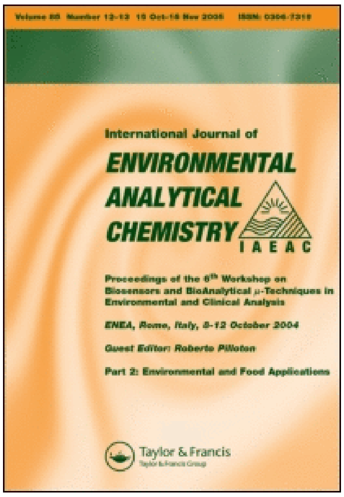

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Phenylurea and Triazine Herbicides in the Garonne River (France) During High Flood and Low Water Periods

S. Dupas[a]; P. Scribe[a]; H. Etcheber[b]; A. Saliot[a]
[a] Laboratoire de Physique et Chimie Marines, CNRS-UA 353, Universite Pierre & Marie Curie, Paris cedex 05, France [b] Département de Géologie et Océanographie, Centre de Recherche sur les Environnements Sédimentaires Oceaniques, CNRS-UA 197, Université de Bordeaux I, Talence cedex, France

To cite this Article Dupas, S. , Scribe, P. , Etcheber, H. and Saliot, A.(1995) 'Phenylurea and Triazine Herbicides in the Garonne River (France) During High Flood and Low Water Periods', International Journal of Environmental Analytical Chemistry, 58: 1, 397 — 409

To link to this Article: DOI: 10.1080/03067319508033141

URL: http://dx.doi.org/10.1080/03067319508033141

Intern. J. Environ. Anal. Chem., Vol. 58, pp. 397-409
Reprints available directly from the publisher
Photocopying permitted by license only

PHENYLUREA AND TRIAZINE HERBICIDES IN THE GARONNE RIVER (FRANCE) DURING HIGH FLOOD AND LOW WATER PERIODS

S. DUPAS*, P. SCRIBE*†, H. ETCHEBER‡ and A. SALIOT*

**Laboratoire de Physique et Chimie Marines, CNRS-UA 353, Université Pierre & Marie Curie, Tour 25, 4 Place Jussieu, 75252 Paris cedex 05, France;*

‡Centre de Recherche sur les Environnements Sédimentaires Océaniques, CNRS-UA 197, Université de Bordeaux I, Département de Géologie et Océanographie, 351 Cours de la Libération, 33405 Talence cedex, France

(Received, 10 September 1993; in final form, 21 January 1994)

Phenylureas and triazines were analysed by reversed-phase liquid chromatography using UV detection at 254 nm after an on-line preconcentration step on a PRP-1 copolymer in order to determine pesticides in river water at μg/l level or lower. Running water was sampled in the Garonne from a station located at La Réole, upstream from Bordeaux and from a small tributary, the Dropt. Water samples were collected mainly at several periods between December 1989 and September 1990 at a low water time (December 1989) and during two high flood periods (February 1990 and May 1990). Atrazine, simazine, de-ethylatrazine, diuron, chlortoluron and isoproturon were detected and quantified. In the Garonne river, atrazine, simazine, de-ethylatrazine and diuron were usually present at the sampling time, whereas chlortoluron and isoproturon maximised during the winter flood (February). In the Dropt river, triazine concentrations were normally between 1.0 and 0.1 μg/l and maximised at 2.2 μg/l during the spring flood (June 1990). De-ethylatrazine/(Atrazine + Simazine) ratio seems to be significantly higher than in the Mississippi river and may be in relation to the use of simazine in the drainage basin. These data are in agreement with seasonal applications of phenylurea and triazine herbicides and hydrologic and pluviometric conditions.

KEY WORDS: Phenylureas, triazines, Garonne river, liquid-solid extraction, on-line precolumn technology

INTRODUCTION

Thousands of tons of herbicides are applied each year in France as pre- and post-emergent weed-control agents on crops. France is the third highest pesticide consumer in the world after the USA and Japan, with around 8000 tons of triazines, 6800 tons of phenylureas and 7700 tons of aryloxyacids per year[1].

Substantial amounts of these synthetic organic compounds and their degradation products

---

† Author to whom correspondence should be addressed

are detected in surface waters draining agricultural areas[2,3,4]. Because herbicides are relatively water soluble, there is the potential for leaching into surface and ground water.

Many pesticides applied to crops are transported to surface water by various processes, such as runoff, ground water discharge and atmospheric deposition. In contrast to triazines, there is little information in the literature on the occurrence and behaviour of phenylurea herbicides in aquatic environments.

A multiresidue method[5] for the determination of phenylureas, triazines and their degradation products at µg/l or lower levels was applied to their monitoring in riverine waters. On-line solid phase extraction using a precolumn fed with PRP-1 copolymer was carried out and followed by liquid chromatography-UV detection and in some cases thermospray mass spectrometry with time-scheduled ion monitoring (SIM)[6].

This paper deals with the first data obtained in 1989 and 1990 for the Garonne river and one of its tributaries: the Dropt river.

