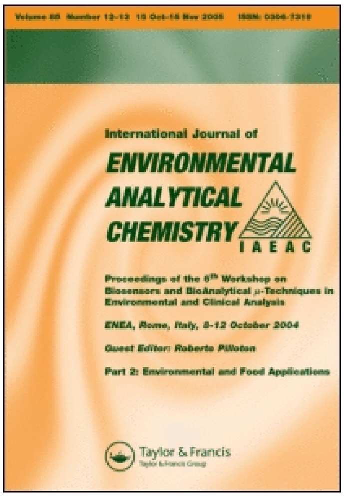

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Two Years of Pesticides Monitoring in a Belgian Watershed

Sabine Beernaerts[a]; Marie Gerard[b]; Philippe Debongnie[a]; Jean-Paul Barthelemy[b]; Luc Pussemier[a]; Alfred Copin[b]
[a] Veterinary and Agrochemical Research Centre (VAR), Ministry of Small Enterprises, Tervuren, Belgium [b] Unit of Analytical Chemistry and Crop Protection Sciences, Agricultural University of Gembloux (FUSAGx), Gembloux, Belgium

To cite this Article Beernaerts, Sabine , Gerard, Marie , Debongnie, Philippe , Barthelemy, Jean-Paul , Pussemier, Luc and Copin, Alfred(2003) 'Two Years of Pesticides Monitoring in a Belgian Watershed', International Journal of Environmental Analytical Chemistry, 83: 6, 469 — 480

To link to this Article: DOI: 10.1080/0306731031000101419

URL: http://dx.doi.org/10.1080/0306731031000101419

Intern. J. Environ. Anal. Chem.
Vol. 83, No. 6, pp. 469–480, June 2003

Taylor & Francis
Taylor & Francis Group

TWO YEARS OF PESTICIDES MONITORING IN A BELGIAN WATERSHED

SABINE BEERNAERTS[a], MARIE GERARD[b], PHILIPPE DEBONGNIE[a],
JEAN-PAUL BARTHELEMY[b,*], LUC PUSSEMIER[a] and ALFRED COPIN[b]

[a] *Veterinary and Agrochemical Research Centre (VAR), Ministry of Small Enterprises, Traders and Agriculture, Leuvensesteenweg, 17, 8030 Tervuren, Belgium;*
[b] *Unit of Analytical Chemistry and Crop Protection Sciences, Agricultural University of Gembloux (FUSAGx), Passage des Déportés, 2, 5030 Gembloux, Belgium*

(Received 15 October 2002; in final form 10 February 2003)

A monitoring study was carried out in 1998–1999 on a medium-sized (c. 4580 km^2) watershed of the Dyle (or Dijle) river in central Belgium, composed of both rural and urbanized areas. This watershed may be considered as representative of a large part of the country. Samples were taken each month from seven sites along the course of the river, plus one from its major affluent the Demer. The eight molecules monitored were the main herbicides used on the major crops in the area, plus some used in nonagricultural sectors. The concentrations found were mostly in the 0–3 μg/L range, with some peaks between 3 and 14 μg/L. The averages over all spring and summer samples analyzed ranged from 0.14 (bentazone) to 1.54 μg/L (diuron). Time and space specific patterns could be observed.

Keywords: Monitoring; Surface water; Herbicides

INTRODUCTION

Monitoring surveys carried out in different countries for many years have shown that agricultural and nonagricultural uses of pesticides lead to the presence of residues in surface and ground waters [1–5]. Diffuse contamination of surface and ground waters is still an important environmental problem [6]. The 80/778/EEC [7] and 98/83/EU [8] directives have set the maximal concentration allowed in drinking water at 0.1 μg/L for each pesticide and 0.5 μg/L for the sum of all pesticides. These concentrations may be exceeded in surface waters, and influence the cost of their potabilization.

In order to better manage this environmental issue, different prediction models were elaborated, as PESTLA, GLEAMS, PELMO, etc. [9] and different possibilities to remove pesticides from waters were developed, as adsorption on activated carbon, ozone treatment, etc. [10–15].

---

*Corresponding author. Fax: +32-81-62 22 16. E-mail: barthelemy.jp@fsagx.ac.be

ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/0306731031000101419

Besides these aspects, it is useful to have data on the current status of surface waters in different countries. In order to comply with the E.C. Guidelines, the Belgian Authorities launched monitoring surveys of pesticides in surface waters. Upon their request, we have selected the watershed of the river Dyle in central Belgium as representative of a large part of this country. This basin is composed of agricultural and urban areas, with various types of topography, and presents the major crops grown in Belgium. The present article gives the results of two years (1998–1999) of monitoring of eight herbicides in eight sites of the Dyle basin. In a first approach, we decide to dedicate the monitoring of pesticides except metabolites and breakdown products in the water part exclusively.

EXPERIMENTAL

Analytical Methods of Pesticides in Water

Analytical Methods for Bentazone, Chloridazon, Lenacil and Metolachlor

LC analyses were performed with a HPLC Beckman with GOLD System, including a Programmable Solvent Module 126 and a Diode Array Module 168 Detector. The injection loop is 50 μL. GC analyses were performed with a GC Carlo Erba Top 8000 including a NPD Detector and an On column Injector.

