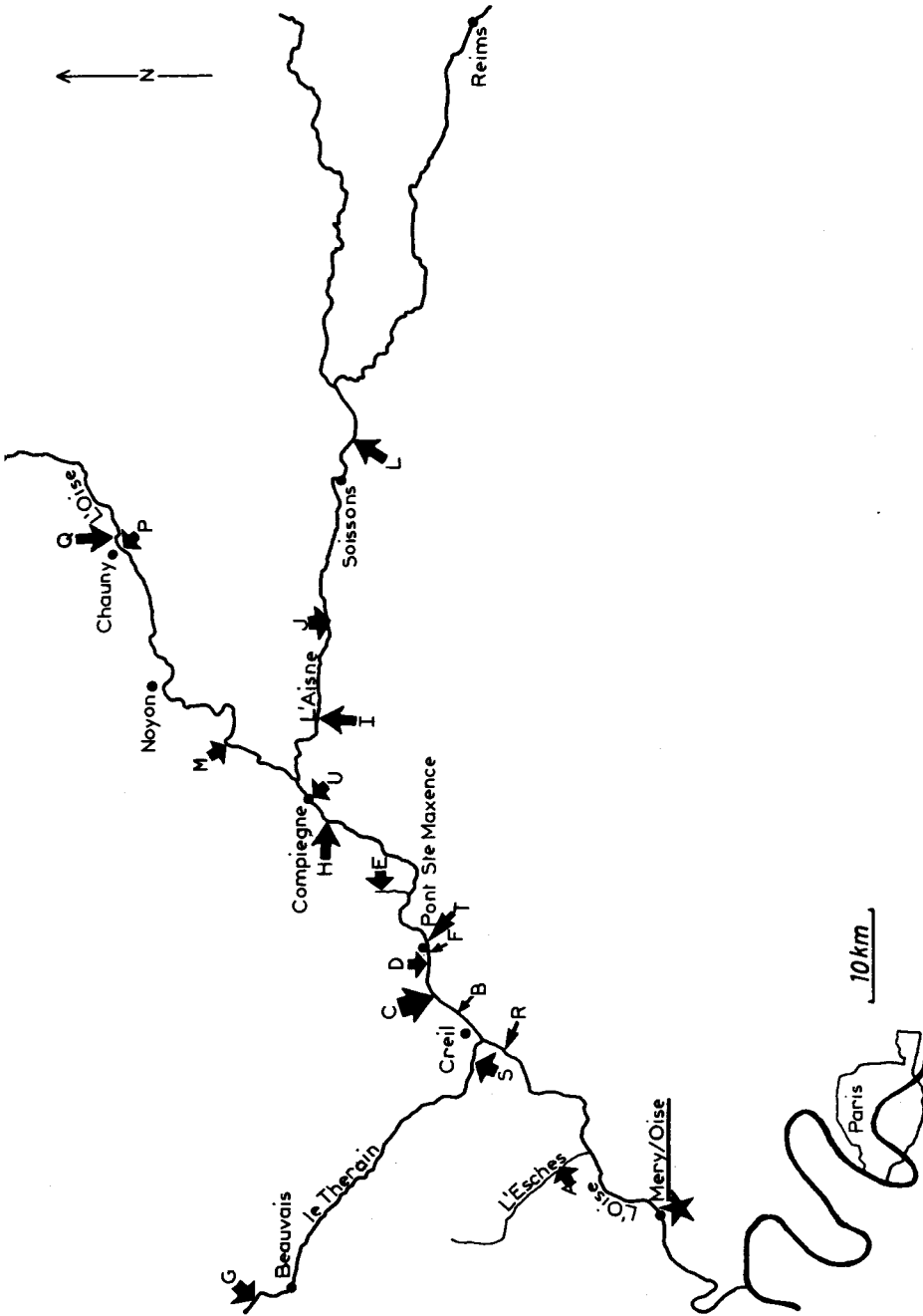


FIGURE 1 Geographical locations of the major factories in the Oise river valley. The size of the arrows is indicative of the relative discharge flow rate.

TABLE I
Major sources of pollution in the Oise valley

Factory	Distance from Méry/Oise (km)	Discharge flow rate (m ³ /d)	Type of industry
A	13.5	900	polymers, diverse organic chem.
R	24	6000	paints
S	26	8000	diverse organic chem.
B	26	175	glass wool
C	29	45000	dyes
D	37	6400	paper
T	37	1600	waste water treatment
E	52	3000	sugar
G	58	2400	ice cream, food processing
H	62	10000	vegetable oil
U	62	10500	waste water treatment
I	78	5000	diverse chem.
M	76	360	glue, diverse chem.
J	85	2600	potato chips
L	108	10000	paper
P	110	2000	ion exchange resins
Q	110	17000	inorganic acids

Générale des Eaux, has been concerned that potentially toxic pollutants from these industries are entering their water treatment plant at Méry/Oise. We have undertaken the task to identify these chronic industrial pollutants at Méry/Oise and to ultimately identify their sources. The eventual goal of this study is to provide evidence to force the offending industries to make appropriate improvements in their waste water purification process. In order to direct our efforts in the most efficient manner, we have decided to begin by qualitatively identifying the major problems in the river within the limits of our chosen techniques and to recognize their relative magnitude. Follow-up studies would address these problems in a more quantitative manner by tailoring the analyses to the pollutants of greatest interest.

Surveys of organic pollutants in river water are often limited to a group of "target" or "black listed" compounds of known environmental danger.^{1,2} However, this approach can ignore other pollutants which present a greater danger to that particular river. Other studies attempt to identify all the components of a single highly concentrated sample.^{3,4,5} The source or sources of these compounds is often left to mere speculation. We have combined both of these approaches. The compounds discharged by each industry were compiled into our "black list", while, at

the same time, we have attempted to establish the identities of the chronic pollutants found in the river at Méry/Oise throughout the year. This can be viewed as a mutual search strategy, i.e., the river water is searched for the discharged compounds and the discharge waters are searched for the compounds found in the river.