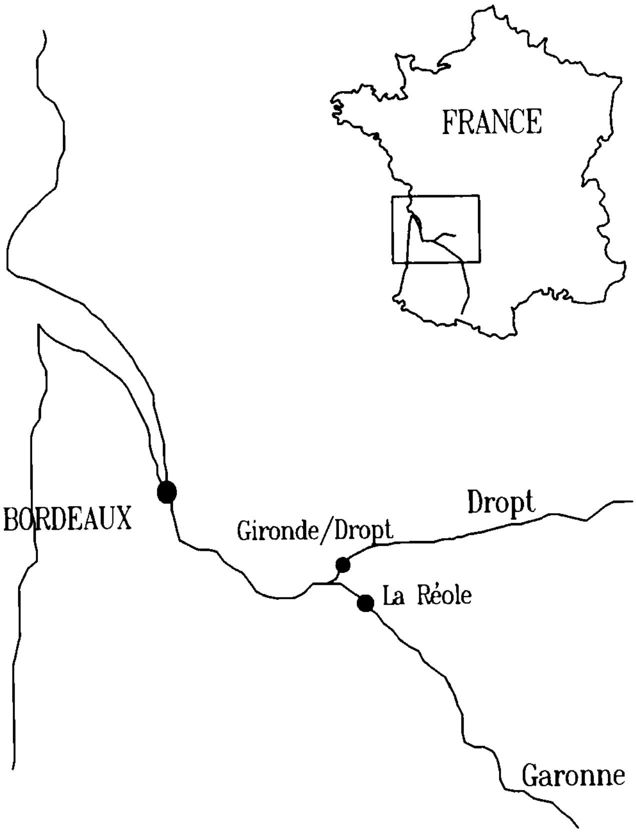

Figure 1 Sampling sites on the lower Garonne river and one of its tributaries (the Dropt river)

EXPERIMENTAL

Sampling site

The Garonne river is the second largest river in France after the Rhône. It flows 575 Km from its source in the Pyrenees to the draining basin outlet (Figure 1). Its annual average discharge is 450 m^3/s, range 300 to 600 m^3/s. The drainage basin of the Garonne river is mainly composed of forest (32%), herbaceous lands (31%), non-agricultural areas (13%) and miscellaneous farming (14%), in the order of decreasing importance: corn, sunflower and vineyard[1].

The Garonne river (yearly average $Q \approx 450$ m^3/s) and the Dropt river ($Q \approx 1$ m^3/s) were at low flow stage till the end of January 1990 and under drought conditions. The late winter flood came after a 10 months drought and the Garonne river discharge was permanently lower than the yearly average. The two highest floods of the year reached 2200 m^3/s and 1500 m^3/s and occurred during late winter and spring, respectively (Figure 2a).

Sample collection

Samples were collected monthly from December 1989 to September 1990 (except in July and August 1990) with special attention to the peak winter (February 16) and spring flood (May 28) (Figure 2a). The Garonne river water was sampled from a bridge at PK-70 called La Réole and the Dropt tributary from the right bank in 500 ml glass bottles and stored at 4°C until analysis.

Apparatus

On-line percolation of water samples was performed with a LC-6A pump (Shimadzu, Kyoto, Japan). Precolumn elutions and analyses were carried out with two Model 510 high-pressure pumps coupled with a Model 680 automated gradient controller equipped with a 486 tunable absorbance detector (Waters, Milford, MA, USA) and a Coulochem model 5100A electrochemical detector (ESA, Bedford, MA, USA). Precolumn and analytical column switching was done using a Rheodyne valve (Cotati, CA, USA). Quantitative measurements of peak areas were provided by an Apex Chromatography Workstation (Autochrom Incorporated, Milford, MA, USA).

Stationary phases and columns

Water samples were preconcentrated on a 2.3 cm × 3 mm ID stainless-steel precolumn packed with 10 μm styrene-divinylbenzene copolymer PRP-1 from Hamilton (Reno, NV, USA). The precolumn was flushed with pure acetonitrile and with methanol. The analytical column was a 25 cm × 4.6 mm ID stainless-steel column packed with a 5 μm octadecyl silica Spherisorb ODS2 from Interchim (Montluçon, France).

