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CONTAMINATION OF IRRIGATION WELL WATER BY RESIDUAL HERBICIDES IN SPANISH CITRUS AREAS

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Abstract. **The main residual herbicides applied to citrus in Spain are atrazine, bromacil, diuron, simazine, terbuthylazine, terbumetone, terbutryn and terbacil. Some of the orchards are on continuous non-tillage system, with one or sometimes two treatments a year of the above mentioned products. Water samples from more than fifty irrigation wells located in or near citrus orchards were analysed during the last five years. Many of the water samples do not contain herbicide. There is a close relationship between rainfall episodes and herbicide detection. Concentrations are in the low range of µg/l. Bromacil was the product most commonly found. Some herbicide degradation products also appeared: DCPMU was found more frequently than DCPU; also des-alquil-s-triazines were observed. In two very shallow wells, 1 m depth, located on a sandy soil area, hydroxy-triazines were also detected.**

Non tillage in Spanish citrus orchards is the most important soil management method nowadays (Gómez de Barreda et al. 1994). In the new plantations where drip irrigation is generally followed, no till methods are quite common. Diuron was the first citrus selective soil residual herbicide used, in the sixties. In the seventies simazine, bromacil, terbacil, terbuthylazine, terbumetone, terbutryn and trifluralin were introduced. In the eighties glyphosate was first used alone but in the nineties it has also been applied in mixtures with simazine or terbuthylazine. Some orchards in Spain received continuous treatments of residual herbicides for more than twenty years, without any cultivation. Groundwater pollution with agri-chemicals has been a matter of concern in intensive agricultural production during the last two decades (Ernst, 1973; Hance, 1987; Muir and Baker, 1976; Rao et al. 1985).

The purpose of this paper is to present the results of a five year survey in which irrigation wells have been sampled and analyzed for the main residual herbicides used in several citrus areas.

Materials and Methods

The selection of wells was done according to the following criteria:

They should be surrounded by citrus orchards.
Their NO_3 concentration, had to be higher than 100 mg/l.

Instead of reporting all the wells surveyed, four types of different situations, will be presented here:

1) *Wells with high risk of contamination.*
   Two shallow (level of water around 1 m depth) wells, named Pinedo 1, and Pinedo 2, were selected. The orchards near these wells used s-triazines and glyphosates for weed control. The weed control program is done with two s-triazine formulated products atrazine 20% + terbuthylazine 15% + terbumetone 15%, at the rate of 6 l/ha of the commercial product the spring and terbuthylazine 15% + terbumetone 15% + terbutryn 20% in autumn and spot treatments with 10 l/ha of a commercial mixture composed of glyphosate 10% + simazine 28% to control the perennial weed species.
2) *Wells near orchards with long history of continuous non tillage use of residual herbicides.*
   A citrus orchard with the longest period in Spain of continuous no tillage system with residual treatments was selected in the Benifayó area. The soil is sandy loam and has a well with the level of water at 15 m depth.
3) *Wells near a large farm (200 ha; for the Spanish sizes), surrounded by mountains.*
   The orchard selected, is located in Rafelguaraf (Valencia) in a very deep sandy soil and has four wells. The figure 1, shows the situations of the four wells, named R-1, R-2, R-3 and R-4, and the level of water is very deep (around 50 m).
4) *Drip herbigated orchard.*
   Three other wells were also included in this paper because they were located in another very different Spanish citrus area, in the south of Spain, near Ayamonte (in the province of Huelva). In this last orchard the soil is acid (in the rest of the orchards surveyed, the soil pH is generally neutral or mostly basic) and it is herbigated.

Water sampling was done throughout the year; particular attention has been paid after rainy episodes. Two samples were al-

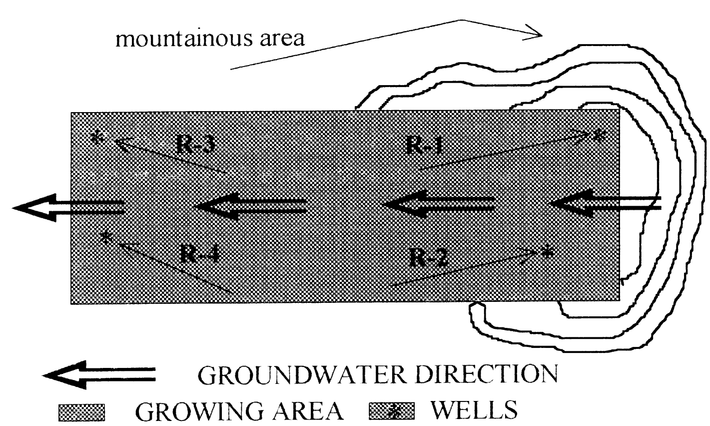

Figure 1. Rafelguaraf citrus orchard.

ways taken in each well, at ten minutes interval after starting

Table 1.