The semi-quantitative study has been limited to compounds which are amenable to glass capillary gas chromatography. Simple, single column retention time comparisons using a flame ionization detector (FID) are inadequate to verify the presence of discharged compounds since several have been found to coelute. A more solid characterization of the extracted compounds is necessary. Mass spectrometry provides the most powerful means of characterization and it is essential for compound identification. However, mass spectra often can be ambiguous and in complex mixtures, can be confused by fragment ions of unresolved neighboring peaks. Selective detectors used simultaneously with the FID can supply necessary complementary information to aid the identification process. Also, these selective detectors, which include electron capture (ECD), nitrogen-phosphorus (NPD), and flame photometric (FPD) are sensitive to certain compounds normally undetected by the more universal FID. The ECD has been used routinely during this portion of the study. While the NPD and the FPD have demonstrated their utility when the ECD is inadequate, their use has not yet been fully exploited.

Volatiles which elute before xylene have been studied concurrently. The results, which will be reported elsewhere, are less useful in identifying pollution sources because most of these volatile pollutants are not unique to a single discharge.

Samples collected throughout the river were also analyzed to determine the geographical points of appearance in the river of the chronic pollutants found at Méry/Oise. The correlation of a pollutant's point of appearance with the geographical location of the suspected source lends strong support to these assignments.

EXPERIMENTAL

Sampling

All sampling was performed by the Compagnie Générale des Eaux, Paris, France. Discharge water samples were collected with an ISCO automatic sampler, generally at a rate of 100 mL every 15 min during a 24 hour period. River water samples were collected as grab samples at points upstream from the plant at the time of the discharge water collection, at the major confluences of the Oise river with its tributaries, and at the

Méry/Oise purification plant with a time delay according to the distance from the discharge and the river velocity. Samples were stored in amber bottles at 4°C until extraction, normally within two weeks of collection.

Extraction procedure

The extraction procedure is outlined in Figure 2. The water samples were first filtered with Whatman glass fiber filters (1.2 μm) to remove particulate matter. The filtered water (0.2–2 L) was passed through a 10 cm \times 1 cm mixed bed (1:1) column of XAD 4/8 (Rohm and Haas, Philadelphia, PA),^{6,7} and the water which passed through the column was recollected and acidified with HCl to pH 2. The adsorbed compounds were eluted with 25 mL of distilled methylene chloride. The acidified water was passed through the column a second time and extracted in the same manner. The methylene chloride fractions were passed through short columns (3 cm \times 0.5 cm) of sodium sulfate to remove traces of water. An aliquot

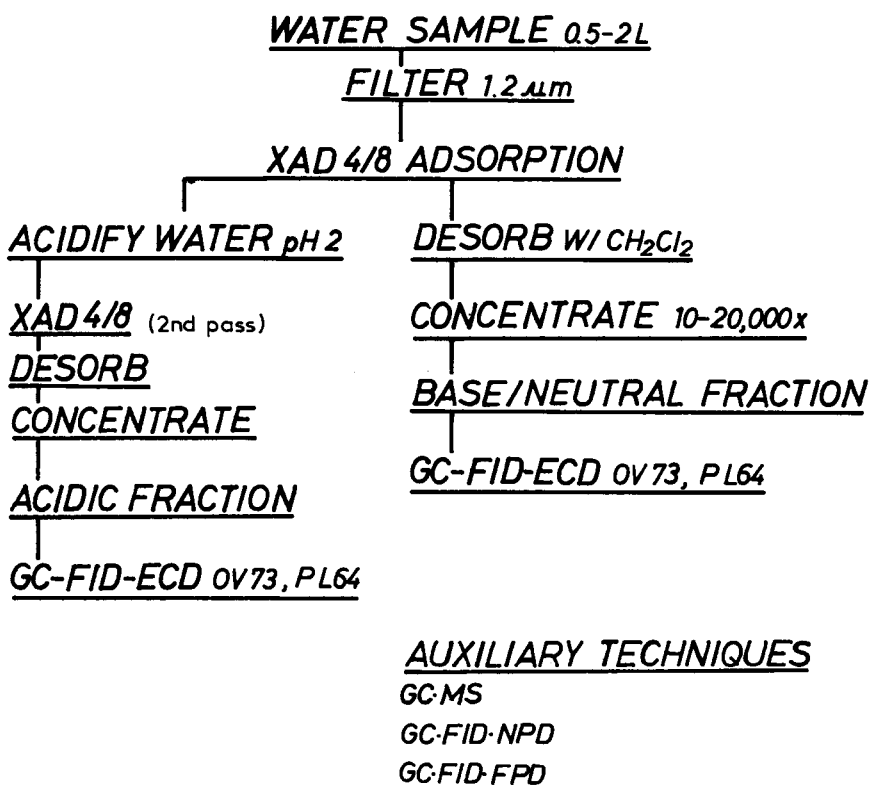


FIGURE 2 Basic scheme for the analysis of the water samples.

(5 μ L) of three internal standards: bromooctane, bromodecane and bromotetradecane (250 μ g/L) was added to each extract for volume correction factor purposes. The "base neutral" and "acidic" fractions were concentrated to approximately 2 mL with a rotary evaporator (Büchi, Switzerland), followed by evaporation to an appropriate volume (0.10 mL–1.0 mL) using a gentle stream of nitrogen. No further sample preparation was used before GC analysis except a solvent change to methanol when the nitrogen-phosphorus detector was used.

Analytical instrumentation

Two types of glass capillary columns of widely differing polarities, OV73 (apolar) and PL64 (polar) were used.^{8,9,10} The polar columns (17 m \times 0.27 mm i.d., 0.20 μ m film thickness) were made shorter than the apolar columns (30 m \times 0.27 mm i.d., 0.15 μ m) in order to elute the heavier components within the lower temperature limits of the phase. Polar columns were temperature programmed from 60–220°C after solvent elution (2 min) while apolar columns were programmed from 60–260°C (3 min hold). All injections (2 μ L) were splitless.¹¹

For dual FID/ECD detection, a Varian 3800 gas chromatograph equipped with ⁶³Ni electron capture and flame ionization detectors was employed. Nitrogen was the carrier gas. A post-column splitter consisting of glass lined tubing similar to that described by Yang¹² was fabricated to allow simultaneous detection. A make-up gas flow of 20 mL/min was required to eliminate the effects of extra column dead volume. Electrometer attenuations were adjusted to achieve a 6:1 peak height ratio between the FID and ECD responses of the bromoalkane internal standards. Dual NPD/FID and FPD/FID detection were accomplished with Perkin-Elmer 3920B and Varian 3800 gas chromatographs, respectively. The same post-column splitter design was used. GC/MS analyses were performed using a Dupont model 21-492-B mass spectrometer interfaced to a model 094-B data system.

