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Field study of methidathion in soil amended with biosolid and a cationic surfactant under different irrigation regimes. Solute transport modeling

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Abstract

Four experimental plots located in Granada (Spain) were used to investigate the potential movement of the insecticide methidathion during three treatments in a period of three years. To increase pesticide soil retention a municipal biosolid and the cationic surfactant, tetradecyl trimethyl ammonium bromide (TDTMA), were used as soil amendments. The presence of the insecticide was monitored in soil and water samples at different depths up to one meter. Soil solution was sampled by ceramic suction cups installed at three depths (25, 75 and 100 cm). No effect of the amendments on pesticide mobility was observed. Experimental results showed that pesticide leaching occurred in the upper soil layer. Although some sporadic high water soil concentrations were found, these were attributed to preferential flow processes. This was confirmed by the absence of high pesticide concentration in soil samples at similar depths. Pesticide mobility was mainly affected by the irrigation employed. Experimental results were compared with theoretical data simulated with the mathematical model FocusPelmo. The resemblance between theoretical and experimental soil data seems to confirm the preferential flow processes. Otherwise, the lack of fit between the soil water data were attributed to the ceramic devices employed, that could suffer an "ageing process" which would cause bias in the determinations.

Keywords: Field test; Pesticide; Mobility; Ceramic cups; Preferential flow; Model; Ageing; Methidathion

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1. Introduction

In arid and semiarid regions the use of groundwater for human supply is a normal practice. For this reason, Public Institutions should develop monitoring programs to evaluate the safety of groundwater systems. Among the different substances that could modify this medium, pesticides are one of the organic contaminants currently applied to the soil. Their use is indispensable in modern agriculture, but their application to the field has contributed to groundwater contamination problems. In the Southeast of Spain several studies have detected the presence of insecticides, such as methidathion, in surface and groundwater (Hernández et al., 1996; Garrido et al., 2001).

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The occurrence of pesticides in groundwater requires the study of transport processes in soil. Usually pesticide mobility is tested in the laboratory using soil columns (Romero et al., 1997; Abu-Zreig et al., 2000; Sánchez et al., 2003a) due to their low cost, high reproducibility, low volume and ease of preparation (Malterre et al., 2000). Ceramic suction cups have been largely used for sampling water soil solution (Grossmann and Ufluft, 1991; Beier et al., 1992; Lord and Shepherd, 1993; Moreno et al., 1996; French et al., 2001; Kalbitz, 2001; Muñoz-Carpena et al., 2002; Zechmeister-Boltenstern et al., 2002; Siemens et al., 2003) but their application in the study of pesticide behaviour has not been frequent (Beltrán et al., 1995a; Close et al., 1998; Guzzella et al., 2000; Pang et al., 2000; Domange et al., 2004). Field studies are more scarce (Beltrán et al., 1995b; Guzzella et al., 2000; Gardner and Branham, 2001; Jindal et al., 2002) because of their high cost and difficulty, but at the same time they provide more representative results and more accurate predictions of pesticide movement.

Recent studies (Barriuso et al., 1995; Abu-Zreig et al., 2000; Graber et al., 2001) have focused on the addition to the soil of exogenous organic matter and surfactants as amendments to increase pesticide sorption and minimize pesticide leaching. Both amendments have shown a high efficacy to modify pesticide behaviour (Sánchez et al., 2003a,b), but little is known about their efficacy under field conditions.

In this study the mobility of the insecticide methidathion was studied in an agricultural field placed near Granada (Southeast of Spain). During three treatments, the annual application at a usual dosage of the insecticide was combined with the addition of the cationic surfactant tretadecyl trimethyl ammonium bromide (TDTMA) and a municipal biosolid. Methidation was periodically determined in soil and water samples at different depths during three consecutive years.

Field results were compared with predicted pesticide concentration using the pesticide leaching model FOCUS-PELMO.

2. Materials and methods

2.1. Amendments

Dewatered biosolids, from a municipal sewage facility of Granada, were used. This material has a pH of 7.2, 40% OM content, equivalent to an organic C content of 23.5%, and an elemental composition which complies with the European legislation (Sánchez et al., 2003b). The cationic surfactant used was tetradecyl trimethyl ammonium bromide (TDTMA), 99% purity (Aldrich Chem., Madrid, Spain), with a critical micellar concentration (cmc) of $0.1\ \mathrm{g\,l^{-1}}$.

2.2. Field experiments

The experimental field was located in Vegas de Genil (longitude: 3°41′10″, latitude: 37°11′17″), in the province of Granada. The soil is a calcareous silt loam type (typic xerofluvent). The main soil properties at three depths (0–25, 50–75 and 100–125 cm), were analysed according to official methods (MAPA, 1986) (Table 1).