The HPLC analytical column was 25 cm × 4 mm I.D. packed with 5-μm Nucleosil 100-5 C18 HD (Machery-Nagel). The G.C. was provided with a WCOT column (30 m; 0.32 mm I.D.; 0.25 μm CP-Sil 8 CB (Chrompack)). The SPE cartridges which were used for water extraction are special cartridges. 500 mg bulk C18 (Waters) are added to a cartridge Oasis 3cc (60 mg).

All organic solvents were purchased "chromatographic grade". LC-quality water was prepared by purifying distilled water in a Milli-Q filtration system (Millipore). Other chemicals were obtained from Merck. The various pesticides were supplied by Dr. Ehrenstorfer. Stock standard solutions of 100 mg/L of each pesticide were prepared by weighing and dissolving them in methanol. These standard solutions were stored at 4°C and were used for the preparation of dilute working standard solutions and for spiking water samples.

The analytical method for bentazon, chloridazon and lenacil is based on a SPE (off-line)-HPLC-DAD method which is described elsewhere. The analytical method for metolachlor is based on a SPE (off-line)-GC-NPD method which is equally described elsewhere [18].

The recoveries for each pesticide correspond to the European demands of 91/414/EEC-guideline on residue analytical method, that set SPE recovery values between 70 and 110% with R.S.D. below or equal to 20%. These methods allow to reach the quantification limit for each product of 0.05 μg/L in distilled water.

Analytical Methods for Atrazine, Isoproturon, Simazine and Diuron

These analyses were performed by on-line SPE-LC-DAD, by a method described elsewhere [19,20]. Briefly, 20 mL of sample prefiltered on 0.22 μm "Anodisc" (Whatman filters) were injected using a Gilson "222 XL" XYZ-arm robot and a ThermoQuest

P4000 pump on a "Sentry Nova-Pak" C-18 guard column (3.9 mm × 20 mm, 4 µm beads, Waters). The herbicides retained on the guard column were then eluted on a "Alltima" C18 analytical column (4.6 mm × 250 mm, 5 µm beads, Alltech). Each sample was injected twice and eluted with different gradients (from 5% ACN to either 100% ACN or 50:50 MeOH:ACN in 40′). The recoveries vary between 102 and 110%, with standard deviations < 10%. The limits of quantification reach 0.05 µg/L or better in pure water. An intern standard (metoxuron) was added in each sample.

Watershed Description

The Dyle (or Dijle) basin is located in the center of Belgium in the two Brabant provinces, with mainly loamy sand soils. It has three large subbasins: Demer, Gette and Senne (or Zenne). Annual precipitations are between 750 and 800 mm.

General and agronomic information is given in Table I. The surface of the basin and subbasins represents 15% of the total surface of Belgium and 14% of the total agricultural surface in Belgium. The major crops are cereals, beets and maize, but some vegetables are also cultivated in these areas. A great part of the Belgian fruit crop is located in the Demer subbasin.

The molecules followed and their major crop applications are given in Table II. These are important herbicides used in the major crops and in the nonagricultural sector (municipalities, gardening companies and private uses).

The estimated amount applied for each molecule followed is given in Fig. 1. These amounts were taken from SEPTWA (System for the Evaluation of Pesticide Transfer to Waters) [20]. This expert system has been developed at VAR and is based on pesticide use data from the Ministry of Agriculture – DG 4 (surveys of the average amounts actually applied per hectare and per year for each crop) and from the National Institute of Statistics (areas devoted to each crop). For the nonagricultural sector (municipalities, private, garden keeper and railway), the amounts applied are estimated on the basis of data from the companies (total amounts sold, and repartition of these sales into agricultural and nonagricultural sectors), and these estimates were checked insofar as possible through comparisons with the results of VARs surveys of municipalities' and railways' uses.

TABLE I Inhabitants and major crops in the Dyle basin and subbasins (Demer–Gette–Senne)

	Dyle basin	*Subbasins*	*Total*	*% Belgium*[c]
Inhabitants[a]	1 749 721	821 216	2 570 937	25
Total area (ha)	183 800	274 135	457 935	15
Agricultural area (ha)	66 306	132 129	198 435	–
Agricultural area (%)	36	48	43	14
Major crops (ha)[b]				
Cereals (winter wheat and winter barley)	29 100	34 285	63 385	24
Beets	11 485	14 874	26 359	26
Maize	10 582	15 775	26 357	13

[a] In 1993; [b] in 1998; [c] fraction of the total value in Belgium.

TABLE II The physico-chemical properties and uses of the eight molecules followed in the Dyle monitoring. K_{oc} = soil/water distribution coefficient (K_d) divided by organic carbon content of the soil (mobility criteria)

Molecule	*Pesticide group*	*Crop application*	K_{oc}	*Solubility in water* (mg/L) *at* 20°C[b]
Atrazine	Triazine	Maize	97[b]	33
Simazine	Triazine	Nonagricultural sector[c] (and fruit)	102[a]	6.2
Diuron	Phenylurea	Nonagricultural sector[c] (and fruit)	399[a]	42
Isoproturon	Phenylurea	Cereals	483	65
Metolachlor	Chloroacetamide	Maize and beets (and bean)	172	488
Chloridazon	Pyridazinone	Beets	110[a]	0.34
Lenacil	Uracil	Beets (and spinach)	17	6
Bentazone	Benzothiadiazinone	Maize (bean and pea)	42[b]	570

[a][16]; [b][17]; [c]uses by municipalities, private, garden keeper and railways.