Concentrations were estimated based on peak heights in the FID chromatograms compared to known amounts of injected standards of the same or similar compounds. Quantitation with the ECD was made only when standards were available. Otherwise, "less than" values were used when a peak was undetected in the FID and the appropriate standard was lacking for ECD quantitation.

RESULTS AND DISCUSSION

Source characterization

Each of the industries studied has been characterized according to

distance from the Méry/Oise purification plant, flow rate(s) of the discharge(s), Kovats indices of each major peak (FID, ECD, NPD or FPD) on each column (OV73 for all detectors, OV73 and PL64 for FID/ECD), selective detector/FID response factors, and the most precise identification possible. An example of this characterization is shown in Table II. Factory A, the closest factory to Méry/Oise, produces acrylates and polymethacrylates in addition to a variety of specialized chemicals. The plant has three principal discharge outlets which together have a flow rate of approximately 900 m³/day. Each major peak has been given a number between 1 and 300 according to its retention order in the OV73 chromatogram. Figure 3 is the FID/ECD chromatogram of one of the three discharges. The ECD/FID response factor estimations were based on a scale of 1 to 5, 1 being equivalent to the response of the bromoalkane internal standards and 5 being equivalent to that of δ -lindane.

In order not to spend excess time on pollutants of minor importance to the study, the criterium for pursuing the identification of a peak which was not satisfactorily identified by the computer mass spectral matching

TABLE II

Characterization of the discharges of Factory A

Distance from Méry/Oise: 13.5 km. Type of industry: polymers, diverse chem.

Peak no.	R.I. OV73 (apolar)	R.I. PL64 (polar)	$I_{\text{ECD}}/I_{\text{FID}}$	Identification (GC-MS)
17	980	1080		butyl crotonate
19	1020	1200	2	<i>p</i> -dichlorobenzene
20	1030	1315		
21	1040	1230	2	<i>o</i> -dichlorobenzene
33	1110	1405		
53	1225	1725		phenoxy ethanol
69	1280	1615		<i>n</i> -alcohol (C ₁₀)
71	1320	1635		dialkyl benzene
82	1330	1595	4	2,3-dichloronitrobenzene
84	1340	1545		
111	1470	1560		<i>n</i> -alcohol (C ₁₂)
148-158	1700-1780	2250-2325		alkyl(C ₉) phenols
158	1780	1875		alkyl(C ₉) methacrylate
174	1875	1965		alkyl(C ₁₀) methacrylate
191	1975	2060		alkyl(C ₁₁) methacrylate
206	2070	2160		alkyl(C ₁₂) methacrylate
220	2155	2355	2	chloroalkyl acrylate
230	2225	2395	2	chloroalkyl acrylate
233-240	2520-2590	>2800		alkyl acrylate