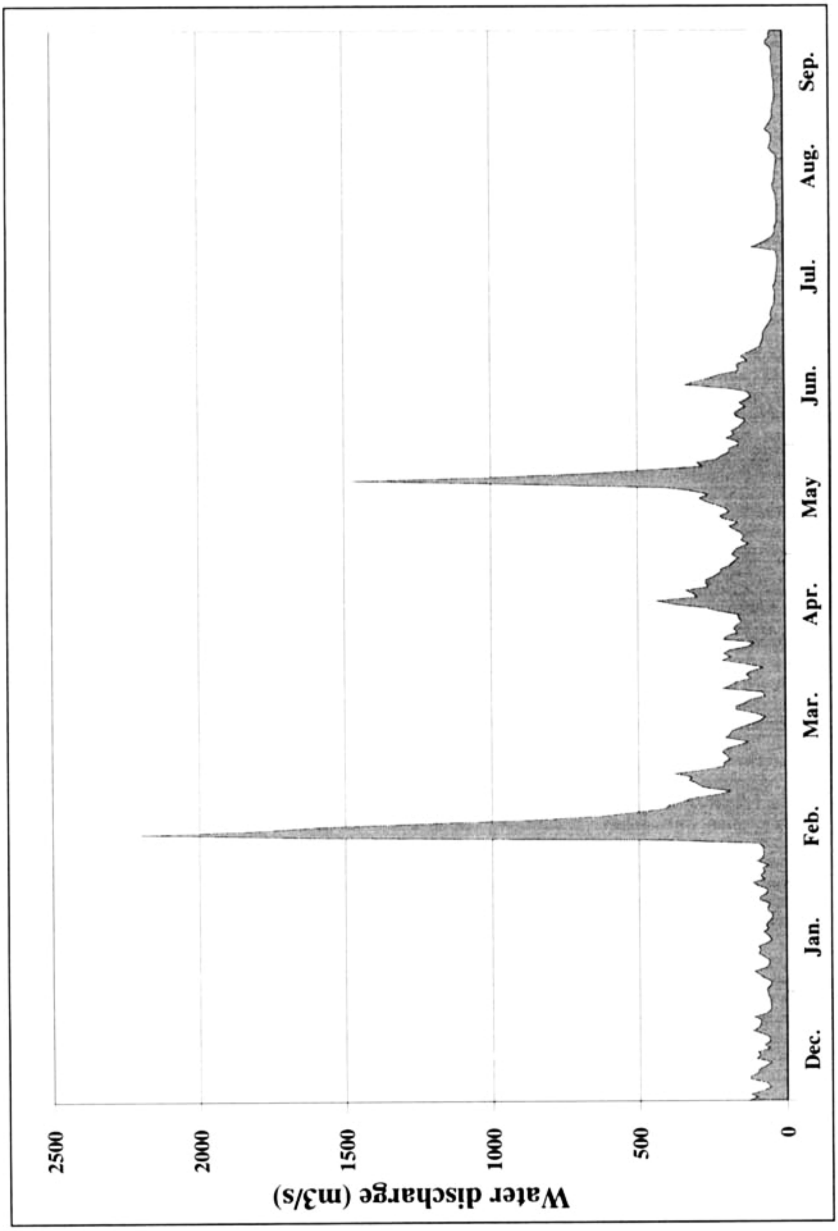

Figure 2a Hydrogram of the Garonne river between December 1989 and September 1990

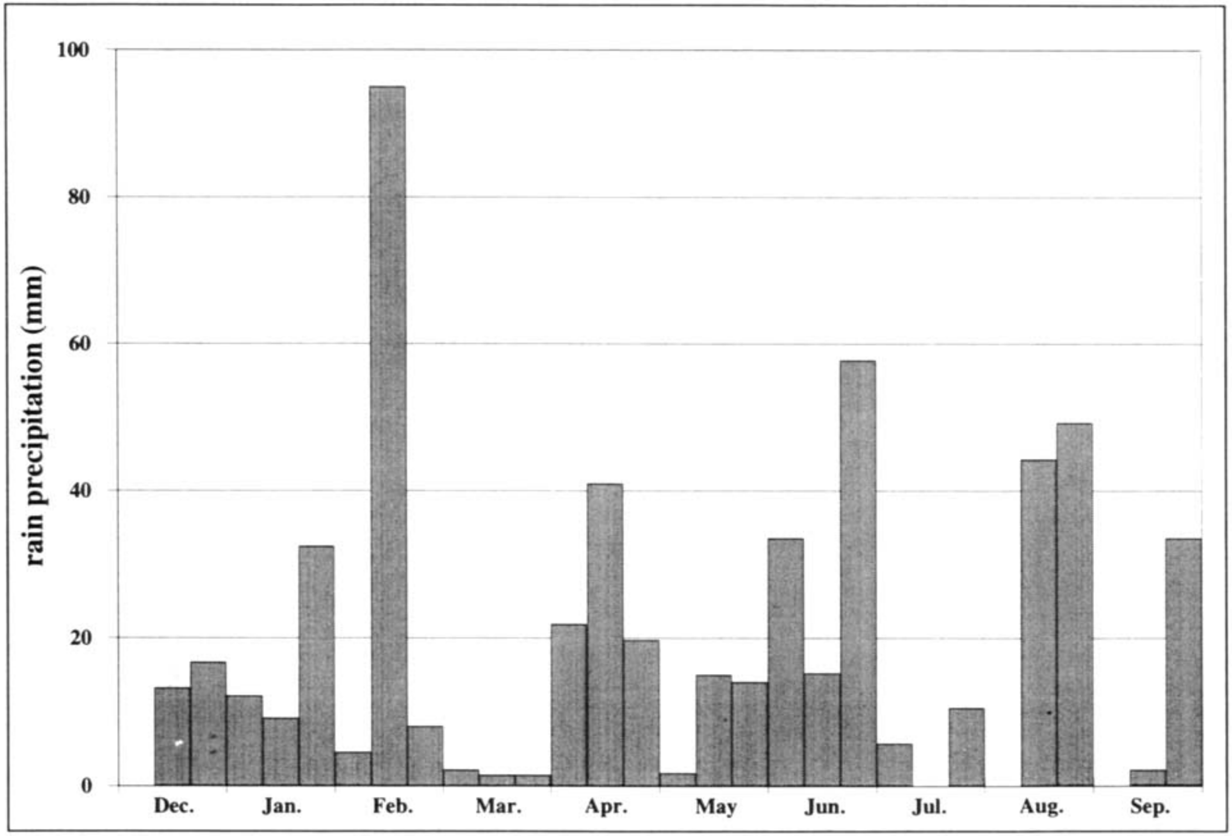

Figure 2b Rain precipitation recorded at the nearest meteorological station (St-Loubert) to the sampling station on the Dropt river (Gironde sur Dropt) between December 1989 and September 1990

Chemicals

HPLC-grade acetonitrile was from Rathburn (Walkerburn, UK) and methanol from Prolabo (Paris, France). LC-quality water was prepared by purifying water in an alpha-Q filtration system (Millipore, Bedford, MA, USA). The phenylureas and triazines were supplied by Cluzeau (Sainte Foy, France). Other chemicals were from Prolabo (Paris, France).