Four experimental plots, of 25 square meters, were laterally confined with vertical soil walls 40-cm high. The experimental design included one unamended plot (S), and the remaining three plots amended with sewage sludge (SB), surfactant (SS) and both amendments (SBS). To collect soil solution, three ceramic suction cups of about 10 cm length, 4.3 cm i.d. and 0.5 cm thick (Bowman et al., 2002) were installed in each plot at three different depths: 25, 75 and 100 cm. Their installation followed the conventional procedure (Webster et al., 1993; Guzzella et al., 2000), which consisted in excavating a borehole of a diameter slightly greater than the cup, inserting the suction cup, and filling the space around the cup with a slurry of water and sieved (<2 mm) upper soil, to avoid preferential flow.

In order to validate the use of ceramic cups for soil solution sampling, additional experiments were carried out by submerging a porous suction sampler in a beaker containing water spiked at $1\ \mu\mathrm{g\,l^{-1}}$ of methidathion. Vacuum was applied during 24 h, and the aqueous solution collected inside and outside the cup was analysed.

2.3. Treatments

One treatment per year was homogenously applied on the soil with a portable knapsack sprayer, at usual field dosage, $1.2\ \mathrm{kg\,ha^{-1}}$ (de Liñán, 2004). A methidathion formulation of wettable powder at 40% a.i. (Supracid 40WP) was used. In the 1st treatment (November, 1998), 120 kg ($45\ \mathrm{t\,ha^{-1}}$) of biosolid was incorporated to the plots SB and SBS. In the 2nd (February, 1999) and 3rd treatments (January, 2000), similar quantities of biosolid were added. In all additions, the upper soil was mixed with the biosolid before insecticide application. Since no agricultural activities were carried out between treatments, the biosolid amendment accounted for 3%, 6% and 9%, if the first 10 cm of soil are considered. Each plot was irrigated with 100–190 mm of water before insecticide application (24 h) to reach saturated soil conditions.

The cationic surfactant was mixed with the insecticide aqueous solution in the portable knapsack sprayer, and applied at two dosages. In the 1st treatment, plots SS and SBS received 12 g of TDTMA which corresponded to 10 times the critical micellar concentration (cmc) in the applied solution. The 2nd and 3rd treatments were conducted applying 120 g of TDTMA (100 cmc) in the same conditions.

Table 1
Physicochemical characteristics of the soil

Soil depth (cm)	pH	Sa/St/Clay[a] (%)	OM (%)	C (%)	N (%)	Ca/Mg/K (cmol kg^{-1})	CEC (cmol kg^{-1})	Phyll.[b] (%)	Mont.[c] (%)	Water content (1/3 bar) (%)
0–25	8.5	31/58/11	1.59	0.92	0.13	35.6/3.2/0.19	7.9	30	6	27
50–75	9.0	33/60/7	0.78	0.45	–	33.6/2.7/0.10	6.2	33	10	24
100–125	8.5	28/63/9	0.63	0.36	–	37.2/3.6/0.09	6.8	39	6	28

[a] Sa/St/Clay = Sand/Silt/Clay.
[b] Phyll. = Phyllosilicates.
[c] Mont. = Montmorillonite.

2.4. Irrigation and meteorological conditions

Water supply proceeded from a groundwater well located in the experimental field. Previous analysis revealed that water was free of methidathion residues. Irrigation was applied using a sprinkler irrigation system.

In the 1st treatment, a low irrigation supply of 380 mm was applied, which corresponds to half of the annual irrigation supply in the agricultural zone. The irrigation was increased by three times (900 mm) the 2nd year and reduced to an intermediate level (470 mm) the 3rd year, in order to avoid a rapid lixiviation.

Precipitations were negligible during the three treatments and temperatures ranged between −5 and 25 °C.

2.5. Water and soil sampling

Water soil samples were collected by applying a vacuum of 60 cbar to the cups 24 or 48 h before water sampling. The cups were kept in the field during the 3 years, and only those which failed to collect water were changed.

Soil samples were obtained from 0 to 20, 50 to 75 and 100 to 110 cm horizons. In the 1st year, a small shovel for sampling the upper soil was employed, being the deeper samples collected with a tube-type soil sampler. The last two years all the soil samples were taken with a tube-type soil sampler. To avoid preferential flow, soil holes were filled with a slurry of sieved (<2 mm) clean upper soil.

2.6. Analysis

In general, the time elapsed between soil and water collection and analysis was short ($\leqslant$24 h). When storage was necessary, soil samples were frozen and kept at −18 °C until analysis.