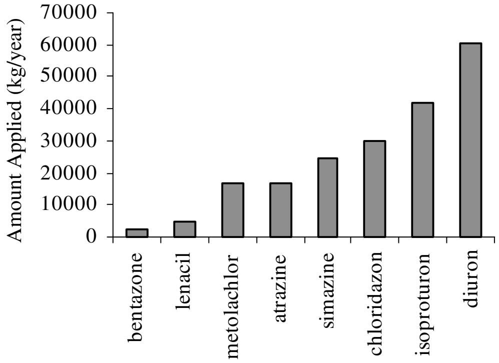

FIGURE 1 Estimated amount of the eight herbicides followed in the monitoring annually applied in the basin (and subbasin).

Sampling Strategy

Samples were taken every month from seven sites along the course of the river, plus one from its major affluent the Demer, just before the confluence point. The location of the sampling sites are shown in Fig. 2 and details about each sampling point are given in Table III. The aim was to see whether differences due to local agronomical, urban, and/or pedological conditions could be observed.

Those herbicides which are likely to be applied over long periods (nonagricultural uses of diuron, simazine and possibly atrazine) or at different times of the year (isoproturon on summer and winter cereals) were measured throughout March 1998 to October 1999. Lenacil, bentazone, chloridazon and metolachlor, used essentially in the spring, were measured only in the spring and summer.

RESULTS AND DISCUSSION

The concentrations measured for the eight herbicides monitored are given in Figs 3–6. Most of these concentrations were in the 0–3 μg/L range, with occasional higher peaks

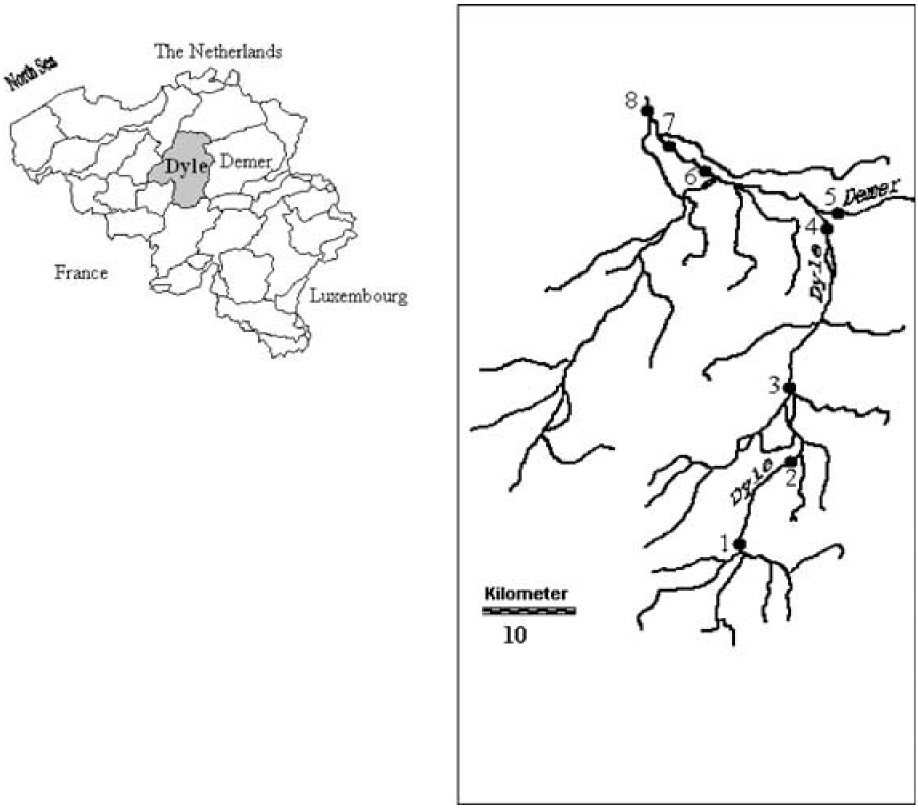

FIGURE 2 Location of the eight sampling sites in the Dyle basin: site 1, Dyle in Court-Saint-Etienne; site 2, Dyle in Gastuche; site 3, Dyle in Sint-Joris-Weert; site 4, Dyle in Werchter; site 5 Demer (affluent) in Werchter; site 6 Dyle in Muizen; site 7 Dyle in Battel and site 8 Dyle in Battenbroek.