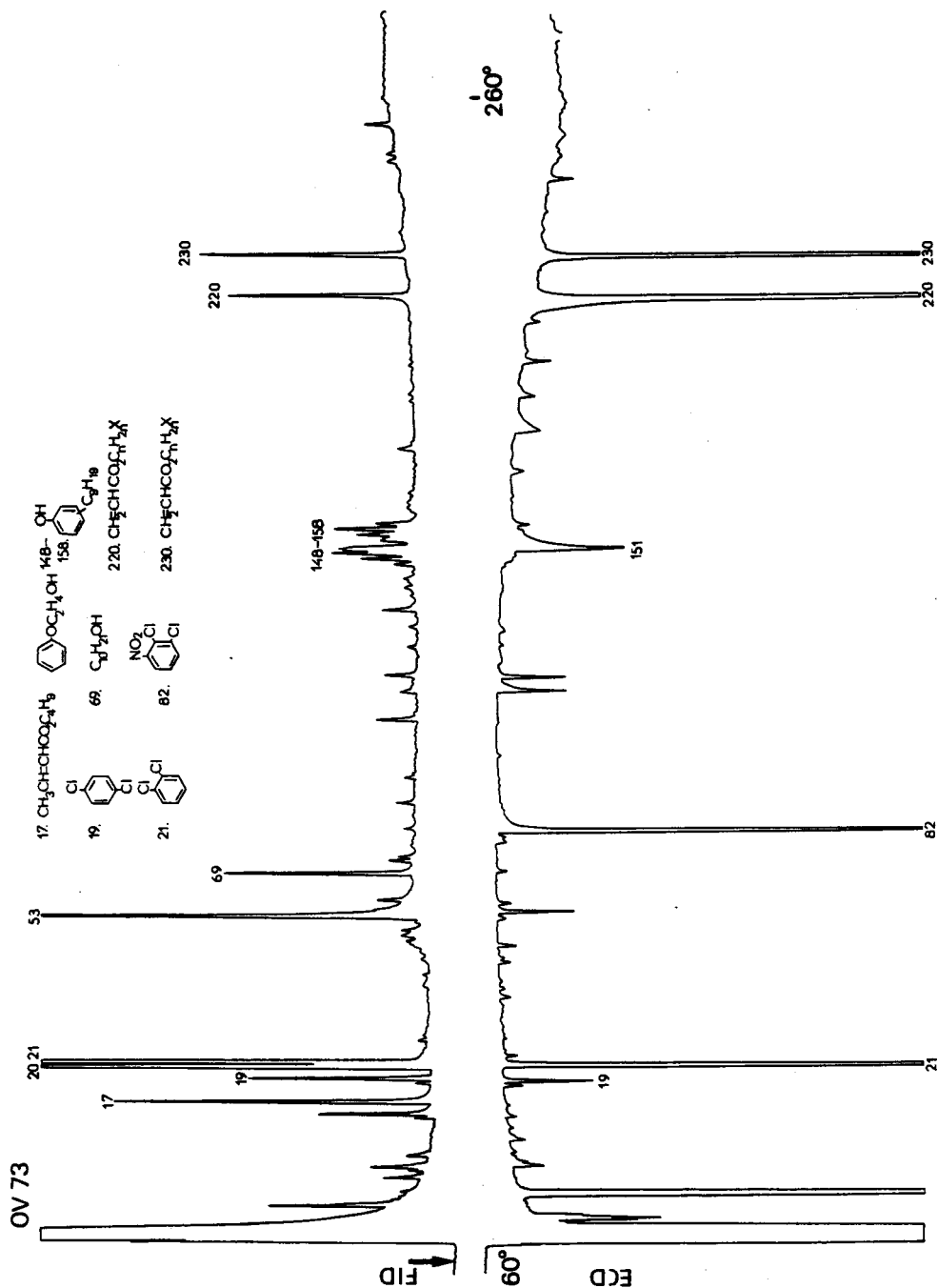


FIGURE 3 Simultaneous FID/ECD chromatogram of the base/neutral fraction of discharge A, concentration factor: 20 x.

system was its reappearance in the river downstream. Peaks 33 and 84 are examples.

Compound 82 would have been overlooked if detection only by flame ionization and mass spectrometry had been used. Fortunately, it was easily detected with the ECD in the discharge water (Figure 3) as well as in the Esches river, 1 km downstream from the plant (Figure 4). A closer examination of the mass spectra at retention indices approximately equivalent to the ECD chromatogram eventually revealed peak 82 to be 2,3-dichloronitrobenzene.

While the mass spectra of peaks 220 and 230 indicated they were identical to other peaks identified as acrylates of long chain alcohols (no.'s 233–240), the ECD response suggested possible halogenation. This not only increased our interest in the compounds due to their increased toxicity potential but it also improved their detectability in the river. In the Esches river extract chromatogram (Figure 4) peak 220 is indeed quite evident. However, peak 230 has disappeared. Evidently, peaks 220 and 230 are not as closely related as their mass spectra and response factors indicate.

The nonyl phenols (148–158) and alkyl acrylates (233–240) were found in the Esches river at concentrations consistent with a simple river water dilution of the discharge. The dichlorobenzenes and 2,3-dichloronitrobenzene are found at relatively lower concentrations suggesting that removal mechanisms have already affected these pollutants 1 km from the plant. This chromatogram provides valuable information as to which compounds have the greatest potential of being found further downstream at Méry/Oise.

Verification of a source identification

Factory C which produces dyes has the highest discharge rate on the river and a high concentration of toxic compounds, as the chromatogram of one of the factory's three discharges illustrates (Figure 5). All three discharges were quantitated in terms of their mass flux, in kg/day, which reflects the discharge flow rates as well as their concentrations, as shown in Table III. Not surprisingly, at Méry/Oise, 29 km downstream, the pollutants from factory C of greatest environmental concern (nitrobenzene, nitrotoluenes, and di- and tri-chlorobenzenes) were present in the river (Figure 6) at mass flux values (considering the flow rate of the river) within a factor of 10 of the summation of all three discharges (Table III). In contrast, peaks 26 and 31 have been reduced substantially.

Equally important in confirming this source was the non-detection (Table III) of these rather common pollutants either in the river upstream