Water samples were analysed using C18 cartridges (Waters, 500 mg). Volumes between 40 and 200 ml were passed trough (Sánchez et al., 2000) and the insecticide was eluted using toluene, concentrated to dryness with N_2, and dissolved in 1 ml hexane. To this solution, 25 µl of an internal standard, bromophos (99.9%, Labor Dr. Ehrenstofer) at a concentration of 100 mg l^{-1} in hexane, was added. Linearity of the response was checked between 0.1 and 1 mg l^{-1}. Recovery tests ($n = 5$) were carried out on water samples spiked with the insecticide at 0.1 µg l^{-1}, using different water volumes (50, 100 and 200 ml). The limit of quantification for the standard solutions was 0.01 mg l^{-1}, and depending on the volume passed through the cartridge the final LOQ would range between 0.25 and 0.05 µg l^{-1}.

Aliquots of approximately 25 g from each soil layer were extracted per duplicate using Soxhlet extraction as previously described (Sánchez et al., 2003a). Recovery tests were carried out with soil samples ($n = 6$) incubated at 1 µg g^{-1} at 15 ± 0.1 °C for 2 h in a thermostatic chamber. Linearity of the response was checked between 1 and 20 mg l^{-1}, providing a LOQ of 1.37 mg l^{-1} for the standard solutions. For soil samples, LOQ was calculated as 0.05 µg g^{-1}.

Residues of methidathion in soil and water samples, were quantified by injection (1 µl) into a Hewlett-Packard 5890 gas chromatograph equipped with a flame photometric detector (Sánchez et al., 2000). Chromatograms of methidathion in soil and water soil samples are shown in Fig. 1. Results were expressed on dry weight basis for soil samples, after the determination of soil humidity. Methidathion recoveries in the different soil treatments were 101.9 ± 5.1% (S), 92.1 ± 7.8% (SB), 95.5 ± 3.8% (SS) and 90.4 ± 5.4% (SBS). For water samples recovery was 104.2 ± 13.6%.

2.7. Simulation with FOCUS-PELMO

Simulation of methidathion behaviour in the four experimental plots (S, SB, SS and SBS) and under the different field experimental conditions described before was conducted using the mathematical model FOCUS-PELMO 1.1.1. The equations which describe transport and transformation of pesticides in this model have been selected on the basis of different scenarios. PELMO (Pesticide Leaching Model) estimates the leaching potential of a pesticide in a compartmental model which considers that the soil is separated into different horizons up to 1 m depth. The thickness of these compartments can be fixed. We have used three horizons (0–30, 30–

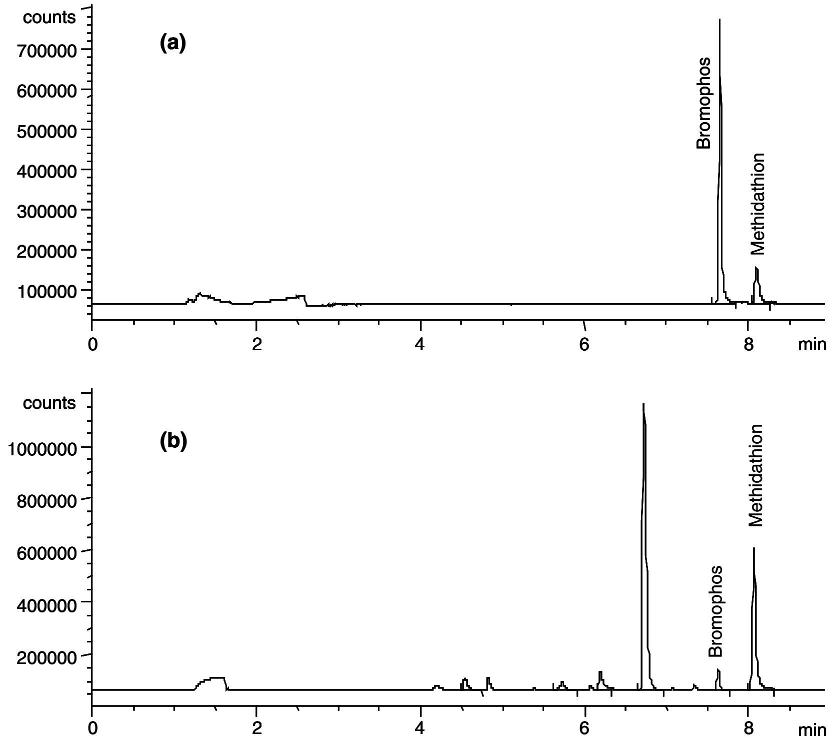

Fig. 1. Chromatogram of soil sample (a) and soil solution (b) from the 3rd treatment in the experimental plot SBS (0–25 cm).

