Short communication

Dissipation of some citrus selective residual herbicides in an irrigation well

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Abstract

The aim of this work was to study the behaviour of some of the main citrus selective residual herbicides in the water of an irrigation well. The chemicals used were: atrazine, simazine, terbuthylazine, terbutryn, terbumeton, bromacil and diuron. The simetric triazines and bromacil were analyzed by gas chromatography and diuron by HPLC. The mentioned pesticides were introduced in the well in order to simulate a point-source contamination. Levels of contamination of the well due to herbicide application were about 1 mg/l, however, dissipation of the herbicides was almost complete 8 days after application, except for bromacil and diuron which persisted longer than the *s*-triazines.   © 1998 Elsevier Science B.V.

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1. Introduction

The *s*-triazines bromacil and diuron are, among the residual herbicides, the most frequently applied for weed control in citrus orchards. These pesticides can be applied alone or, more frequently, in mixtures, to control a broad spectrum of weeds. Fig. 1, shows the chemical structures of these herbicides.

Gómez de Barreda et al. [1–3] reported data from several surveys in wells of citrus orchard areas, showing *s*-triazines and diuron at very low levels (range between less than detection limit and 11 µg/l) and higher levels of bromacil (range between limit of detection and 22.7 µg/l), but the samplings were always done in orchards with a high risk of contamination, like a long history of continuous use of herbicides and/or unusual periods of heavy rain.

In general, these herbicides have a very low water

solubility, except for bromacil which achieves 815 mg/l, even the K_{oc} of the uracil derivative is very low (32 ml/g). Bromacil is a good candidate for leaching and, therefore, a groundwater contaminant. In addition, triazines and diuron have high persistence in soils which makes them risky herbicides in flood irrigated citrus orchards. However, high temperatures and lack of rainfall during most of the year have reduced the problem of leaching to weak applications with high doses in light soils or leaking due to accidents near wells. Perhaps, leakage from sites used for rinsing of tractors and sprayers could be the main cause of groundwater contamination in this area.

Diuron, atrazine and simazine, were detected during 1993 in wells around the Belgian town of Louvaine-la-Neuve. The range of concentrations were around 0.7–1.6 µg/l for atrazine and 0.6–3.4 µg/l for diuron [4].

There is still considerable uncertainty as to
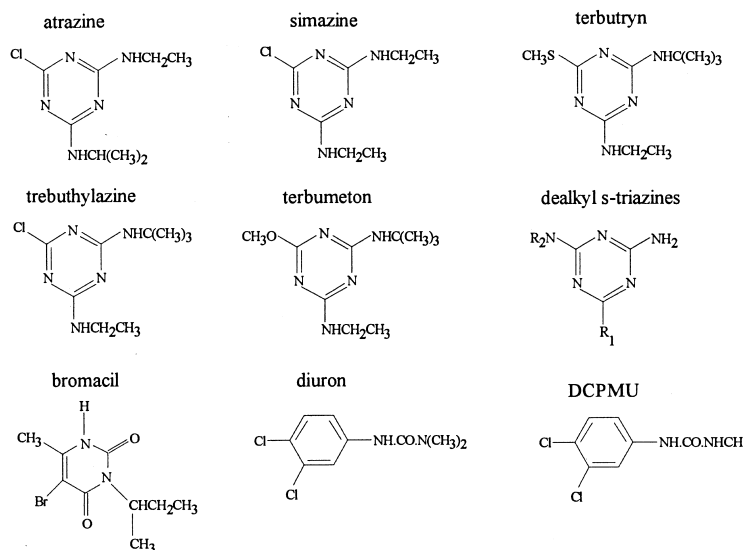
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Fig. 1. Chemical structures of the seven herbicides applied and degradation products analyzed.

whether such contamination results from the widespread use of pesticides in agriculture, their more limited but higher rate non-agricultural usage or from individual point source events [5].

The purpose of this paper is to show the dissipation of the seven herbicides in a particular well as a consequence of a leakage simulation.

2. Experimental

The herbicides, were diluted in a stainless steel vessel, introduced in the well with a 45-m rope tightened to the external parts of the well and thoroughly mixed by an up and down movement of the rope. The temperature of the water in the well was $11\pm1°C$. The theoretical initial concentration that we wanted to achieve was 10 $\mu g/l$.