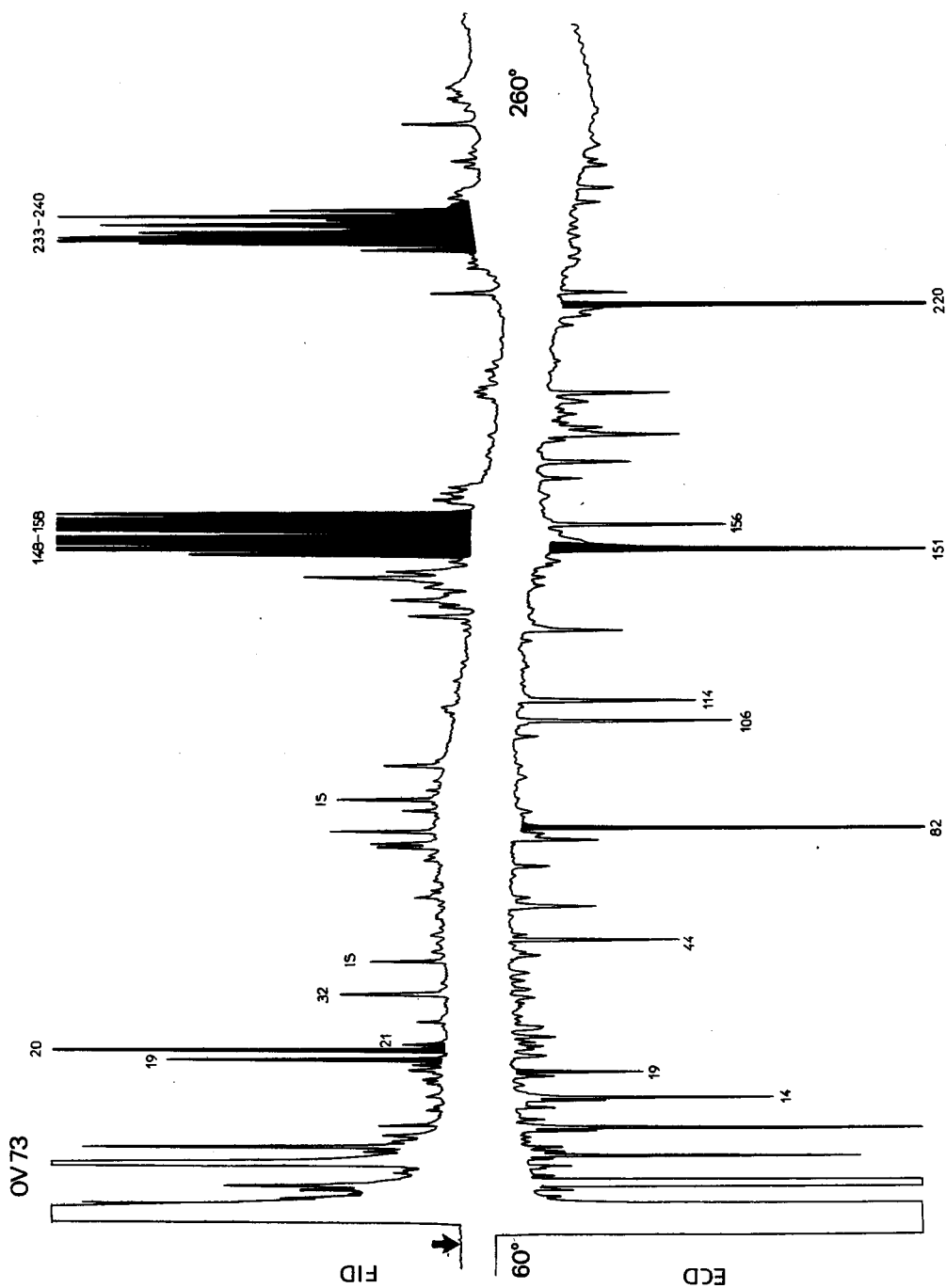


FIGURE 4 Simultaneous FID/ECD chromatogram of the base/neutral fraction of the Esches river water, 1 km downstream from factory A, concentration factor 5,000x. Compounds found in discharge A are blackened.

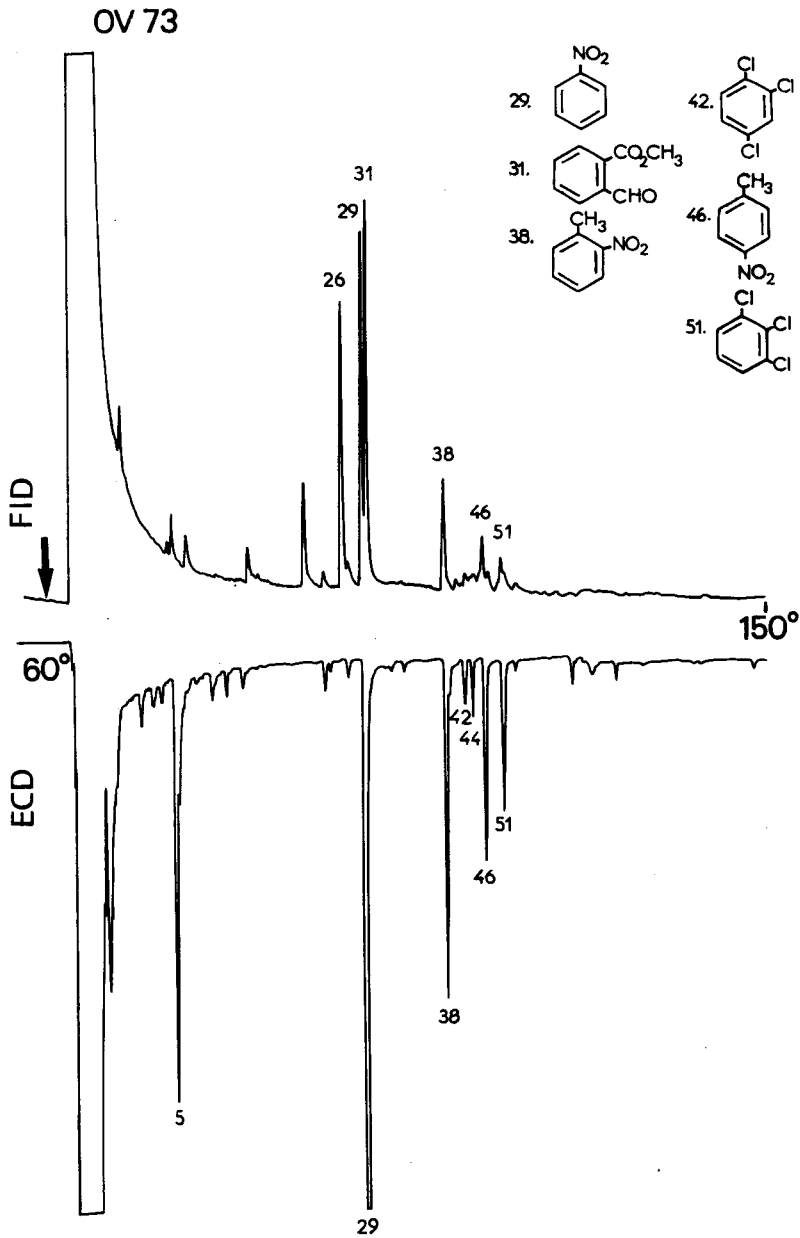


FIGURE 5 Simultaneous FID/ECD chromatogram of the base/neutral fraction of discharge no. 143 of factory C, concentration factor: 10 \times .