70 and 70–100 cm) in relation with changes in soil properties with depth and amendment addition in the upper layer. The soil hydrology, a key process of the program, is estimated by using a capacity model with the field capacity and the wilting point as the most important soil parameters. Daily evapotranspiration was estimated using the Haude equation. PELMO assumes equilibrium between pesticide concentration in the soil matrix, soil air and soil water after one day. The model calculates depth dependent temperature in soil by using daily air temperatures.

Input parameters were water supply (irrigation plus precipitations), mean temperature and air humidity at 2 p.m. Data were supplied by the Meteorological National Institute (Ministerio de Medio Ambiente, Spain). Other parameters include soil density (1.5 g cm^{-3}), organic carbon content, sand, silt and clay (Table 1). Sorption Freundlich constants (K_f and $1/n$) and degradation constants (k, and $t_{1/2}$) were obtained from previous lab experiments (Sánchez et al., 2003b,c). Application dosage and depth (1 cm) were also included.

In the biosolid-amended plots, OC contents for the first 10 cm of the upper layer increased with every treatment.

3. Results and discussion

3.1. Water soil samples

Pesticide analysis using ceramic suction cups to monitor pesticide mobility is a low cost method, easy to manage, which permits replicated analysis along the time (Grossmann and Ufluft, 1991). However there are also

Table 2

Efficiency (%) of ceramic suction cups collection at three depths, in the four experimental plots during the three treatments

Depth	Plot S[a]			Plot SB			Plot SS			Plot SBS		
	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
25 cm	84	100	100	100	100	86	84	100	86	100	100	86
75 cm	80	100	60	100	100	100	40	100	100	80	100	100
100 cm	40	40	50	80	100	75	0	100	75	40	100	100

[a] S: natural soil; SB: amended with the biosolid; SS: amended with the surfactant; SBS: amended with the biosolid and the surfactant.

some drawbacks such as bias in the determination of concentrations or low reproducibility at low volumes (Domange et al., 2004).

Before field installation, laboratory assays showed that ceramic walls did not absorb methidathion at low concentrations (0.1 μg l^{-1}). Under field conditions with the vacuum applied, the water volume collected ranged from 50 to 700 ml in average, similar to that obtained by other authors (Adams and Thurman, 1991; Sánchez-Pérez, 1994; Gatzweiler et al., 1999) but cups did not collect water in all the cases. The highest sampling yield corresponded to the highest irrigation (2nd treatment, 900 mm) (Table 2) and diminished with depth. Failures (values below 100%) could be explained by low soil humidity or because the sealing around the cups was broken (Gatzweiler et al., 1999). Cups which did not collect water were replaced.

Table 3 shows pesticide concentrations in the leachates at different depths during the treatments. Pesticide concentrations in the upper soil (25 cm depth) during the 1st treatment ranged between 3 and 6.7 μg l^{-1}. Values at other depths were in general <1 μg l^{-1}. A value of 1.15 μg l^{-1} in plot SB at 100–110 cm, 27 days after pesticide application could be attributed to preferential flow or to a fraction transported by dissolved organic matter, as described by other authors in amended soil (Nelson et al., 1998; Graber et al., 2001).

In the 2nd treatment, using the highest irrigation volume (900 mm), pesticide concentration in the upper cups was lower (<4 μg l^{-1}) than that obtained in the 1st treatment, while higher concentrations (between 1.45 and 4.48 μg l^{-1}) where determined at intermediate and lower depths in the 6th day in plots S, SS and SBS.

During the 3rd treatment a new reduction of pesticide concentrations in upper cups was observed (<0.5 μg l^{-1}) for all the plots, except for plot SBS. At others depths, methidathion concentration was around 2 μg l^{-1}, although in one case (day 7, plot SB and 50–75 cm depth) the concentration peaked up to 17 μg l^{-1}.

The exceptional high pesticide concentrations found during the 2nd and 3rd treatments can be attributed to preferential flow, and to the irregular performance of the suction cups. Preferential flow is considered to be one of the most important factors which contribute to groundwater contamination (Steenhuis et al., 1990; Flury, 1996; Reichenberger et al., 2002). Pesticide mobility to deeper soil layers has been observed for methidathion and dimethoate (Beltrán et al., 1995b) using ceramic suction cups, as well as for monolinuron and linuron (Guzzella et al., 2000). Preferential flow depends of soil properties, on the irrigation methods, on the presence of worms, or on agricultural practices, which determine the existence of cracks. In the present work, the cup insertion into the soil, together with the high irrigation supply during the 2nd treatment could contribute to crack formation. In the 3rd treatment the preferential

Table 3
Methidation concentration (μg l^{-1}) in the soil water samples from the four experimental plots at three depths during the treatments