Procedure

The sample was filtered through a glass microfibre filter (Whatman, GF/F) and 200 ml was percolated through the PRP-1 precolumn at a flow-rate of 4 ml/min. The precolumn was coupled to the analytical column by switching a valve and backflush-eluted by an acetonitrile-water gradient via the LC pump. For separating pesticides on the Spherisorb column, the initial mobile-phase composition was 80 % water, containing 0.1 mol/l acetate buffer (pH 4.7) and 20 % acetonitrile. This was programmed linearly to 80 % acetonitrile after 45 min with a flow-rate of 1 ml/min. The herbicides were monitored with the UV-detector set at 254 nm and the electrochemical-detector set at 0.7 and 0.8 V. The concentrations of pesticides in river water were calculated by measuring the peak area or peak height of each pesticide and comparing them with those obtained from standard solutions. Replicate samples were analysed several times during the sampling period. Field equipment and laboratory blanks were found to be devoided of the analytes under investigation. Recoveries of the analytes of interest were determined by spiking milli-Q water at different concentrations. Concentration values reported are uncorrected for per cent recovery. Recoveries of the solutes were calculated from milli-Q water spiked at a concentration of 0.2 µg/l; standard deviations are given in brackets: Atrazine: 91 % (7), Simazine 89 % (8), Diuron: 85 % (6), Chlortoluron: 82 % (3), Isoproturon: 83 % (10), de-ethylatrazine: 73 % (5), de-isopropylatrazine: 18 % (15). The lower limit of detection of analytes in water samples on both sites was 10 ng/l. De-isopropylatrazine was generally always detected but not quantified since it co-elutes with interferents at the maximum of the unresolved peak of organic matter at the early step of the chromatogram.

RESULTS AND DISCUSSION

Several triazines and phenylureas were identified, including: atrazine, simazine and their degradation products de-ethylatrazine and de-isopropylatrazine, diuron, chlortoluron and isoproturon. All these compounds were quantified by calibrated UV detector and their structure was confirmed by LC-MS[6] (Tables 1 and 2).

Atrazine and simazine are the dominant and the most ubiquitous herbicides[7] in the mainstem of the Garonne river, <0.05–0.68 µg/l and <0.05–0.3 µg/l, respectively, for 1990 to 1992 (Agence de l'eau Adour-Garonne, Toulouse). In this work, their concentrations were at the maximum in May-June, 0.7 µg/l and 0.4 µg/l (Figure 3a), respectively, which corresponds to the spring flood period after their application on cereals and corn for both

Table 1 Concentrations (ng/l) of herbicides in water samples from the Garonne river between December 1989 and September 1990. DIA: de-isopropylatrazine; DEA: de-ethylatrazine; n.d.: not detected; n.q.: not quantified (interferents coeluted); DAS: de-ethylatrazine/(atrazine + simazine) ratio; Sim/Atr: simazine/atrazine ratio.

	Sampling date								
Compound	*20-Dec*	*30-Jan*	*16-Feb*	*23-Feb*	*26-Mar*	*24-Apr*	*28-May*	*07-Jun*	*12-Sep*
DIA	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
DEA	221	258	n.q.	228	247	138	105	n.q.	255
Atrazine	64	106	125	308	77	115	707	324	148
Simazine	<10	n.d.	79	n.d.	15	133	435	198	36
Chlortoluron	n.d.	n.d.	46	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Diuron	12	<10	11	23	<10	62	<10	n.d.	16
Isoproturon	n.d.	n.d.	36	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DAS	3.11	2.43		0.74	2.68	0.55	0.09		1.38
Sim/Atr	>0.11		0.63		0.19	1.16	0.62	0.61	0.24

compounds and on vineyards for simazine. In the Dropt river, the highest concentrations of atrazine and simazine, 2.1 µg/l and 2.3 µg/l, respectively, were observed one week later (Figure 3b). This one week shift in peak triazine levels can be explained by the fact that the drainage basin of the latter which is normally at a low level at this period had received abundant precipitations during the first ten days of June (Service Météorologique Interrégional Sud-Ouest, Mérignac) (Figure 2b). The water discharge before June 6 is normally about 0.6 m^3/s (Agence de l'eau Adour-Garonne, Toulouse).

De-isopropylatrazine (DIA) and de-ethylatrazine (DEA) were present in all the samples whatever the season. As indicated above, DIA was not quantified since it coelutes with unidentified interferents. Atrazine, degraded by soil bacteria yields mainly DEA and DIA among other degradation products whereas simazine yields only DEA, because of the symmetry of its C3 and C5 carbons that both bind to ethyl substituents.