EAC B

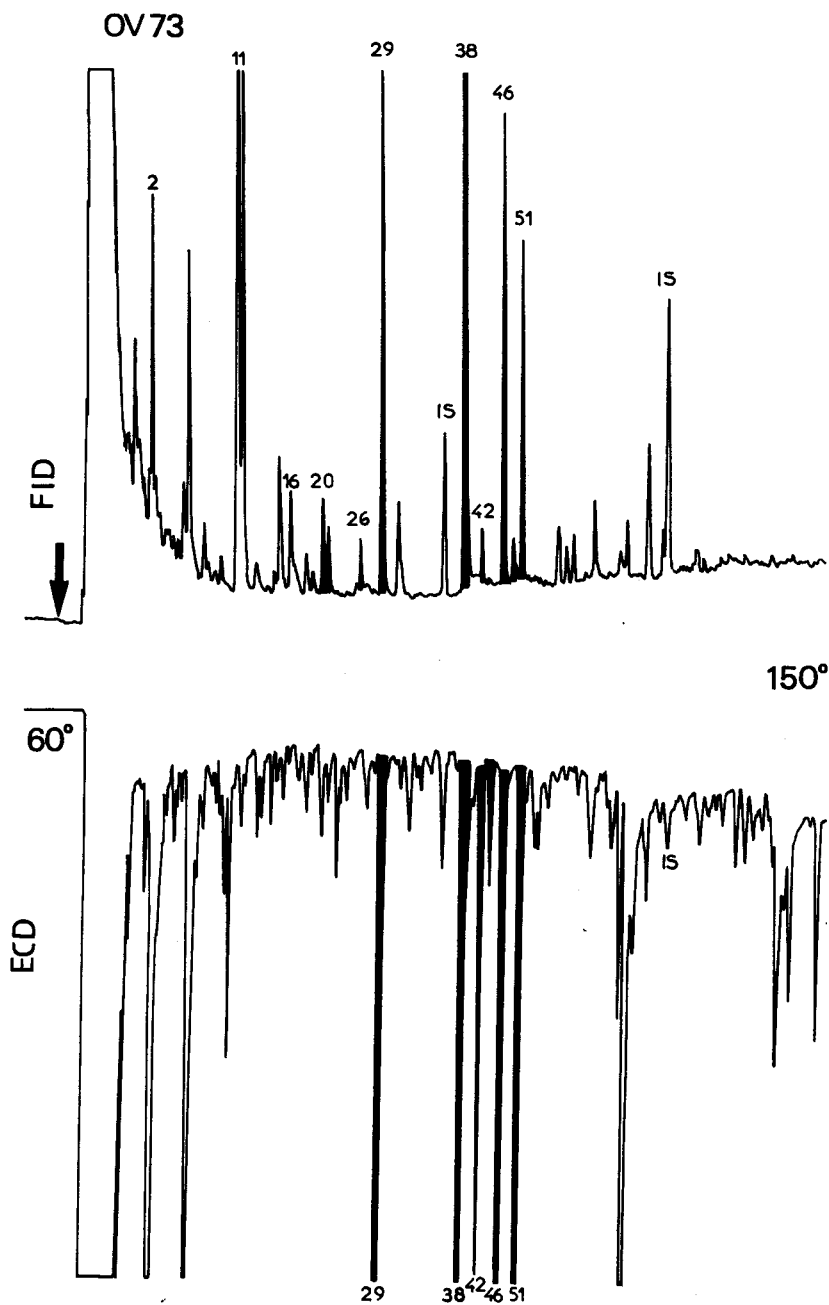


FIGURE 6 Simultaneous FID/ECD chromatogram of the base/neutral fraction of the Oise river water at Mery/Oise, concentration factor: 10,000 ×. Compounds found in the factory C discharges are blackened.

TABLE III

Comparison of the mass flux of pollutants from Factory C in its discharge and in the Oise river

Peak no.*	Discharge mass flux (kg/d)			River mass flux (kg/d)		
	no. 143	<i>N</i>	<i>S</i>	Total	Méry/Oise	Upstream C
21	0.9	0.06		1.0	0.08	<0.004
26	3.0	0.06		3.0	0.04	<0.001
29	4.0		0.4	4.0	0.5	<0.0005
31	5.0			5.0	<0.004	<0.004
38	0.9	0.2	0.2	1.0	0.8	<0.0005
42	0.04	0.06	0.1	0.2	0.04	<0.0001
44	0.09	0.003		0.09	0.09	<0.08
46	0.3			0.3	0.4	<0.0005
51	0.2	0.04	0.08	0.3	0.3	<0.0005

*See Figure 5 for peak identification.

Discharge flow rates: no. 143=4,400 m³/d, *N*=14,400 m³/d, *S*=41,000 m³/d. River flow rate: 60 m³/d.

from the factory (with the exception of peak 44) or in the tributaries entering the river downstream as shown earlier in Figure 4 (with the exception of peak 21).

The utility of selective detectors

While the ECD has been the routine selective detector of this project, the other selective detectors have been utilized when the ECD was inadequate. The discharge from Factory L, a paper factory, illustrates how the NPD can complement the capabilities of the ECD. The strongly scented pyrazines which exhibit little sensitivity toward the ECD show a strong response in the NPD (Figure 7). The possible misidentification of many interfering peaks in this crowded region of the chromatogram (Figure 5) can be avoided through the use of the NPD. Peaks 2 and 16 in Figure 5 have the same retention times as methyl and methyl ethyl pyrazine, however, the NPD did not confirm their presence. Nitrobenzene and the nitrotoluenes, however, were confirmed in the river water with the NPD.

Points of appearance of chronic pollutants

A key tool in isolating the industrial sources was the geographical mapping of the points of appearance or the concentration maximum of the recurring compounds in the river. These assignments are shown in Figure 8. This can add support to the identification of a source (factories

