



## RESEARCH ARTICLE

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## Testing of leachability and persistence of sixteen pesticides in three agricultural soils of a semiarid Mediterranean region

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### Abstract

Leaching, the movement of water and chemicals into deeper soil layers and groundwater is a subject of worldwide interest because a high percentage of drinking water is extracted from groundwater. The objective of this study was to evaluate the potential leaching and persistence of sixteen pesticides (one fungicide, three nematicides/insecticides, and twelve herbicides) for three Mediterranean agricultural soils with similar texture (clay loam) but different organic matter content (1.2-3.1%). Adsorption was studied in batch experiments and leaching was tested using disturbed soil columns (40 cm length × 4 cm i.d.). Degradation studies were carried out during 120 days under laboratory conditions. Mobility experiments showed that pesticides can be grouped according to their potential leaching. Thus, pesticides showing medium leachability were included in group 1 (referred as G1) while those with high leachability were termed as G2. The differences observed in the leachability can be attributed to the different organic carbon (OC) content in the soils (0.7-1.8%). Values of  $\log K_{OC}$  were higher in the order: soil C > soil B > soil A, which agrees with the OC content in each soil. The calculated half-lives ranged from 4.2 days for carbofuran in soil A to 330 days for prometon in soil C. As a general rule, when higher OC content in the soil the greater persistence of the pesticide was observed as a consequence of the increased adsorption. The first order kinetics model satisfactorily explains the disappearance of the studied pesticides in the soil.

**Additional key words:** aqueous/soil environment; groundwater pollution; pesticide leaching; soil half-lives.

**Abbreviations used:** BTC (breakthrough curves);  $C_e$  (concentration after equilibrium);  $C_i$  (initial concentration);  $C_s$  (concentration adsorbed);  $DT_{50}$  (the time for 50% disappearance); GUS (groundwater ubiquity score);  $K_d$  (distribution coefficient);  $K_{OC}$  (the soil organic partition coefficient);  $K_{ow}$  (octanol/water partition coefficient); LOD (limit of detection); LOQ (limit of quantitation); MCP (mean concentration of pesticides); OC (organic carbon); PV (pore volume);  $S_w$  (water solubility);  $t_{1/2}$  (half-life time).

**Citation:** Garrido, I.; Vela, N.; Fenoll, J.; Navarro, G.; Pérez-Lucas, G.; Navarro, S. (2015). Testing of leachability and persistence of sixteen pesticides in three agricultural soils of a semiarid Mediterranean region. Spanish Journal of Agricultural Research, Volume 13, Issue 4, e1104, 11 pages. <http://dx.doi.org/10.5424/sjar/2015134-8339>.

**Received:** 20 Jul 2015. **Accepted:** 17 Nov 2015.

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**Funding:** Spanish Ministry for Science and Innovation (project AGL2010-20458-C02-01); 'Ramón and Cajal' Subprogram; FEDER and European Social Funds; INIA, Spain (project RTA2011-00022-00-00).

**Competing interests:** The authors have declared that no competing interests exist.

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### Introduction

Pesticides are widely applied to control pests and produce good quality food at reasonable prices and costs. Their use is constantly increasing and also the probability of causing any unwanted side effects in the natural environment. These undesirable effects must be identified and as far as possible eliminated, but some risks are inevitable because pesticides can provoke an impact in nature through spray drift, leaching and runoff into water, or effects on living organisms exposed (Rao *et al.*, 1983).

Upon application, the concentration of pesticides in the environment varies due to several processes as scattering, volatilization, chemical and biological degradation and leaching (Shestopalov & Molozhanova, 1992), and the extension in which happens every process depends on the physicochemical properties of each compound, the properties of water and soil, the climatic conditions of the area and the method of application (Navarro *et al.*, 2007).

The persistence and mobility of pesticides in soil is directly related to their adsorption to soil components

and their degradation. Persistence may be defined as the tendency of a given compound, a pesticide in this case, to conserve its molecular integrity and chemical, physical and functional characteristics in a medium through which it is transported and distributed after being released into the environment. Sorption will determine whether the pesticide will persist or not, be transported and become a pollutant or not, especially to groundwater and, often, whether it will be efficacious or not (Wauchope *et al.*, 2002). Under certain conditions, these substances may move through the soil to groundwater from normal field applications and pollute those resources of water (Arias-Estévez *et al.*, 2008). This movement of pesticides, the named leaching, is mainly influenced by chemical and physical properties of the soils (texture, clay and organic content, and permeability) and pesticides involved and weather conditions (Kreuger, 1998) being the organic carbon (OC) content the most important factor implicated in the adsorption and mobility of pesticides in soil. As a general rule, the higher the OC content is, the greater the pesticides adsorption is and the lower the mobility, reducing leaching (Spark & Swift, 2002; Alister *et al.*, 2011).