The experiment was repeated with the same herbicides, but trying to achieve 1 $\mu g/l$ as first concentration.

The first experiment began on the 31st March 1995 and six samplings were done: 0, 4, 8, 36, 63 and 96 days after application. The second experiment began on 7th September 1995 with seven samples taken 0, 0.25, 4, 8, 38, 91 and 174 days after application. In both experiments, two 1-l bottles were

taken in each sampling and they were immediately frozen or analyzed.

Fig. 2, represents a section of the irrigation well. It is an old well, with a first drilling of 3-m diameter to a 46-m depth and a second drilling of 0.25-m diameter to a 64-m depth. The perforation cuts two gravel aquifers, the first one at 28-m depth and the second at 63-m depth. There is a 40 CV electric
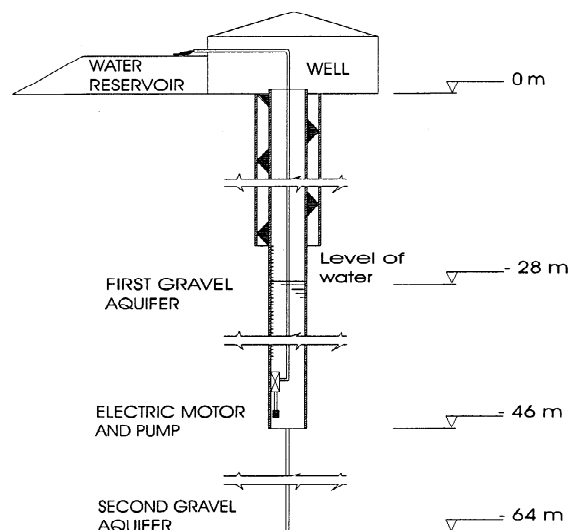

Fig. 2. Section of irrigation well.

engine with a vertical pump which delivers 29 l/s of water (1 CV≈735.5 w).

Several papers [6–8], dealing with the same residual herbicides were considered before beginning the analyses.

2.1. Extraction from water

A 1-l volume of water was filtered through a filter paper and 5 ml of methanol was added. A Bond Elut column C_{18} (size 6 ml, 500 mg) from Varian (Harbour City, CA, USA) was conditioned with 10 ml of ethyl acetate, vacuum was applied and 5 ml of methanol was added. Water was filtered through the Bond Elut column for 30–60 min, then the column was dried for 30 min.

The sample was eluted with 3×7 ml of ethyl acetate and a vacuum pump. The extract was collected in a 50-ml flask and evaporated at 35°C, in a rotary vacuum evaporator till dryness. The residue was redissolved in 1 ml of ethyl acetate and transferred to a vial, ready for gas chromatography determination of bromacil and the *s*-triazines. For

diuron determination on HPLC, the vial was dried under a nitrogen stream and redissolved in the mobile phase, methanol–water (70:30, v/v).

2.2. HPLC and GC determination

2.2.1. Standard materials
All materials were of the highest purity available. Bromacil 99,8% and diuron 99% from Dupont (Wilmington, DE, USA), simazine 99% and ter-butryn 99% from Agan Chemicals, atrazine 96%, terbuthylazine 97% and terbumetone 96,4% from Ciba (Basel, Switzerland.

Fig. 3, shows a GC chromatogram of a mixture of standards of bromacil and the *s*-triazines and Fig. 4, an HPLC chromatogram of a diuron standard.