TABLE III Characteristics of the region down the sampling points in the Dyle basin

Site number	*Sampling point*	*Particularities*
1	Court-Saint-Etienne	Arable land, loamy soil, hilly region
2	Gastuche (Just after municipal waste water treatment plant)	Arable land, Urban center (town of Wavre), loamy soil, hilly region
3	Sint-Joris-Weert	Arable land, loamy soil, hilly region
4	Werchter (Dyle)	Urban center (town of Leuven), fairly flat region, sandy soil
5	Werchter (affluent : Demer)	Fruit farming (Demer), Urban centers
6	Muizen	Urban centers, vegetables farming, fairly flat region, sandy soil
7	Battel (Just before municipal waste water treatment plant)	Urban center (town of Mechelen), vegetables farming, fairly flat region, sandy soil
8	Battenbroek (Mouth)	Just after the confluence with Zenne, (subbasin with an important urban, center)

(up to 14 μg/L chloridazon in Site 1, May 99). For the ease of comparison, the same *y*-axis (0–3.3 μg/L) was used for all graphs, and an axis break was added where necessary. The application periods expected on the basis of normal agricultural and/or nonagricultural practices are indicated as dashed boxes.

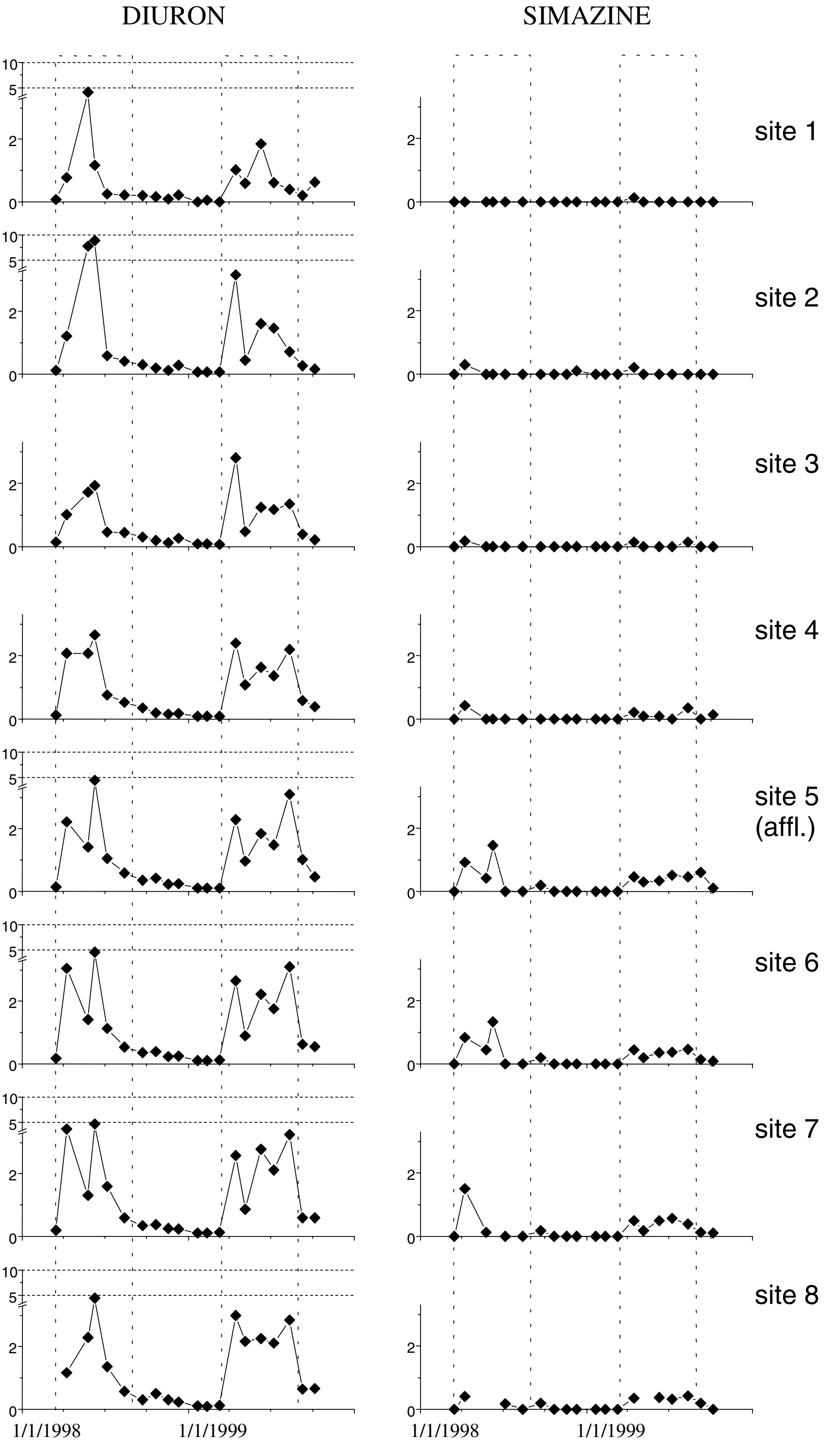

FIGURE 3 Diuron and simazine concentrations in 1998–1999 at eight sampling sites in the Dyle basin.