		RANGE OF CONCENTRATIONS (µg/l)																	
		Parent Compounds									Degradation Compounds								
Wells	Duration of sampling	atra	bro	sim	ter.cl	ter.o	ter.s	tri	diur	dcp	a-des	a-desis	s-des	tcl-des	to-des	ts-des	H-at	H-si	HETT
Pinedo-1	30-6-93 27-6-94	<ld 7.1	n.u.	<ld	0.4 3.8	0.4 6.1	<ld	n.u.	n.u.	n.u.	<ld 4.0	<ld	<ld	0.8 4.9	0.8 7.4	<ld	<ld 0.5	0.8 2.4	2.5 10.0
Pinedo-2	22-7-93 27-6-94	0.5 11.0	n.u.	<ld	0.3 0.5	0.5 0.7	<ld	n.u.	n.u.	n.u.	<ld 1.9	<ld	<ld	<ld 1.2	<ld 4.0	<ld	* 1.7	* 3.7	* 38.8
Benifayo	5-7-89 12-5-92	<ld 1.2	<ld 19.5	<ld 0.9	<ld 1.8	<ld 6.3	<ld	<ld 4.1	*	*	<ld 3.5	<ld 3.0	<ld	<ld 1.0	<ld 3.5	<ld	*	*	*
Huelva-1	28-2-91 22-11-93	<ld	<ld	<ld	<ld	<ld	<ld	<ld	n.u.	n.u.	<ld	<ld	<ld	<ld	<ld	<ld	*	*	*
Huelva-2	28-2-91 22-11-93	<ld	<ld	<ld	<ld	<ld	<ld	<ld	n.u.	n.u.	<ld	<ld	<ld	<ld	<ld	<ld	*	*	*
Huelva-3	28-2-91 22-11-93	<ld	<ld	<ld	<ld	<ld	<ld	<ld	n.u.	n.u.	<ld	<ld	<ld	<ld	<ld	<ld	*	*	*
R-1	27-6-91 3-5-95	<ld 0.2	<ld 0.5	<ld 0.1	<ld 0.4	<ld 0.4	<ld 0.2	<ld	<ld 0.4	<ld	<ld	<ld	<ld	<ld	<ld	<ld	*	*	*
R-2	27-6-91 3-5-95	<ld 0.1	<ld 7.4	<ld 0.1	<ld 0.6	<ld 0.2	<ld 0.2	<ld	<ld 0.8	<ld	<ld	<ld	<ld	<ld	<ld	<ld	*	*	*
R-3	6-11-90 9-5-95	<ld 3.0	0.5 22.7	<ld 0.3	<ld 1.2	<ld 1.6	<ld 0.5	<ld	<ld 1.4	<ld	<ld 0.6	<ld 2.5	<ld	<ld 0.6	<ld	<ld	*	*	*
R-4	6-11-90 3-5-95	<ld 1.2	0.4 8.8	<ld 0.1	<ld 0.5	<ld 0.6	<ld 0.2	<ld	<ld 0.7	<ld	<ld 0.5	<ld	<ld	<ld 0.2	<ld 0.7	<ld	*	*	*

atra = atrazine; bro = bromacil; sim = simazine; ter.cl = terbuthylazine; ter.o = terbumeton; ter.s = terbutryn; tri-trifluralin; diur = diuron; dcp = DCPMU; a-des = deethylatrazine; a-desis = deisopropylatrazine; s-des = deethylsimazine; tcl-des = deethylterbuthylazine; to-des = deethylterbumeton; ts-des = deethylterbutryn; H-at = hidroxyatrazine; H-si = hidroxysimazine; HETT = hidroxyethylterbutyltriazine. <ld = less than limit of detection. * = not analyzed. n.u. = not used.

pumping. The samples were immediately transported and placed in the refrigerator prior to the analysis. The analysis, was done by gas chromatography for bromacil and s-triazines, and by liquid chromatography for diuron. The methods are described in previous works (Gómez de Barreda et al. 1991; Gómez de Barreda et al. 1993).

Results

In table 1 are presented the results of water analyses in different citrus orchard wells. The table shows the concentration range of herbicides, found between the first and last sampling date of the entire survey.

From the s-triazines terbutryn was less frequently found, as mother compound or des-alquil-compound. This is in agreement with a first survey that was reported previously (Gómez de Barreda et al. 1994). In general terbumetone was found in higher concentration than terbuthylazine. The commercial product used contained both s-triazines, in the same proportion (25%) and means therefore that terbumetone is more leachable and persistent than terbuthylazine; this phenomenon also happens with the des-alquil-degradation compounds.

We have not found data in the literature hydroxy-s-triazine in groundwater. Khan and Marriage (1977), applied 4.5 kg/ha for eight consecutive years in a peach orchard and 18 months after the treatment found more hydroxy atrazine than atrazine or desalkyatrazine. We believe the reason for not detecting hydroxy-compounds is twofold: 1) it is difficult to analyze these compounds and, 2) these have no herbicide properties. Saez et al. (1996), proposed a simple analytical method to solve the first problem.

The concentration of hydroxy-ethyl-terbuthyl-triazine is very high in many sampling dates (38.8 µg/l in June 27th, 1994), but it must be remembered the weed control program; the hydroxy-thyl-terbuthyl-triazine degradation compounds could be degraded from three parent compounds: terbuthylazine, terbumetone and terbutryn.