The DEA/atrazine ratio (DAR) proposed by Thurman *et al.* (1991) as an indicator of groundwater recharge by atrazine laden-waters, varies from < 0.1 to 0.4 in surface runoff depending on the sampling time and may reach values > 1.0 in contaminated groundwater[3].

Table 2 Concentrations (ng/l) of herbicides in water samples from the Dropt river between December 1989 and September 1990. DIA: de-isopropylatrazine; DEA: de-ethylatrazine; n.d.: not detected; n.q.: not quantified (interferents coeluted); DAS: de-ethylatrazine/(atrazine + simazine) ratio; Sim/Atr: simazine/atrazine ratio.

	Sampling date									
Compound	*15-Dec*	*20-Dec*	*30-Jan*	*16-Feb*	*23-Feb*	*26-Mar*	*18-Apr*	*28-May*	*07-Jun*	*12-Sep*
DIA	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
DEA	386	279	168	648	500	242	299	213	287	288
Atrazine	103	299	228	716	373	194	446	270	2173	173
Simazine	557	317	206	1056	395	390	763	n.d.	2327	522
Chlortoluron	n.q.	255	123	199	92	n.d.	n.d.	n.d.	n.d.	n.d.
Diuron	17	12	22	42	20	42	136	213	188	n.d.
Isoproturon	n.d.	n.d.	n.d.	53	58	n.d.	n.d.	n.d.	n.d.	n.d.
DAS	0.58	0.45	0.38	0.36	0.65	0.41	0.24	0.79	0.06	0.41
Sim/Atr	5.41	1.06	0.90	1.47	1.06	2.01	1.71		1.07	3.02

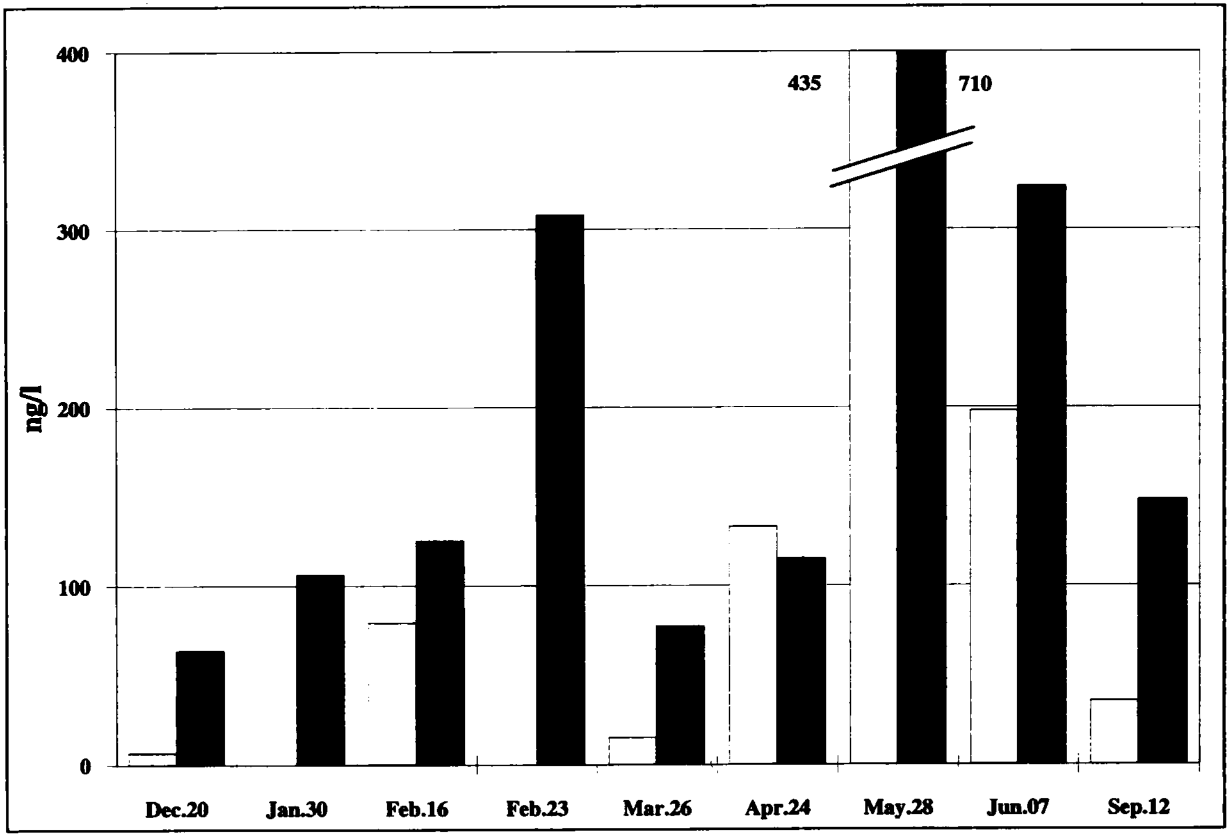

Figure 3a Histogram of the concentration (ng/l) of atrazine ■ and simazine ☐ in the Garonne river between December 1989 and September 1990