		1st Treatment								2nd Treatment						3rd Treatment						
	Days	3	6	10	13	20	27	57	60	3	6	11	17	24	60	1	3	7	10	14	21	28
S[a]	0–25 cm	–	5.54	–	0.17	0.09	0.56	–	0.96	0.15	0.13	0.09	0.05	<LOQ[b]	<LOQ	0.11	<LOQ	0.05	<LOQ	<LOQ	0.25	<LOQ
	50–75 cm	–	–	–	0.37	0.10	0.13	–	0.09	–	1.45	0.09	0.05	<LOQ	<LOQ	–	–	0.20	–	–	0.08	0.12
	100–110 cm	–	–	–	–	–	0.40	0.05	0.18	–	0.55	–	0.27	–	–	–	–	–	–	–	1.69	0.68
SB	0–25 cm	6.72	4.72	–	0.21	0.09	0.14	–	0.07	1.01	4.10	0.15	0.07	0.06	0.10	0.15	0.11	0.16	0.18	0.10	0.16	–
	50–75 cm	–	–	<LOQ	0.15	0.08	0.22	–	0.08	–	0.11	<LOQ	0.06	<LOQ	<LOQ	–	–	17.9	1.59	0.54	0.27	0.24
	100–110 cm	–	–	<LOQ	–	0.12	1.15	0.05	0.09	–	0.38	0.32	0.10	0.05	0.08	–	–	–	–	0.32	0.12	0.21
SS	0–25 cm	–	4.03	–	0.15	0.14	0.42	–	<LOQ	0.08	0.13	0.12	0.08	<LOQ	0.11	0.33	0.05	0.05	–	0.09	0.05	0.05
	50–75 cm	–	–	–	–	0.11	–	–	<LOQ	–	4.48	0.21	0.06	<LOQ	<LOQ	–	–	0.06	0.06	0.05	0.83	0.78
	100–110 cm	–	–	–	–	–	–	–	<LOQ	–	0.13	0.15	0.07	<LOQ	<LOQ	–	–	–	–	0.22	1.73	0.25
SBS	0–25 cm	–	3.17	–	0.48	1.01	0.35	–	0.09	0.17	0.20	0.20	0.16	0.35	<LOQ	–	0.14	2.02	0.17	5.01	0.99	<LOQ
	50–75 cm	–	–	–	0.43	0.09	0.17	–	<LOQ	–	1.79	0.13	0.10	<LOQ	<LOQ	–	–	0.39	0.25	0.05	0.13	0.52
	100–110 cm	–	–	–	–	–	–	0.07	0.12	–	2.01	0.08	0.06	<LOQ	<LOQ	–	–	–	0.29	0.11	0.09	0.15
New cup	0–25 cm															4.74	3.02	2.60	0.70	0.23	0.35	<LOQ

'–' Not sampled.

[a] As in Table 2.

[b] <LOQ: Below the limit of quantification.

flow in SB could also be related with the fraction associated with the dissolved organic matter from the organic amendment. The lixiviation of this fraction with the soil solution in macropores and cracks may be favoured by the absence of agricultural practices.

During the 3rd treatment it is also necessary to stress the differences between the old and the new cup installed in plot SBS (Table 3). In spite of the greater irrigation volume applied in the 2nd and 3rd years, there is a reduction of the volume collected by the cups placed in the upper layer, in relation to the 1st treatment, of 13% and 34%, respectively which could point out to an "ageing" process of the cup surface, because the cups were kept into the field during the three treatments (around three years). The results are in contradiction with other authors (Jones and Edwards, 1993) who recommend a conditioning period of several years to avoid bias in the collection of ionic compounds (Lord and Shepherd, 1993).

Spatial variability using ceramic cups has been reported in the analysis of inorganic cations (Böttcher and Strebel, 1988; Scott-Wendt et al., 1988; Wopereis et al., 1988) or pesticides (Smith and Parrish, 1993; Beltrán et al., 1995b; Guzzella et al., 2000). This variability has been attributed to soil properties (Beier and Hansen, 1992), chemical cup characteristics (Hughes and Reynolds, 1990), soil heterogeneity and preferential flow (Flury et al., 1994; Guzzella et al., 2000; Patterson et al., 2000), but not many references point to ageing phenomena. Beltrán et al. (1995b) using ceramic cups observed a reduction of 10–20 fold in methidathion concentration during a field study in which the insecticide was applied twice in a year. Although no mention was made to the ageing process, it could be due to an analogous phenomenon. Haberhauer and Gerzabek (2000) considered that a long contact time of the ceramic with soil can alter their surface and modify its behaviour. Although some authors (Lord and Shepherd, 1993) report that ceramic cups can be used for years, our results question this assert for pesticide studies.