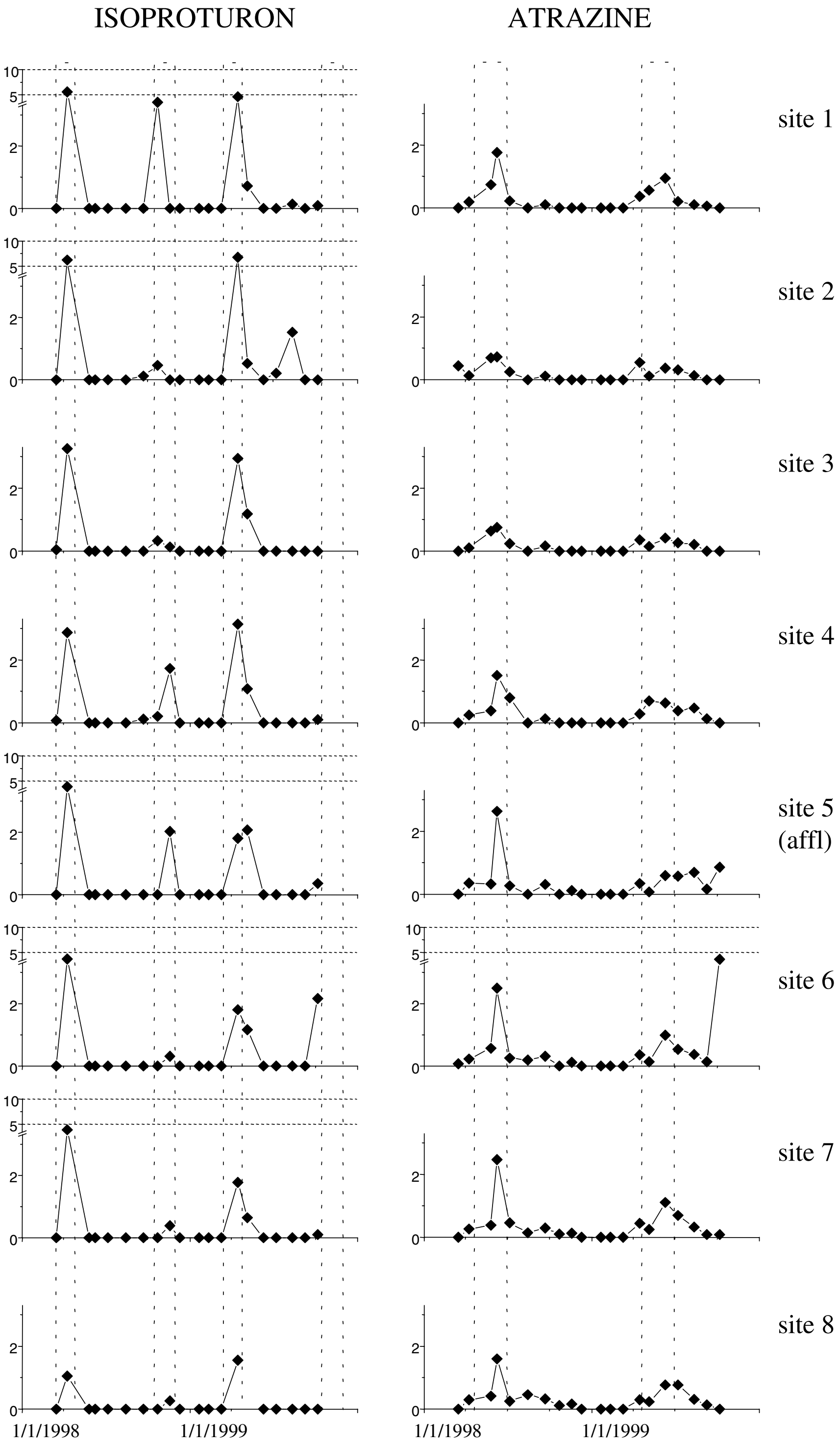

FIGURE 4 Isoproturon and atrazine concentrations in 1998–1999 at eight sampling sites in the Dyle basin.