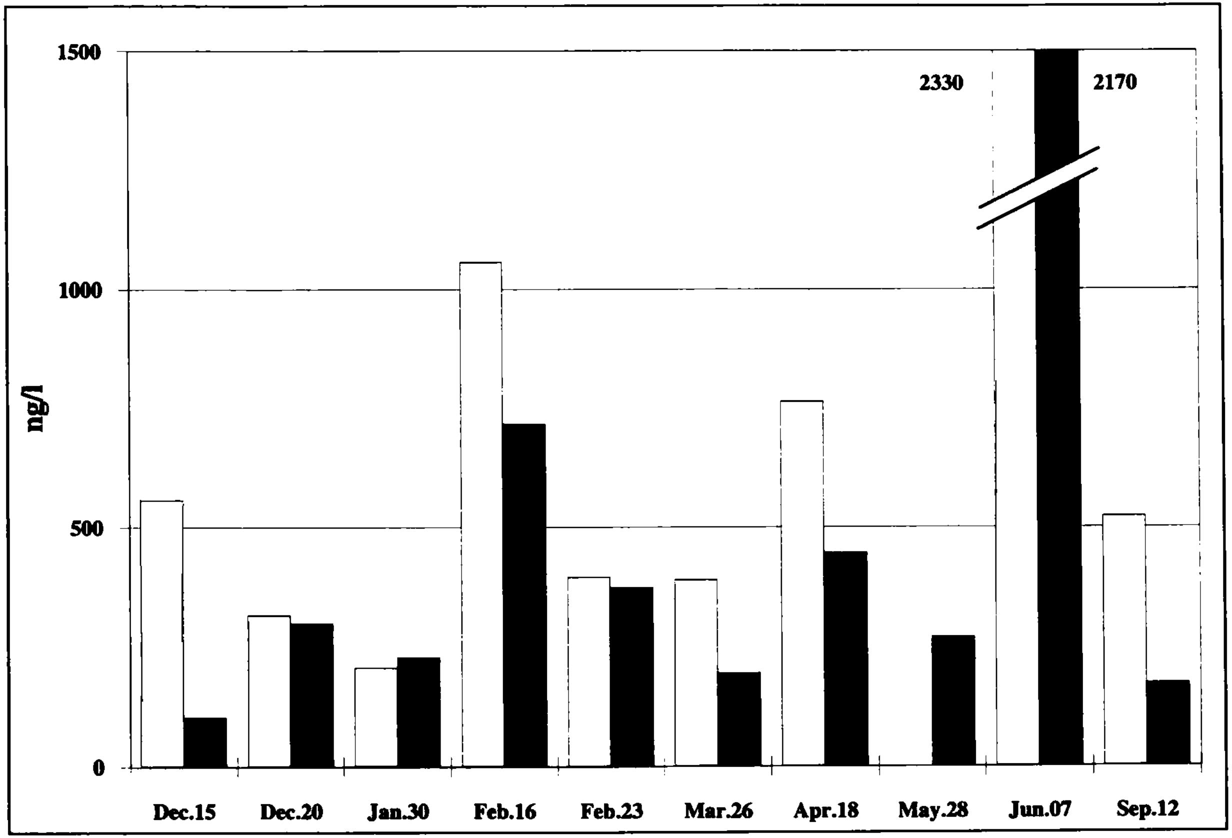

Figure 3b Histogram of the concentration (ng/l) of atrazine ■ and simazine □ in the Dropt river between December 1989 and September 1990

The DAR was constantly about 0.2 in the Mississippi river and its main tributaries in July-August 1991 and reached highest values <1.0 during April-May 1992[10]. It is worth noting the high values of the DEA/(Atrazine+Simazine) ratio (DAS) in the Garonne river (Tables 1 and 2). In fact, the DAR cannot be quantified when simazine is used on the drainage basin in substantial amounts. DAS values in the Garonne river are <1.0 when the water discharge is at its low level. Alluvial aquifers may play a considerable role in herbicide transport by storing them during the rainfall period and releasing them selectively during low water flow, depending on their physical and chemical properties (water solubility, Koc, polarity . . .). The DAS ratio may be related to the high proportion of simazine relative to atrazine but cannot be correlated with simazine levels (simazine/atrazine: Mississippi river 1991–1992[10]<0.1; Garonne river 1989–1990<0.11–1.2 and Dropt river 1989–1990<0.9–5.4 (Tables 1 and 2)). DEA is more water soluble than its precursors: atrazine and simazine which also differ considerably in water solubility (atrazine 33 mg/1; simazine 6.2 mg/l) and polarity. This two factors could contribute to the enhanced transport of DEA in preference to the precursors through the unsaturated zone and is in good agreement with the chromatographic effect suggested by Pereira and Hosettler[10].

Several data concerning the rather hieratic occurrence of phenylurea herbicides have been reported in both surface and ground waters. In France, diuron has been detected (2.2–12 μg/l) in leaching water of vineyard basins[8], in Brittany rivers sometimes at high concentrations, 16 μg/l[9] and in the Garonne river (<0.05 μg/l in 1992; Agence de l'eau Adour-Garonne, Toulouse). Chlortoluron, isoproturon, linuron, metoxuron and neburon have also been found in surface water of numerous French rivers (unpublished results). In the Garonne river, diuron is detected at a low level (< 20 ng/l), except in April whereas chlortoluron and isoproturon are observed at detectable concentrations (45 ng/l and 35 ng/l, respectively), only in February (Figure 4a). In the Dropt river, diuron is also monthly detected (> 15 ng/l) and follows the general trend of the triazines with a maximum of an order of magnitude less than triazines in May and June (Figure 4b). In contrast, chlortoluron shows a maximum during the winter (100–250 ng/l) which can be explained because it is applied as a pre-emergent weed-control agent on crops such as winter cereals and owing to the local rainfall.