2.2.2. Reagents
Methanol and ethyl acetate used for pesticide residue analysis both had a degree of purity of 99.8% and came from Scharlau (Barcelona, Spain). Water was of HPLC grade, obtained from a nanopure II system (Barnstead, Dubuque, USA).
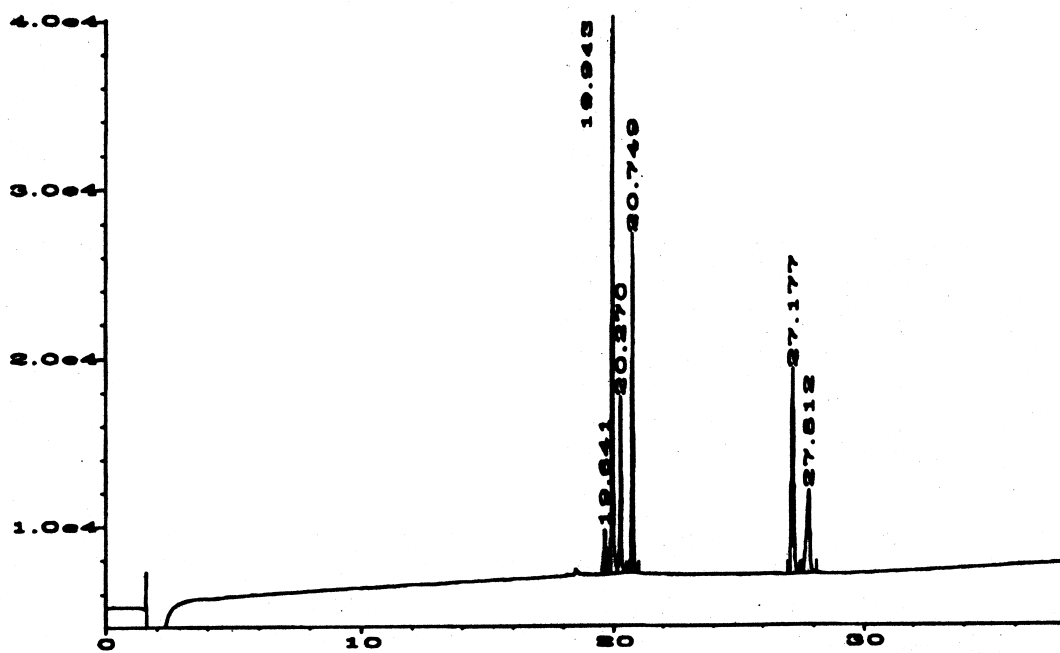

Fig. 3. GC of a standard mixture containing: simazine, atrazine, terbumeton, terbuthylazine, terbutryn and bromacil in order of appearance. Carrier gas, helium; flow-rate, 1 ml/min; nitrogen–phosphorus detector.
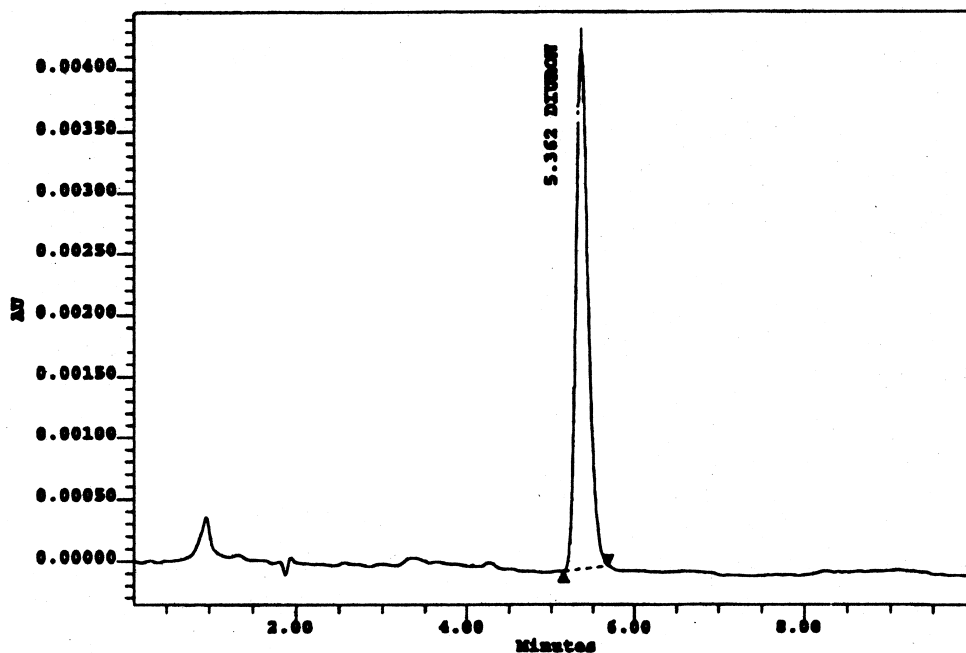
Fig. 4. HPLC of a diuron standard. Mobile phase, methanol–water (70:30, v/v); flow-rate, 1.3 ml/min; photodiode-array detection at 250 nm.