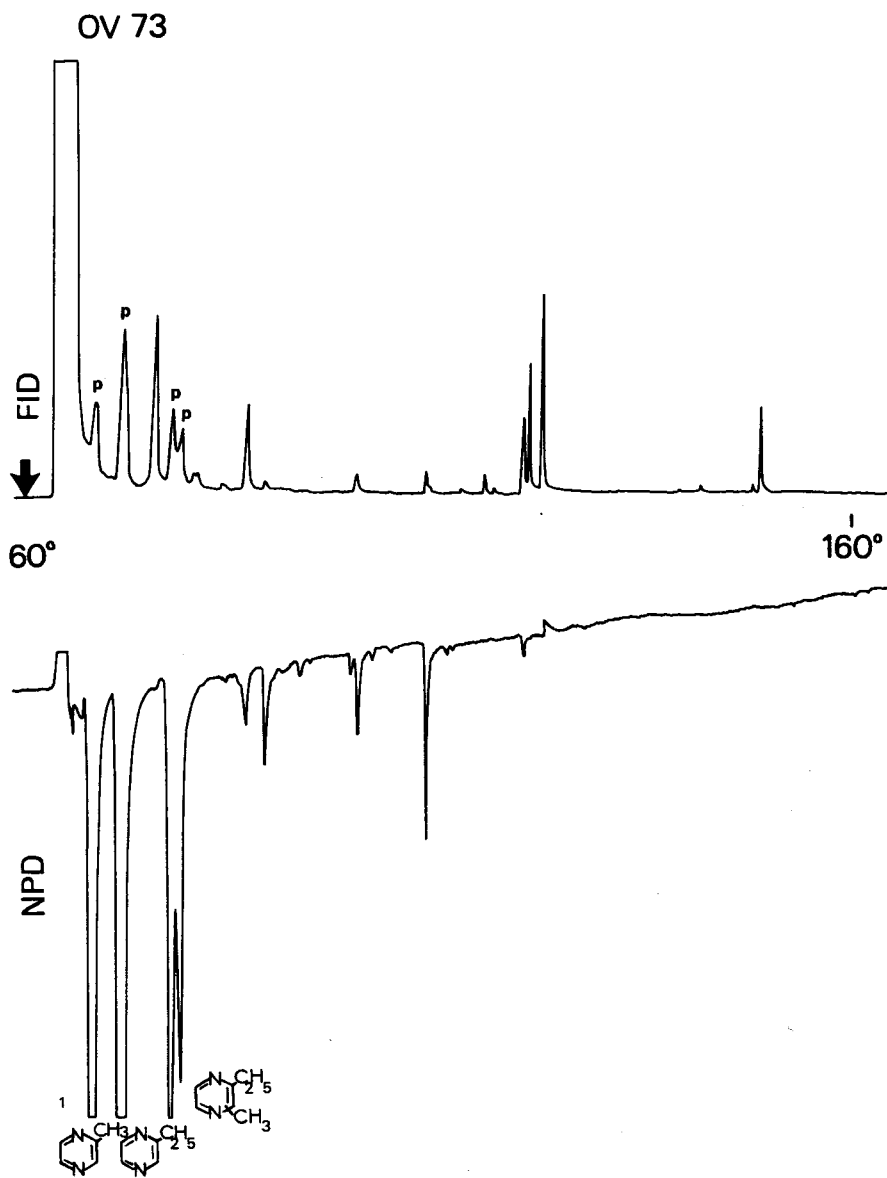


FIGURE 7 Simultaneous FID/ECD chromatogram of the base/neutral fraction of discharge L, concentration factor: 100x. The pyrazine peaks are marked by a "p" in the FID trace.

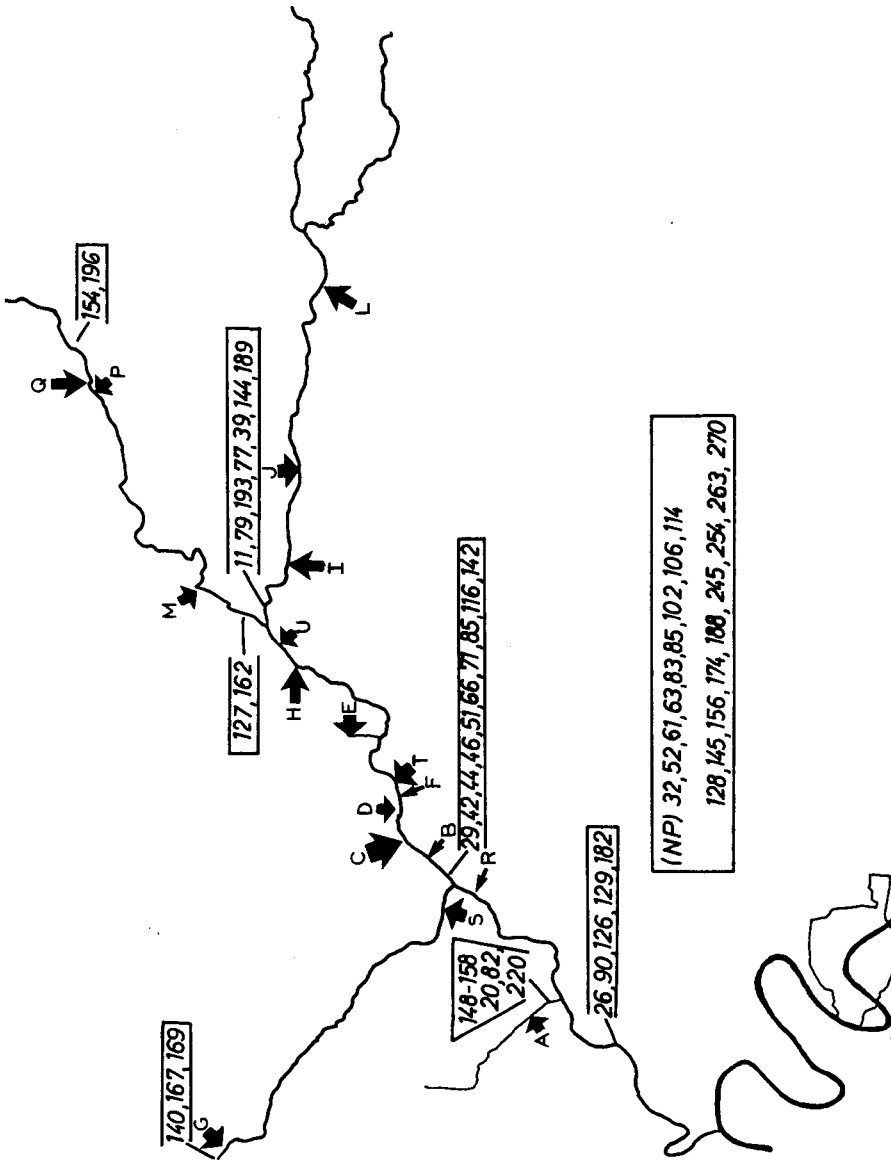


FIGURE 8 Geographical points of appearance of chronic pollutants in the Oise river.

A and C) as well as provide clues to isolate a candidate source. Compound 11 illustrates the latter (Figure 6). This doublet of isomers of pentanol trimethyl silyl ether left a trail of evidence throughout the river from Compiègne to Méry-Oise so that when factory I was characterized, it was no surprise to find concentrations of greater than 2.0 ppm in the discharge (10 kg/d).

Equally important is the recognition of particular peaks which appear at all sampling points in the river with no apparent maximum. These were considered to be from non-point sources (NP) and include phthalate esters and pesticides as well as naturally occurring fatty acids. When these compounds are eliminated from source consideration, the complexity of the study is reduced.

Source identification results

The typical chromatogram of Oise river water (Figure 9) and Table IV of the candidate sources of selected chronic pollutants are presented to show the progress which has been made in identifying the sources of pollution in the Oise river. Table IV indicates the frequency of occurrence of the selected compounds (which appear in Figure 9) in eleven samples collected throughout the year and their average concentrations. The industrial effluents in which they are found are listed along with the most precise identification to date. The most likely source is underlined as determined by its point of appearance in the river.