CONCLUSIONS

In the Garonne river, atrazine, simazine and their degradation products are the dominant herbicides, but diuron also persists in the dissolved phase with a concentration about an order of magnitude lower. This preliminary report suggests that the seasonal application of herbicides and the hydrologic and pluviometric conditions account for the load of atrazine and simazine and some of their degradation products in the Garonne river.

Triazines and their degradation products appear to be a valuable indicator of current contamination of the Garonne river by herbicides; high values of the DEA/(Atrazine+Simazine) ratio are observed during base flow which may be due to the contribution of groundwater to the Garonne river, but further investigations are needed to discover whether if simazine is involved in this phenomenon; thorough evaluation of water quality requires a multiresidue analysis including phenylureas to be taken into account.

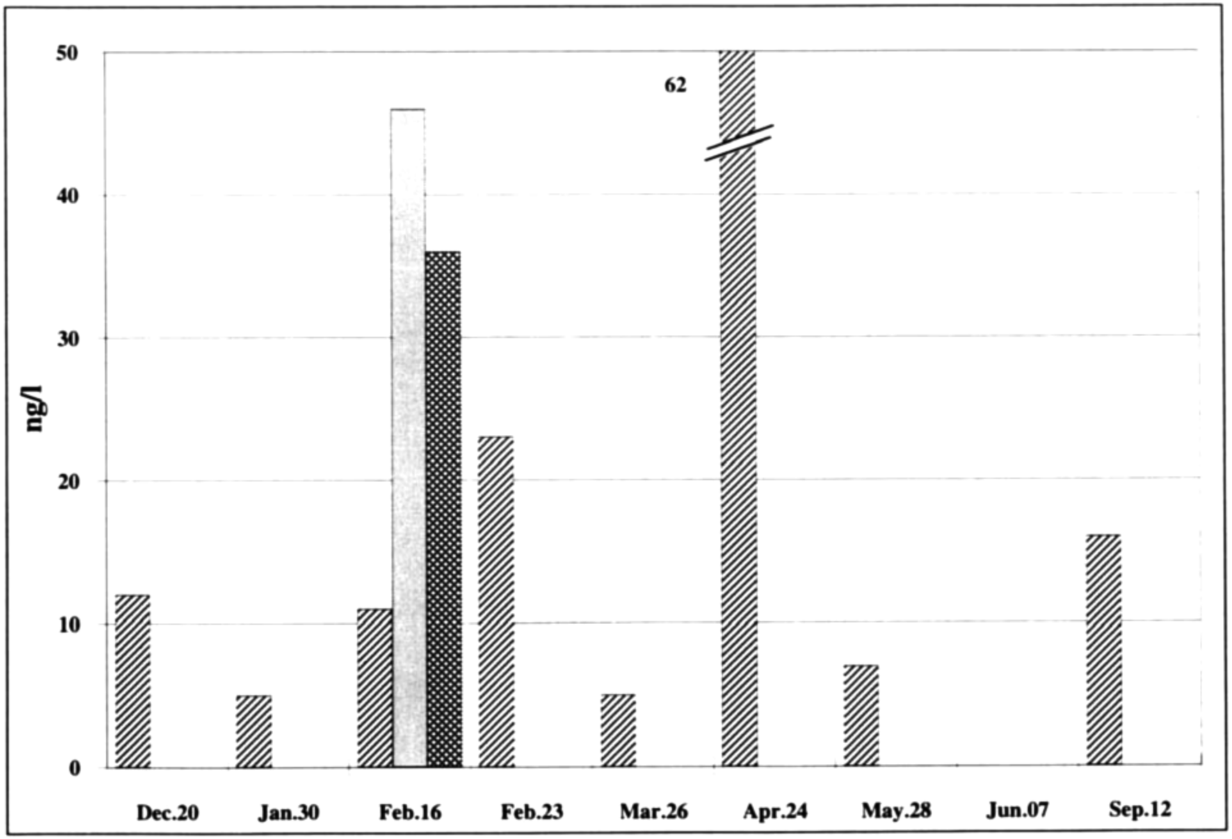

Figure 4a Histogram of the concentration (ng/l) of diuron ▨, chlortoluron ☐ and isoproturon ⊠ in the Garonne river between December 1989 and September 1990