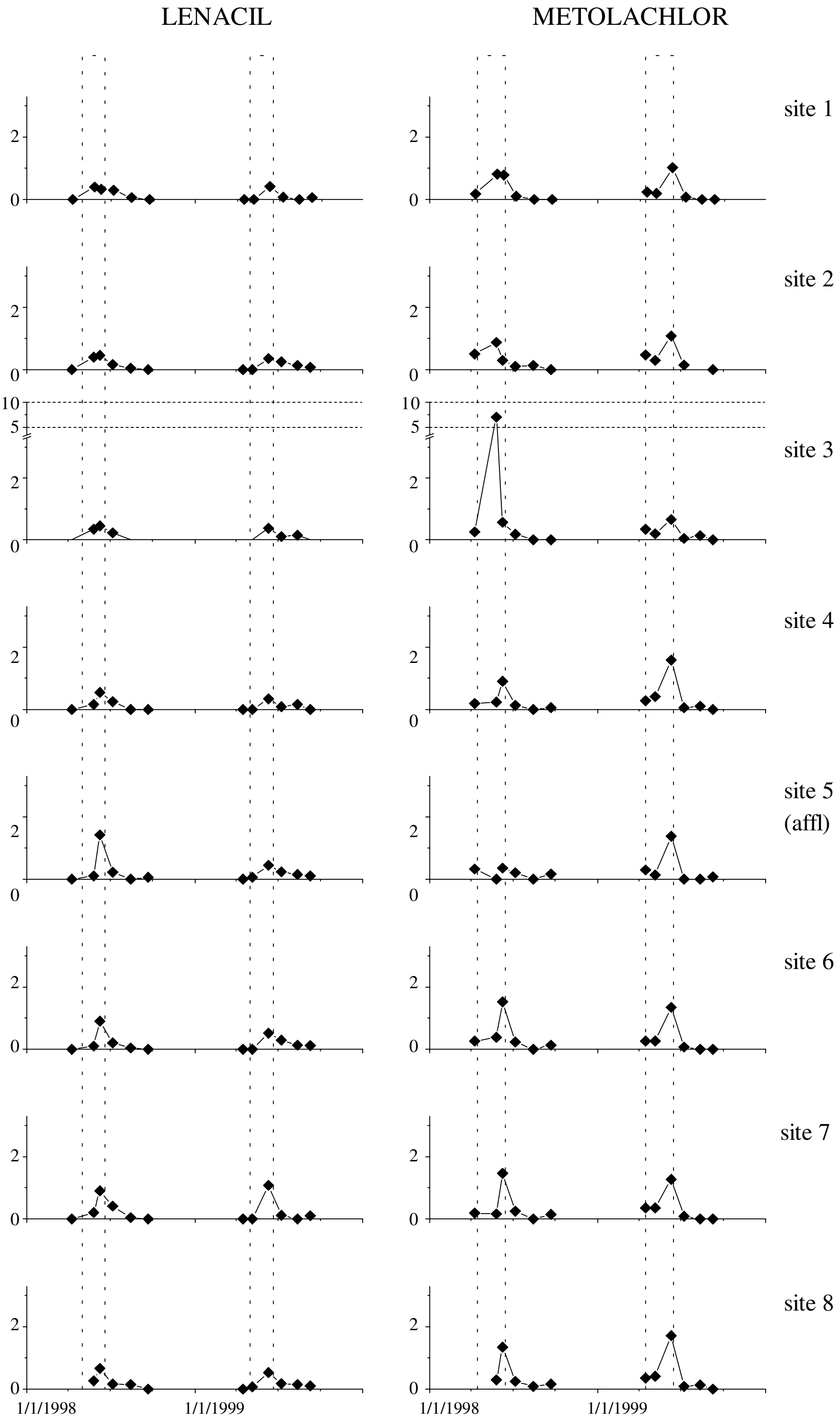

FIGURE 5 Lenacil and metolachlor concentrations in 1998–1999 at eight sampling sites in the Dyle basin.