Clearly, some discharges can be eliminated from source consideration by the small mass flux values of its components. Yet, in the event of a catastrophic spill (or clandestine discharge), we also have discharge characterization information available to attempt to identify its source even if it is normally a minor pollution source.

As Table IV indicates, some questions still remain unanswered. Future work will center on identifying the unknown pollutants such as peaks 20, 26, 79, 127, and 193 more precisely. It will then be possible to modify and optimize the analytical scheme to quantify the pollutants of greatest concern. The end result will be a clearer understanding of the organic pollutants in the Oise river which will facilitate decisions concerning where to direct efforts to eliminate them.

TABLE IV
Candidate sources of selected chronic pollutants

Peak no.	Frequency of occurrence, %	Average concentration (ppb)	Candidate sources	Tentative identification
11	100	2.1	I	pentanol trimethyl silyl ether
19	22	0.7	A	<i>p</i> -dichlorobenzene
20	44	0.5	A	
21	55	1.0	A, C, D	<i>o</i> -dichlorobenzene
26	44	1.1	C	
29	100	1.1	C, D, P, T	nitrobenzene
31	44	1.0	C	methyl,2-formyl benzoate
32	89	0.7	(NP)	nonanal
38	89	1.6	C	<i>o</i> -nitrotoluene
42	89	0.7	C, L	1,2,4-trichlorobenzene
44	78	1.0	C	
46	89	0.8	C	<i>p</i> -notrotoluene
51	100	0.4	C, A	1,2,3-trichlorobenzene
61, 63	100	0.9, 1.2	(NP)	alkoxy alcohol
82	55	0.1	A	2,3-dichloronitrobenzene
106, 114	66	0.1	P, T, (NP)	
127	33	0.2	P	
128	100	0.6	(NP)	diethyl phthalate
145, 156	100	0.1	L, (NP)	α,δ -BHC
188	100	0.8	(NP)	dibutyl phthalate
192	100	1.1	D, G, H, (NP)	palmitic acid
193	44	0.1	L	
220	55	0.2	A	chloro alkyl acrylate
270	100	1.5	D, G, (NP)	di (2-ethylhexyl) phthalate

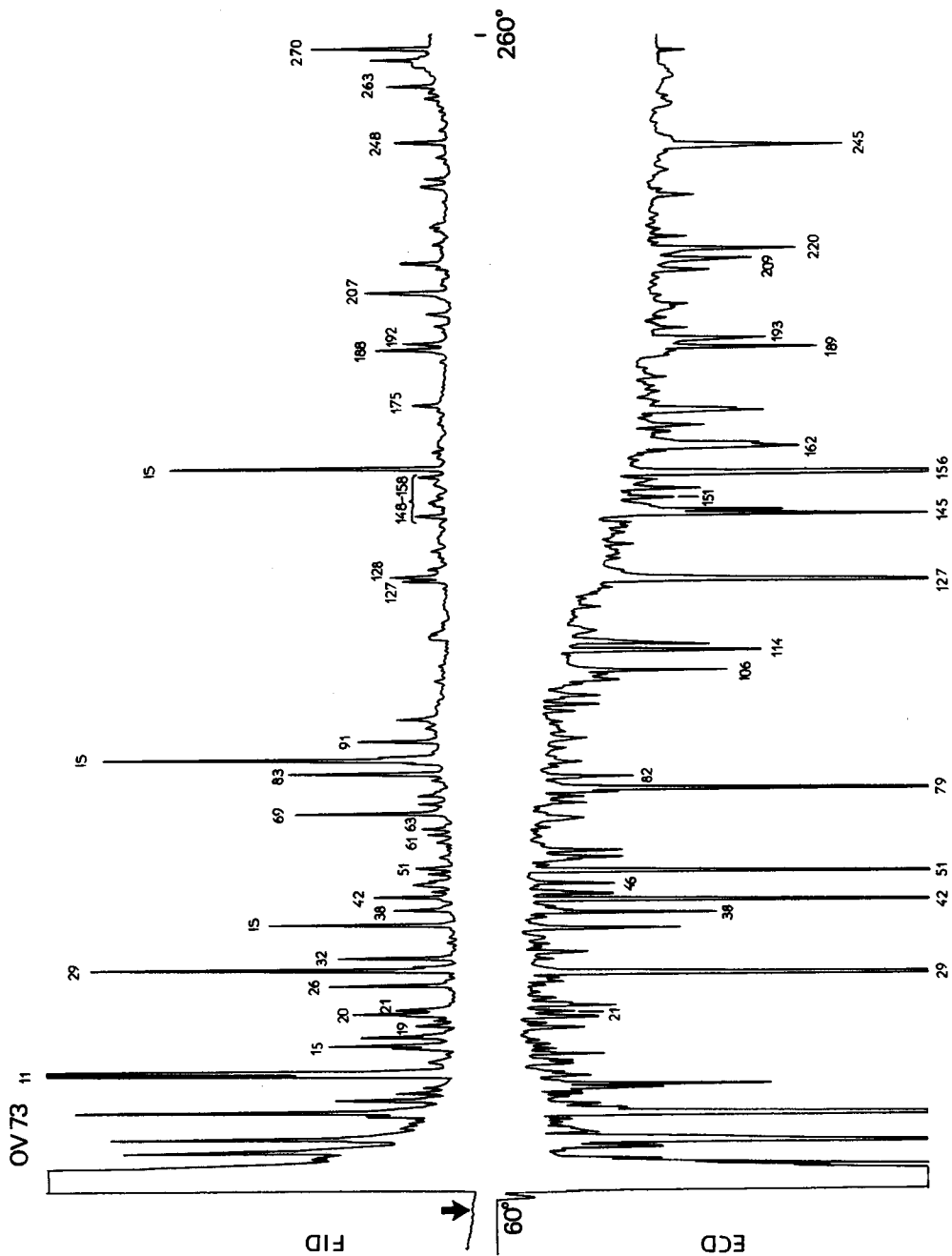


FIGURE 9 Simultaneous FID/ECD chromatogram of the base/neutral fraction of Oise river water at Méry/Oise, concentration factor: 10,000x. Numbers correspond to those found in Table V.

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