Gas chromatography was performed with a HP 5890 A model (Hewlett Packard, Palo Alto, CA, USA) with a nitrogen–phosphorus detector; automatic injector, HP 7674 A; data station, Vectra QS/ 20 HP. HPLC was performed on a model 1090 liquid chromatograph (Hewlett Packard), an autoinjection system and a photodiode array detector. Instrumental control was effected with a model 9000 series Chemstation using LC-PASCAL software (Rev 5.22). Detection limit on GC and HPLC was 0.1 μg/l. Linearity range for the s-triazines was 0–2 mg/l and 0–10 mg/l for bromacil and diuron.

2.2.3. Gas chromatography

Column, methyl silicone (50 m×0.2 mm I.D., film thickness 0.33 μm). The carrier gas was helium with a 1 ml/min flow-rate. The oven temperature programme was: Initial temperature of 100°C for 2 min, then a first ramp of 5°C/min to 180°C and a second ramp of 2°C/min to 200°C, which was the final temperature. The injector temperature was 270°C and the detector temperature 300°C. The injection volume was 1 μl.

Table 1
Recovery data of some of the seven citrus selective residual herbicides in water (concentration 1 μg/l)

Compound	Mean recovery (%)	S.D. ($n=5$)
Diuron	98	4.5
Simazine	114	7.4
Atrazine	113	5.7
Terbuthylazine	94	5.6
Terbumeton	103	13.7

Table 2
First experiment — concentration of herbicides in well water samples (μg/l)

	Days after treatment					
	0	4	8	36	63	96
Bromacil	191.5	191	11.8	6.1	1.1	1.4
Diuron	425.5	290.1	7.1	4.1	1.9	4.45
Atrazine	128.6	3.6	0.5	0.1	0.1	<1d
Simazine	463.8	25.35	1.6	0.6	0.3	0.2
Terbumetone	258.8	8.9		0.3	0.15	0.1
Terbuthylazine	273.6	10.1	1.1	0.3	0.15	<1d
Terbutryn	290.1	10.75	1.1	0.1	0.1	<1d

<1d, less than limit of detection.

2.2.4. High-performance liquid chromatography

The detector was an HP photodiode array detector, 250 nm; bandwidth 20 nm (reference, 390 nm, 110 nm); column, Lichrosorb RP-$_{18}$, 5 μm, 250×4.6 mm, Merck (Darmstadt, Germany); mobile phase, methanol–water (70:30, v/v); flow-rate, 1.3 ml/min; injection volume, 10 μl.

Table 1 shows the results of the recovery test of some of the herbicides used in the experiment.