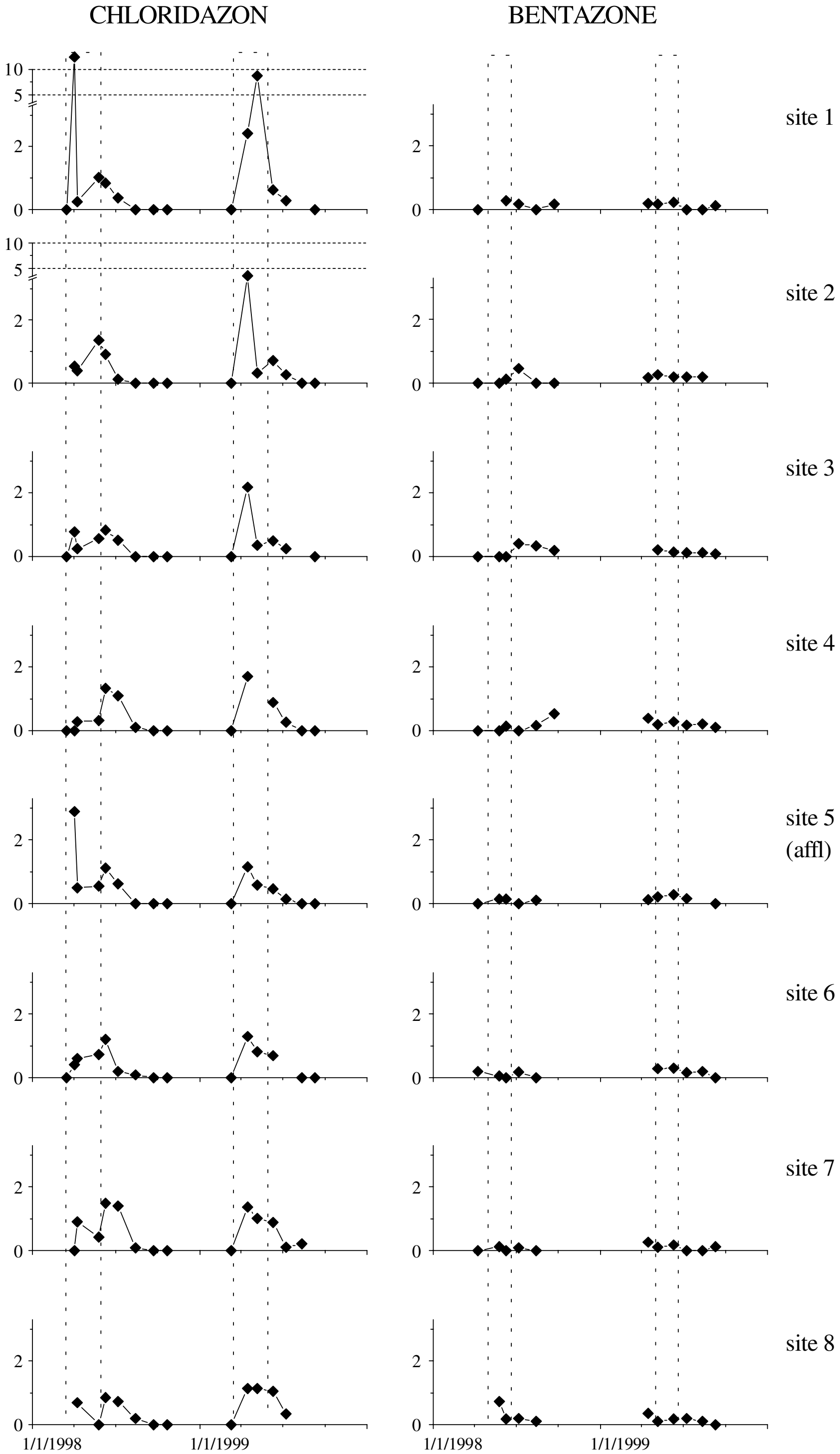

FIGURE 6 Chloridazon and bentazone concentrations in 1998–1999 at eight sampling sites in the Dyle basin.

Time Patterns

The time patterns reflect the application periods expected. Accordingly, isoproturon was observed only in short periods in early spring (April 1998, April–May 1999: 1–7 μg/L), and again in October (0–3 μg/L). All other pesticides were present for longer periods, often throughout spring and summer, expecially diuron (> 0.50 μg/L throughout April–July 1998 and April–September 1999). In 1998 all herbicides measured except isoproturon and bentazone peaked in the beginning of June, which was very wet and followed an unusually dry month of May. In 1999 the concentrations in the lower part of the river were fairly constant throughout April–August for diuron (1–3 μg/L) and simazine (0.3–0.5 μg/L).

All eight pesticides were measured throughout spring and summer 1998 and 1999. The average concentrations found in these periods ranged from 0.14 μg/L (bentazone) to 1.54 μg/L (diuron).

Four herbicides (diuron, isoproturon, atrazine and simazine) were also measured in autumn 1998 to winter 1999. As could be expected, in the coldest part of the year (December 1998 to March 1999), no isoproturon or atrazine was detected, and simazine was found only in one sample (0.1 μg/L, Site 2, December 1998). In contrast, diuron, used mainly in the nonagricultural sector, was still present above 0.10 μg/L in 19 out of the 32 samples, with averages of 0.24 μg/L in December and 0.08–0.09 μg/L in the three following months.

Space Patterns

The concentrations of the different herbicides changed in various ways along the course of the river. The evolution of the concentrations measured on a single day gives a snapshot of the situation on that day. In some cases profound changes between the different sites can be observed. One example is 6th June 1998 (Fig. 7), when (a) diuron peaked at 9.25 μg/L at Site 2, and (b) atrazine, simazine and diuron strongly increased in Site 6, just after the confluence with the Demer. In this particular case the concentrations found in the Demer (Site 5) confirm that this affluent is the main source of this increase, but not the only source, since an increase of atrazine and diuron was already visible in Site 4. In other cases (Fig. 8), such as metolachlor in Site 3 (Sint-Joris-Weert) on

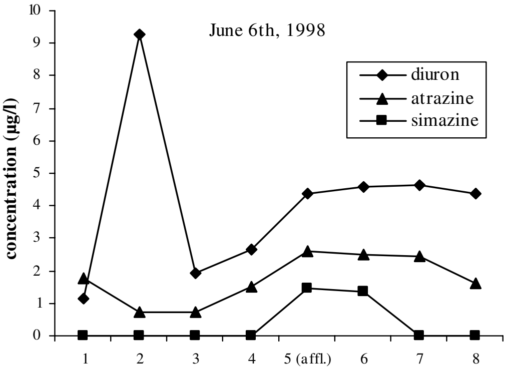

FIGURE 7 Diuron, atrazine and simazine concentrations at eight sites in the Dyle basin on 6th June 1998.

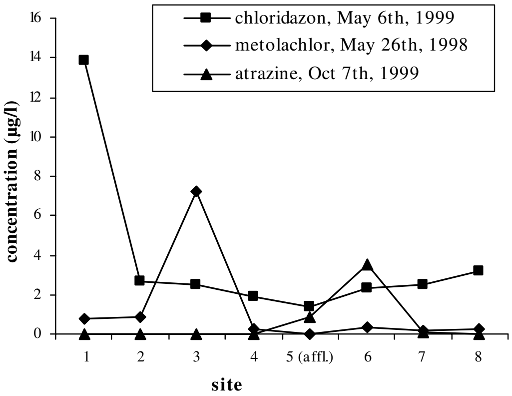

FIGURE 8 Chloridazon, metolachlor and atrazine concentration at eight sites in the Dyle basin on a specific day.