3.2. Soil data

Pesticide soil concentrations in the soil profile are shown in Table 4. In general, methidathion soil mobility was scarce, because the higher concentrations were found in the upper layer. Below this depth, methidathion concentration was very low (in general <0.009 μg g^{-1}) in all the treatments and plots. These data support that the unusual high pesticide concentrations found in some leachates from the deeper layer during the treatments were due to preferential flow processes. The lack of correlation of pesticide data between soil and water soil samples has been found by other authors (Schoen et al., 1999) and attributed to preferential flow.

Table 4
Methidathion soil concentration (μg g^{-1}) in the four experimental plots at three depths during the treatments

		1st Treatment					2nd Treatment							3rd Treatment							
	Days	6	13	20	27	60	0	3	6	11	17	24	60	0	1	3	7	10	14	21	28
S[a]	0–25 cm	1.170	0.352	0.232	0.135	<LOQ	0.475	0.352	0.099	0.045	0.063	<LOQ	<LOQ	1.229	0.649	0.265	0.157	0.180	<LOQ	0.049	0.034
	50–75 cm	–	–	<LOQ[b]	–	<LOQ	–	–	<LOQ	–	<LOQ	<LOQ	<LOQ	–	–	–	–	<LOQ	<LOQ	<LOQ	<LOQ
	100–110 cm	–	–	<LOQ	–	<LOQ	–	–	<LOQ	–	<LOQ	<LOQ	<LOQ	–	–	–	–	–	<LOQ	<LOQ	<LOQ
SB	0–25 cm	1.163	0.425	0.344	0.083	<LOQ	0.303	0.609	0.093	0.074	0.052	0.081	<LOQ	1.956	0.345	0.562	0.559	0.349	0.071	0.087	0.098
	50–75 cm	–	–	<LOQ	–	<LOQ	–	–	<LOQ	–	<LOQ	<LOQ	<LOQ	–	–	–	–	<LOQ	<LOQ	<LOQ	<LOQ
	100–110 cm	–	–	<LOQ	–	<LOQ	–	–	<LOQ	–	<LOQ	<LOQ	<LOQ	–	–	–	–	–	<LOQ	<LOQ	<LOQ
SS	0–25 cm	1.500	0.605	0.396	0.092	<LOQ	1.023	0.769	0.228	0.067	0.039	0.144	<LOQ	1.012	1.165	0.315	0.326	0.599	0.049	0.134	<LOQ
	50–75 cm	–	–	<LOQ	–	<LOQ	–	–	<LOQ	–	<LOQ	<LOQ	<LOQ	–	–	–	–	<LOQ	<LOQ	<LOQ	<LOQ
	100–110 cm	–	–	<LOQ	–	<LOQ	–	–	<LOQ	–	<LOQ	<LOQ	<LOQ	–	–	–	–	–	<LOQ	0.050	<LOQ
SBS	0–25 cm	1.271	0.530	0.260	0.131	<LOQ	0.319	0.703	0.148	0.328	0.056	0.133	0.074	0.752	0.645	0.328	0.533	0.484	0.064	0.198	0.247
	50–75 cm	–	–	<LOQ	–	<LOQ	–	–	<LOQ	–	<LOQ	<LOQ	<LOQ	–	–	–	–	<LOQ	<LOQ	<LOQ	<LOQ
	100–110 cm	–	–	<LOQ	–	<LOQ	–	–	<LOQ	–	<LOQ	<LOQ	<LOQ	–	–	–	–	–	<LOQ	<LOQ	<LOQ

'–' Not sampled.

[a] As in Table 2.

[b] Below the LOQ.

To verify if the amendments had an effect, pesticide concentration in the upper soil layers was plotted in each treatment (Fig. 2). As it can been seen, differences between plots were small, in spite that biosolid addition was two (1999) and three times (2000) higher than that employed in laboratory experiments (Sánchez et al., 2003b). For the surfactant, the dosage employed in the spraying solution (10 and 100 cmc), was similar to or 10 times higher than the concentration employed in previous batch experiments (Sánchez et al., 2003b). The addition of TDTMA at 10 cmc had increased Freundlich sorption constant 25 fold with respect to the unamended soil in batch studies. Differences can be attributed to the relationship TDTMA/soil in both experiments. In a batch experiment this relationship was higher (4×10^{-3} g TDTMA/g soil at 10 cmc) than in the field. If we consider the first 10 cm, the relationship TDTMA/soil would be 3.4×10^{-6} for TDTMA addition at 10 cmc or 3.4×10^{-5} at 100 cmc. Another explanation can lay in the way the surfactant was added to the soil. Some authors (Sánchez-Camazano et al., 1995, 1996) have found that a previous mixture of the surfactant with the soil is more efficient than the incorporation to the irrigation water in lixiviation experiments. Finally, the sorption and the dissipation processes in the different plots and treatments were also influenced by the irrigation volume, and by non-equilibrium processes which could also contribute to explain the absence of amendment effect.