3. Results

Table 2 shows the herbicide content as a function of the sampling date over the first experiment. We wanted to achieve an initial concentration of 10 μg/l, however the first sample had a concentration range between 128–463 μg/l, probably due to a bad estimation of the water volume in the well and the short dilution time between application and first
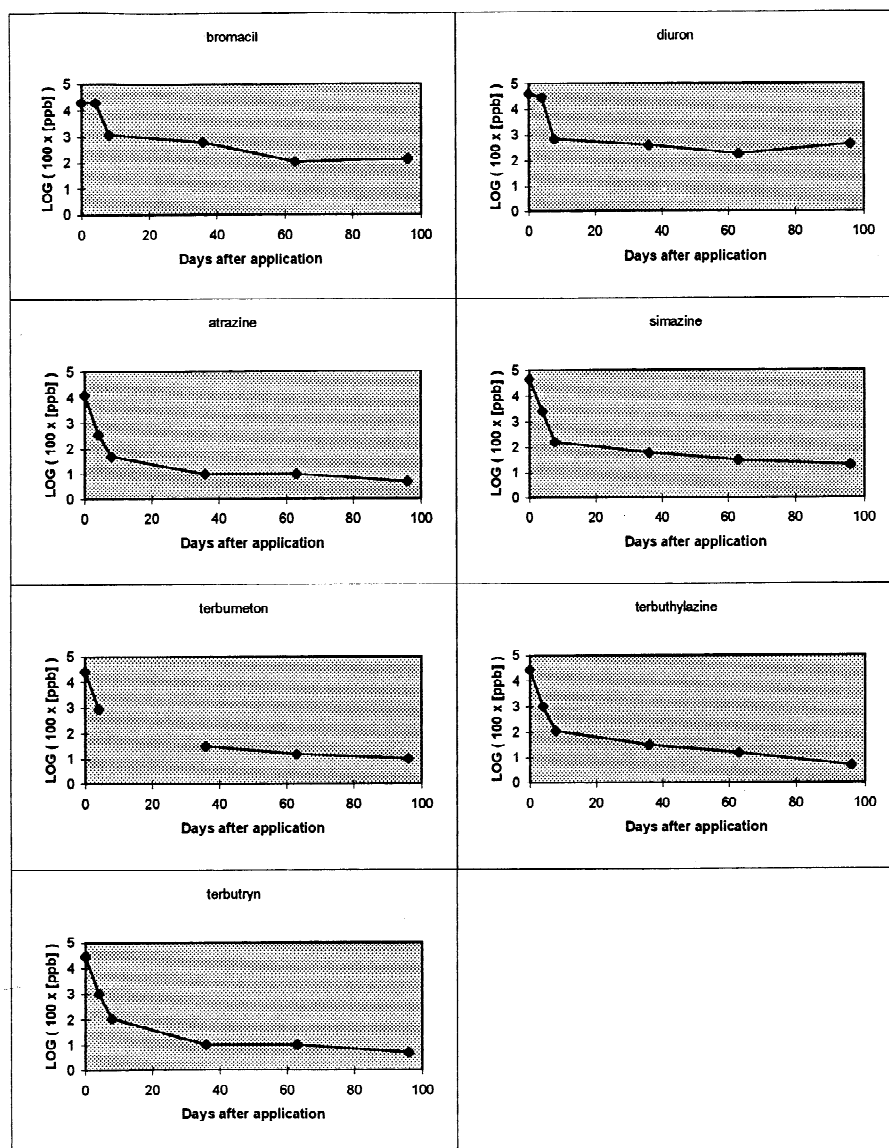

Fig. 5. First experiment: application date: 31-3-1995. Initial theoretical concentration: 10 μg/l.

sampling. It is important to note that 8 days after application the herbicide content in the water samples had decreased remarkably.

Table 3 shows the results of the second experiment. The initial herbicide concentration was about 10 μg/l, decreasing immediately to 0.1–1 μg/l.

Both tables show how bromacil and diuron persisted longer than the *s*-triazines, which were detected at the end of the experiment at doses very

close to the European Union (EU) limits for drinking purposes.

In the first experiment, the next dealkyl *s*-triazines products were detected; in the first sampling, 3.7 μg/l of desethylatrazine; in the second sampling, 0.1 μg/l of desethylatrazine, desisopropylatrazine and desethylterbutryn; in the third sampling, 0.2 μg/l of desisopropylatrazine; in the fourth sampling, 0.1 μg/l of desethylatrazine and 0.2 of desethylterbutryn,