6th May 1998 (7.25 µg/L) or atrazine in Site 6 (Muizen) on 7th October 1999 (3.55 µg/L), the peaks observed are probably due to run-off according to the meteorological conditions or to point source contaminations. But it is impossible to determine where those point sources were situated, since this could be any distance upstream. Indeed, the only way to separate with certainty the contributions of two successive parts of the same river would be to raise the frequency of sampling so that the time interval between two successive samples is shorter than the time it takes the water to travel from one site to the other, i.e. probably only 1 to 2 days from, e.g., Sites 3 to 8. For the same reason, apparent decreases with distance from the source (e.g., chloridazon on 6th May 1999, Fig. 8: from 13.8 µg/L in Site 1 to 1.9 µg/L in Site 4) should not be attributed indiscriminately to processes such as dilution, degradation and/or immobilization on sediments, since they could as well be actually due to this snapshot effect.

SUMMARY AND CONCLUSIONS

During this two-year monthly monitoring of eight herbicides at eight sites in the Dyle basin, the average concentrations measured during spring and summer ranged from 0.14 (bentazone) to 1.54 µg/L (diuron). The spatial trends along the course of the river varied: some pesticides increased (e.g., diuron), while others decreased (e.g., isoproturon), and simazine increased significantly due to the contribution of the Demer (the major affluent of the Dyle).

Such a monitoring can give good snapshots of only parent molecules of studied pesticides at different times and places in the basin, and thus of the general quality of its surface waters. However it must be remembered that, due to transient peaks, the concentrations at any point can change quickly, and that one must, therefore, be very careful in interpreting the results in terms of total loads or of respective contributions of the different parts of the basins. For such purposes, point samples should be replaced by an automatic sampling equipment which can work in direct proportion to time or to flow.

Acknowledgements

The authors are grateful to the Ministry of Agriculture, DG 4 and DG 6 – Research and Development and by Phytofar – Belgian Federation of Producers and Distributors of Pesticides whose funded enable this work.

References

[1] R. Hopman, C.G. van Beek, H.M. Janssen and L.M. Puijker, *H_2O*, **7**, 176–185 (1992).

[2] C. Bertinchamps and R. Savoir, *Bull. Information Anseau,* 57–73 (1993).

[3] M. Schiavon, C. Perrin-Ganier and J.M Portal, *Agronomie*, **15**, 157–170 (1995).

[4] S. Bouland, S. Royer, A. Montiel and B. Welté, *Journal Européen d'Hydrologie*, **29**, 79–87 (1998).

[5] E. Chauveheid, C. Bertinchamps and R. Savoir, *Tribune de l'eau*, **600–601**, 75–83 (1999).

[6] T.A. Albanis and D.G. Hela, *Intern. J. Environ. Anal. Chem.*, **70**, 105–120 (1998).

[7] x1. Council Directive of 15 July 1980 (80/778/EEC) relating to the quality of water intended for human consumption O. J. n° L-229/11 of 30/08/80.

[8] x2. Council Directive of 3 November 1998 (98/83/E.U) on the quality of water intended for human consumption O. J. n° L-330 of 05/12/98, pp. 0032–0054

[9] J. Cornejo and P. Jamet coord, *Pesticide/Soil Interactions. Some Current Research Methods*, INRA Edn., p. 479 (2000).

[10] V. Camel and A. Bermond, *Wat. Res.*, **32**, 3208–3222 (1998).

[11] F.J. Beltran, J. Rivas and B. Acedo, *J. Environ. Sci. Health*, **34**, 449–468 (1999).

[12] S. Chiron, A. Fernandez-alba, A. Rodriguez and E. Garcia-Calvo, *Wat. Res.*, **34**, 366–377 (2000).

[13] N.H. Ince and I.G. Apikyan, *Wat. Res.*, **34**, 4169–4176 (2000).

[14] J. Rositano, G. Newcombe, B. Nicholson and P. Sztajnbok, *Wat. Res*, **35**, 23–32 (2001).

[15] M. Gérard, *Etude de l'adsorption sur le charbon actif et de l'ozonation des eaux sur l'élimination de différents herbicides des eaux potabilisables*, p. 280. PhD Thesis Faculté Universitaire des Sciences Agronomiques de Gembloux (2002).

[16] J.B.H.J. Linders, J.W. Jansma, B.J.W.G. Mensink and K. Otermann, *Pesticides: Benefaction or Pandora's Box? A Synopsis of the Environmental Aspects of 243 Pesticides*, p. 204. National Institute of Public Health and Environmental Protection (rivm)-Report no 679101014-Bilthoven, The Netherlands (1994).

[17] Pesticide Manual – Tenth Edition, p. 1341. Crop Protection Publications, Clive Tomlin (1994).

[18] M. Gérard, J.-P. Barthélemy and A. Copin, *Intern. J. Environ. Anal. Chem.*, **80**, 281–294 (2001).

[19] P. Debongnie, S. Beernaerts and L. Pussemier, In: *The Seventh Symposium on the Chemistry and Fate of Modern Pesticides*, 14–16 September. Lawrence, Kansas, USA (1999).

[20] L. Pussemier and S. Beernaerts, In: *Umweltbundesamt. Pesticide Emissions into Water Bodies – Modelling and Measure*, 30–37 (text 85/99), 12–13 January. Berlin, Germany (1999).