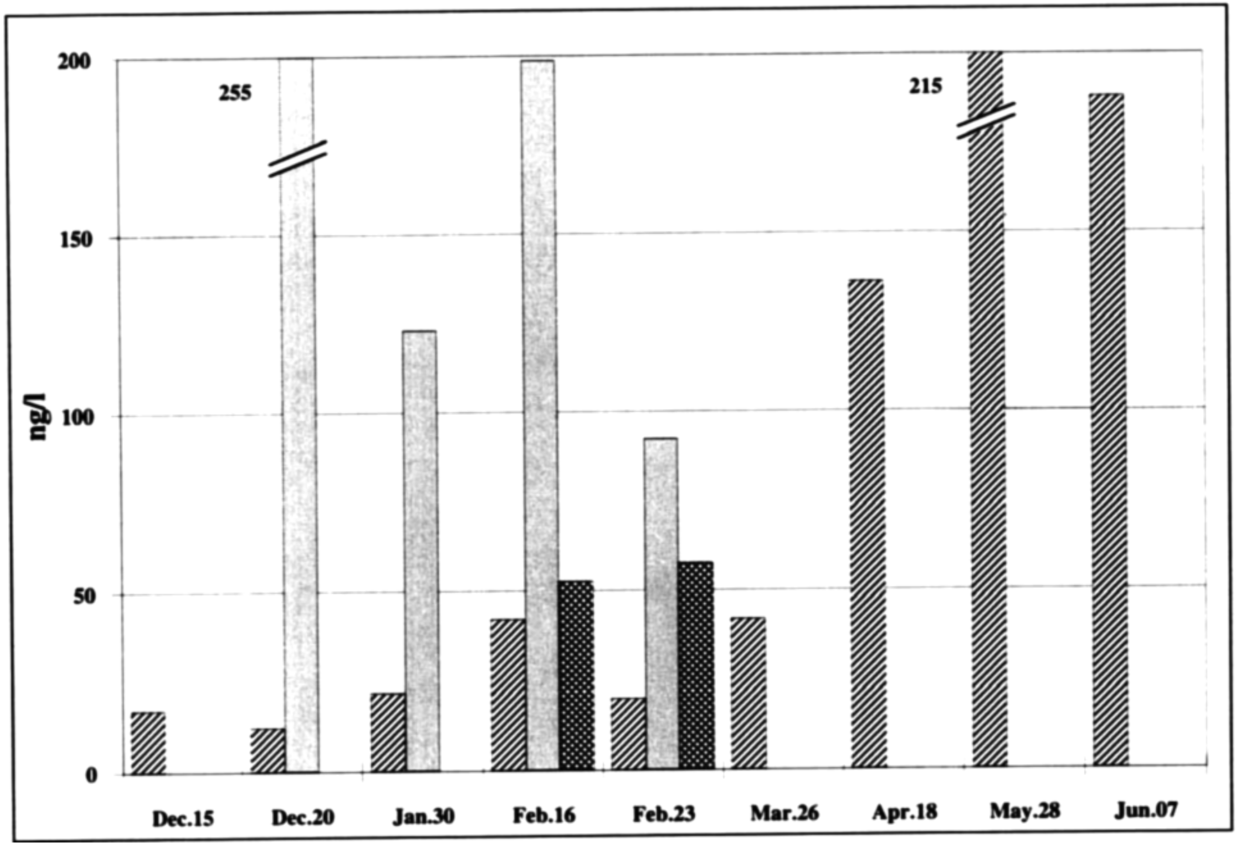

Figure 4b Histogram of the concentration (ng/l) of diuron ▨, chlortoluron ☐ and isoproturon ⊠ in the Dropt river between December 1989 and September 1990

Numerous questions arise concerning transport and fate of phenylurea herbicides in large river systems which are flushed from cropland and non-point sources into the rivers. Further work is necessary to understand the difference in transfer processes of triazine and phenylurea herbicides such as diuron and chlortoluron through the surface water system as pulses in response to the winter and spring rainfalls.

Acknowledgements

This work has been supported by the "Dynamique et Bilan de la Terre" INSU programme (DBT) and the "Observatoire National de Terrain Garonne".

References

1. M. Collet, in: *Evaluation des transferts existants ou potentiels de produits phytosanitaires utilisés en agriculture vers le milieu marin* (Ifremer, Centre de Brest, No. DERO-8804-EL, 1988) pp. 1–111.
2. W. E. Pereira and C. E. Rostad, *Environ.Sci. Technol.*, **24**, 1400–1406, (1990).
3. E. M. Thurman, D. A. Goolsby, M. T. Meyer and D. W. Kolpin, *Environ. Sci. Technol.*, **25**, 1794–1796, (1991).
4. J. Tronczynski, C. Munschy, G. Durand and D. Barceló, *Sci. Total Environ.* **132**, 327–337, (1993).
5. M. C. Hennion, P. Subra, R. Rosset, J. Lamacq, P. Scribe, A. Saliot, *Intern. J. Environ. Anal. Chem.*, **42**, 15–33, (1990).
6. S. Chiron, S. Dupas, P. Scribe and D. Barceló, *J. Am. Soc. Mass. Spectrom.* (in press).
7. B. Bourgouin and S. Safont, *Purpan*, **166**, 105–113 (1993).
8. J. F. Munoz in: *Méthodologie d'étude des produits phytosanitaires. Etude d'un bassin versant viticole: l'Ardière. Mise au point de méthodes analytiques de pesticides* (PhD. Thesis, Université Claude Bernard Lyon I, France, 175pp, 1992).
9. D. Maupas and H. Gillet in: *Premier bilan de la contamination de quelques rivières de Bretagne par les produits phytosanitaires* (Colloque Phyt'eau, 21–22 Octobre 1992) pp. 13–19.
10. W. E. Pereira and F. D. Holsttettler, *Environ. Sci. Technol.*, **27**, 1542–1552 (1993).