3.3. PELMO predictions

PELMO estimates the vertical transport of pesticides in the unsaturated soil system within and below the plant root zone for 1 m depth. The model was used to calculate methidathion behaviour during the three treatments, considering that amendments application modified sorption and degradation constants and induced changes in the OC content in the soil profiles.

3.3.1. Predicted water soil data

Fig. 3 shows the predicted and experimental results, in the upper layer, for plot SBS during the treatments. Similar results were found for the rest of the plots. Theoretical

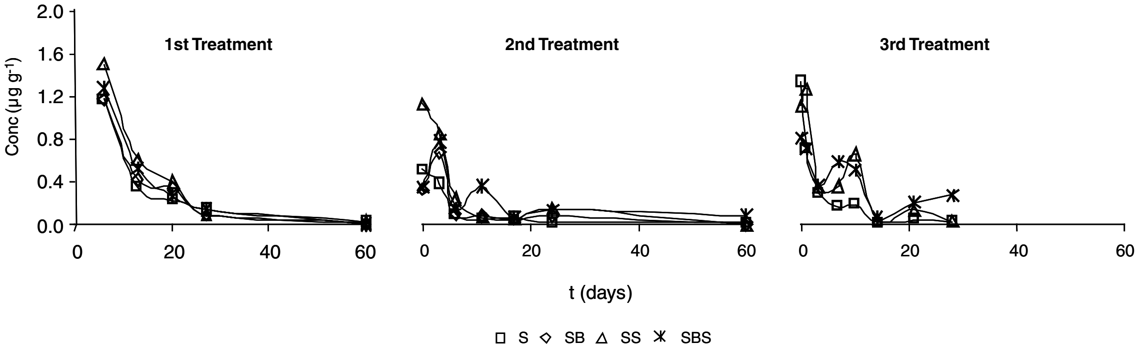

Fig. 2. Experimental methidathion concentration in soil (μg g^{-1}) in the upper layer for the different plots during the three treatments: (□, S) unamended soil, (◇, SB) soil amended with sewage sludge, (△, SS) soil amended with surfactant and (✱, SBS) soil amended with sewage sludge and surfactant.

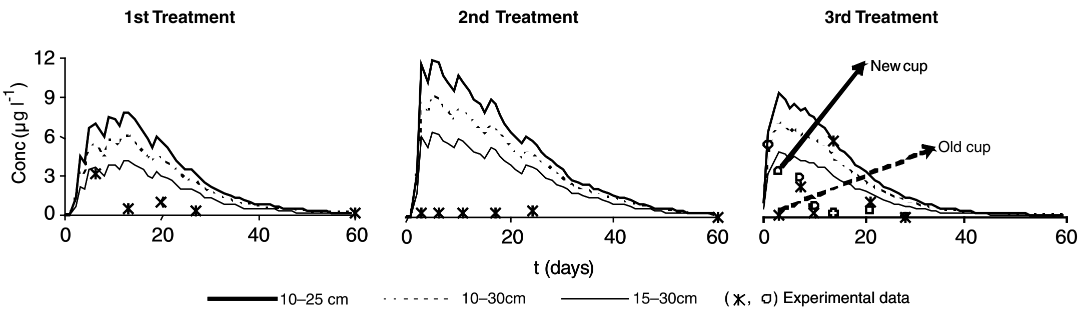

Fig. 3. Predicted (lines) and experimental (✱) methidathion soil water concentration (μg l^{-1}) in the upper ceramic suction cup for plot SBS amended with sewage sludge and surfactant. The predictions assume a zone around the cup of 10–20 (—), 10–30 (- - -) or 15–30 cm (—) measured from the soil surface. In the 3rd treatment, data for the old (✱) and the new (○) cup are presented.

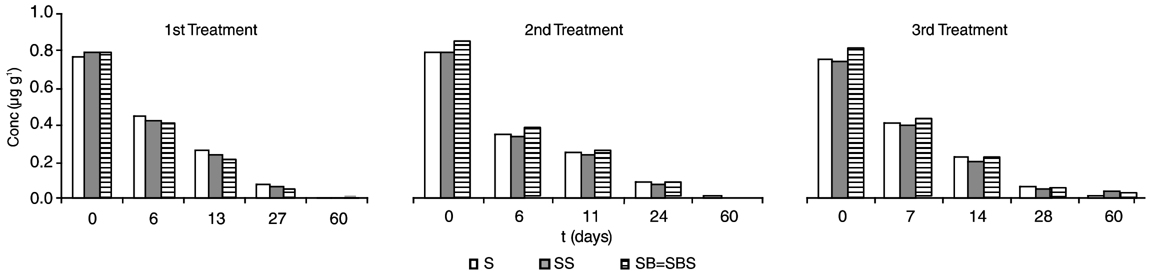

Fig. 4. Theoretical results of methidathion concentration in soil upper layers (µg g^{-1}). Comparison among the plots for the three treatments.