The Benifayó well was the most contaminated in the entire study. This well is on a sandy soil and surrounded by the non tillage orchard with longest records (dated from 1968) of continuous use of residual herbicides. The level of the water is approximately 15 m depth. Trifluralin was detected in 04/04/90 sampling despite its high K_{oc}. The main points of these data are that bromacil was almost always found in all samplings, at higher concentration than the rest of the herbicides, except for terbumetone on 04/04/90. The unusual data, of this last table, is the finding of trifluralin the 04/04/90. How a so high adsorption chemical (Koc 6400-13400) has reached the 15 m depth? A possible reason is that this chemical was herbigated, in a flood irrigated sandy citrus orchard, and therefore it may have arrived to that depth mainly through preferential pathways.

The analysis of 4 wells with water level around 50 m depth in a large citrus orchard with sandy soil, must be considered separately. R-1 and R-2 are situated in the first part of the aquifer pathway (see Fig. 1) and the former almost in the boundary of the orchard, near the mountain, that shields the farm. R-3 and R-4 are within the entire influence of many herbicide plots treatment in the latest part of the aquifer of the farm. As can be observed in this table the more contaminated wells, as could be expected, are R-3 and R-4.

The results of samples from wells located in a big orchard, in the southwestern part of Spain (Huelva 1, 2 and 3), where drip herbigation is practiced, showed no detection of the s-triazines. Besides differences in soil pHs, it is possible that this results are due to the way of herbicide application, that not only reduced the total amount of the herbicides, but perhaps limits also the leaching of the chemicals.

Bromacil was found more frequently than atrazine in this survey. After them terbumetone showed more than terbuthylazine and simazine. Terbutryn is less leachable and persistent (Gómez de Barreda et al., 1995), therefore it has been almost impossible to find it.

In summary, some of the wells selected, that belong to high risk situations of contamination by residual herbicides, during some dates of the year, contain insignificant concentrations, parent compounds or even in some cases, degradation chemicals, above the EC limits for drinking purposes. The concentration found, is in the levels of few µg/l. The main danger in using this water for drinking is more due to the high nitrate levels than to the concentration of the citrus selective residual herbicides studied.

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VARIATION IN GROUNDWATER NITRATE UNDER AN EAST CENTRAL FLORIDA CITRUS GROVE

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Abstract. **Groundwater nitrate levels under a 'Valencia' (*Citrus sinensis* L. Osbeck) on rough lemon (*C. limon* L. Burm.f) grove planted in 1984 near St. Cloud, Florida, were monitored every 30 days from November 1994 to September 1996. The samples were taken from four 5 cm (2.0 in) diameter wells, 3.7 m (12 ft) deep, spaced 87 m (264 ft) apart in the center of the 600 m (1312 ft) × 70 m (230 ft) grove. The wells were jetted in with water and had 1.5 m (5 ft) of finely slotted (0.5 mm [0.02 in]) filter pipe on the lower end. Eight 30 cm (1 ft) deep shallow wells were designed to intercept seepage into drainage ditches on three sides of the grove. To the north side, the land is bordered by swampy woodland from which groundwater drained into the grove. Water in the drainage ditches was also monitored. The water table in the center of the grove was at 1.7 to 2.0 m (5.6 to 6.8 ft), with little fluctuation. The grove was irrigated with microsprinklers, but fertilization was with dry fertilizer only. The grove was fertilized uniformly until April 1995. After that, Plots 1 and 3 received approximately half the amount of N applied to Plots 2 and 4. The high N plots received 244 kg N/ha (217 lb N/acre) in four applications, and the low N plots received 169 kg N/ha (150 lb N/acre) in three applications in 1995. In 1996, N was applied four times between January and September, 106 kg N/ha (95 lb N/acre) to the high N plots in four applications, and 70 kg N/ha (62 lb n/acre) in two applications to the low N plots. Water in the well in Plot 3 and the seepage well on its east side had between 8 and 28 mg/l nitrate N in 1995, while Well No. 2 never exceeded 12 mg/l. Water from Wells 1 and 4 was intermediate and never exceeded 10 mg/l NO_3-N. All four wells were essentially nitrate-free in December 1995. In the first 8 months of 1996, none of the wells had NO_3-N higher than 8 mg/l, with the highest levels in Well No. 2.**

For decades, there has been concern about chemicals applied to agricultural land entering the groundwater (Canter, 1996). The problem can be acute in temperate zone areas where, because of shallow soil and low soil temperatures, high concentrations of pollutants accumulate (Baier and Rykbost, 1976). In the often deep soils of Florida, where higher soil and water temperatures favor faster breakdown of substances and root absorption of nutrient elements, phosphorus has long been blamed for eutrophication of lakes and ponds, but nitrates have received increased attention recently (McNeal et al., 1994). Provisional regulations imposing a 10 ppm NO_3-N limit on all groundwater, even under agricultural land,