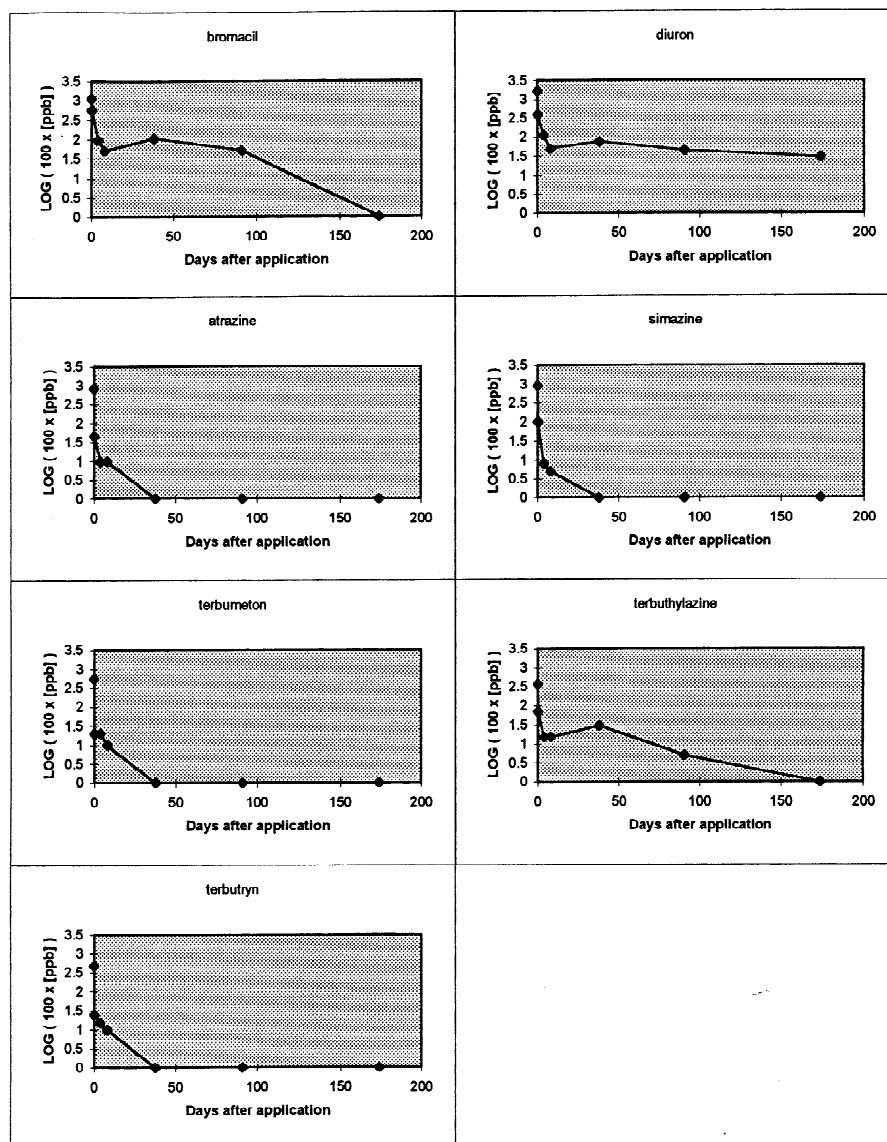Fig. 6. Second experiment: application date: 7-9-1995, initial theoretical concentration: 1 μg/l.

Table 3
Second experiment — concentration of herbicides in well water samples (μg/l)

	Days after treatment						
	0	0.25	4	8	38	91	174
Bromacil	11	5.55	0.95	0.5	1.05	0.5	−
Diuron	16.8	3.95	1.1	0.5	0.75	0.45	0.3
Atrazine	8.3	0.45	0.1	0.1	−	−	−
Simazine	9.3	1	0.08	0.05	−	−	−
Terbumetone	5.55	0.2	0.2	0.1	−	−	−
Terbuthylazine	3.7	0.7	0.15	0.15	0.3	<1d	−
Terbutryn	4.7	0.25	0.15	0.1	−	−	−

<1d, less than limit of detection.

and in the fifth sampling 0.1 μg/l of desethylatrazine and desisopropylatrazine.

Figs. 5 and 6 show the histograms of the behaviour of the seven herbicides during the experiments. Note that the concentration of the chemicals are logarithmics and have been multiplied by 100.

4. Discussion

In more than 100 wells surveyed studied previously [1–3] neither mother compounds nor dealkyldegradation products were found in concentrations higher than 20 μg/l. This type of contamination, could be derived from non-point-sources (diffusive contamination); however, with the point source contamination as the one simulated in this paper, mainly in the first experiment, concentrations of the chemicals, at least during the first week after application, were at levels of hundreds of μg/l.

As shown in the histograms of the two experiments, the concentration of the seven herbicides fall very quickly during the first week after the initial application.

Dissipation of the *s*-triazines is faster than that of bromacil and diuron. Given the *s*-triazines lower water solubility and higher K_{oc} values than bromacil, the only explanation for the dissipation could be that in a water environment, degradation of the *s*-triazines are faster than bromacil and diuron.

The dealkyl *s*-triazines which appeared only in the first experiment were from atrazine and terbutryn,

but never from terbumeton or terbuthylazine. The desethylatrazine was detected always at higher concentration than the others, taking into consideration that the desisopropylatrazine could be derived from both simazine and atrazine.

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