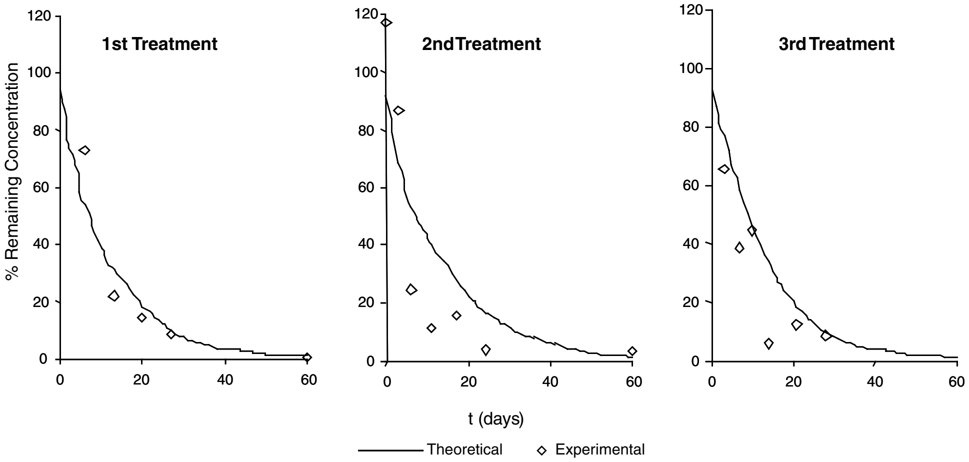

Fig. 5. Predicted (—) and experimental (◇) residual methidathion concentration in soil (%) for unamended soil (plot S) at 0–25 cm depth during the three treatments.

lixiviation values, for cups placed in the upper soil layer, were obtained considering three different areas around the cups from the soil surface (Grossmann and Ufluft, 1991), 10–25, 15–30 and 10–30 cm (Fig. 3). Simulated values below this depth were not represented because they were virtually zero (<0.0006 µg g^{-1}).

Theoretical maximum values for the three treatments in the upper water layer were close to 6, 12 and 9 µg l^{-1} (1st, 2nd and 3rd treatment, respectively), and reached zero values 60 days after the treatment. The differences between treatments were mainly due to the irrigation employed. Theoretical values for plots SB and SBS were similar since the same K_f was used for both plots, because it was assumed that the surfactant did not contribute to an increase in insecticide sorption.

These theoretical values were at odds with the sporadic higher concentrations found at intermediate and deeper levels, but supported that they could be explained by preferential flow processes, because Focuspelmo does not take into account this phenomenon (Steenhuis et al., 1990).

In general, the model predicted small differences between treatments, but theoretical lixiviation values in upper layers did not reached zero values for the 2nd and 3rd treatments, as was observed in the experimental results (Table 3). This corroborated that the experimental values for these years were erroneous, and confirmed that old cups did not work properly. No significant relationship was encountered between theoretical and experimental values (Fig. 3), but the highest similarity corresponded to the data of the 1st treatment and to the data of the new cup in the 3rd treatment, supporting again the above supposition.

3.3.2. Predicted soil data

Predicted values for methidathion concentration in the upper soil layer (0–20 cm) during the three treatments are shown in Fig. 4. The maximum methidathion concentration was below 0.8 µg g^{-1} (day 0) and diminished quickly to 0.12 µg g^{-1} the day 24 after insecticide application. The mathematical model did not predict significant concentrations (<0.0004 µg g^{-1}) below 20 cm so they have not been depicted. These results were in accordance with experimental data (Table 4) since the insecticide concentration between 50 and 100 cm depth was in general <0.009 µg g^{-1}. Therefore, model predictions were only compared with upper soil results. Fig. 5 shows experimental and theoretical values in plot S, during the three treatments. In general, the model provided a reasonable estimation of experimental soil data, with correlation coefficients between 0.67 and 0.88. The model considers first order degradation kinetics for methidathion in soil. Nevertheless, under the experimental field conditions, degradation can be influenced by the soil moisture content (Walker, 1987; Arnold and Briggs, 1990), or as observed in a previous lab experiment (Sánchez et al., 2003c) the dissipation behaviour can be better fitted to different equations which could explain the lower correlation obtained for the 2nd and 3rd treatments (Fig. 5). Another factor to be taken into account was the soil sampling procedure, which was different in the 1st treatment.

Among plots, model predictions were quite similar (Fig. 4). The scarce differences between the predicted data in a plot were in accordance with the experimental results (Fig. 2) and supported that the small differences were mainly due to the irrigation employed, playing the amendments a secondary role in the field experiments.

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