Pesticides can enter in water bodies via diffuse or via point sources. Diffuse pesticide input into groundwater are leaching through the soil and unsaturated zone and infiltration through riverbanks and riverbeds (Reincherberger *et al.*, 2007). Pesticide residues have been detected in groundwater bodies worldwide (Kolpin *et al.*, 1996; Sorensen *et al.*, 2003) and their levels often exceed the drinking water limit established by the European Union (0.1 mg/L for individual pesticides and 0.5 mg/L for total concentrations of all pesticides) to safeguard people from harmful effects (EC, 2006). As a consequence, for a proper risk assessment of these chemicals, it is important to estimate their potential for transformation in soil and for movement (leaching) into deeper soil layers and eventually into groundwater. In contrast to surface water, dilution of pesticides in groundwater is very small. Moreover, pesticide pollution of groundwater is a subject of worldwide interest because it is used for drinking water in many countries.

In this view, the aim of this work was to estimate the leaching of 16 pesticides (one fungicide, three nematicides and twelve herbicides), usually applied by the farmers in different areas of the world during the last decades and with high toxicological profile, using disturbed columns loaded with three soils with different organic matter content, under laboratory conditions. In addition, we have studied adsorption and degradation as other major processes determinants of their behaviour in soil.

## Material and methods

### Chemicals

Pesticide analytical standards ( $\geq 96\%$ ) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The main physical-chemical properties of the active ingredients are shown in Table 1. Experimental values of the octanol/water partition coefficient ( $K_{ow}$ ), soil/organic partition coefficient ( $K_{oc}$ ), aqueous solubility ( $S_w$ ), and groundwater ubiquity score (GUS) index were taken from The Pesticide Properties DataBase (AERU, 2015) and KOCWIN™ included in the EPI Suite v4.11 program provides by USEPA (2015).

Stocks solutions (1000  $\mu\text{g/mL}$ ) of each pesticide standard were prepared in acetonitrile, protected from light and stored at 5°C. Several standard solutions, with concentrations of 0.5-200  $\mu\text{g/L}$ , were injected to obtain the linearity of detector response and the detection limits (LOD) of the compounds studied. Pesticide grade acetonitrile and dichloromethane were supplied by Scharlab (Barcelona, Spain).

### Soils

Three different agricultural soils were chosen for this study. Soil A (Hipercalcic calcisol), soil B (Calcic regosol) and soil C (Haplic calcisol) were taken from the Campo de Cartagena (Murcia, south-eastern Spain). Soil samples were collected from the surface (top 20 cm), air-dried, and passed through a 2 mm sieve. The experimental studies began within four days after sampling and storage under cool conditions. The composition of the soils is shown in Table 2.

The main characteristics of the soil (total organic carbon, pH, alkalinity, texture) were determined by standard soil analysis techniques (Reeuwijk, 2002) The clay content was determined by means of a powder X-ray diffractometer (XRD) on a Philips PW 1700 using Cu-K $\alpha$  radiation at a scanning speed of 1° (2 $\theta$ ) after washing, disaggregation and dispersion of the sample.

### Downward movement of the pesticides through the soil columns

The experiment was conducted according to the OECD guidelines (OECD, 2007). Downward movement of the pesticides was studied in polyvinyl chloride (PVC) columns of 40 cm (length)  $\times$  4 cm (i.d). There were three sets of columns, each filled with 200 g of a different kind of soil: A, B or C. The top 3 cm of the

**Table 1.** Main physicochemical properties of the studied pesticides.

Pesticides	Molecular formula	Molecular mass	Log $K_{ow}$	$S_w^a$	Log $K_{oc}^b$	GUS index <sup>c</sup>
Atrazine	C <sub>8</sub> H <sub>14</sub> ClN <sub>5</sub>	215.7	2.7	35	2.1	3.3 (H)
Cadusafos	C <sub>10</sub> H <sub>23</sub> O <sub>2</sub> PS <sub>2</sub>	270.4	3.8	245	3.1	2.6 (M)
Carbofuran	C <sub>12</sub> H <sub>15</sub> NO <sub>3</sub>	221.3	1.8	322	2.2	3.0 (H)
Ethoprophos	C <sub>8</sub> H <sub>19</sub> O <sub>2</sub> PS <sub>2</sub>	242.3	3.0	1300	3.0	2.4 (M)
Isoxaben	C <sub>18</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub>	332.4	3.9	0.9	3.0	2.9 (H)
Metamitron	C <sub>10</sub> H <sub>10</sub> N <sub>4</sub> O	202.2	0.8	1770	1.7	3.0 (H)
Metribuzin	C <sub>8</sub> H <sub>14</sub> N <sub>4</sub> OS	214.3	1.6	1165	2.2	2.6 (M)
Pencycuron	C <sub>19</sub> H <sub>21</sub> ClN <sub>2</sub> O	328.8	4.7	0.3	3.2	0.6 (L)
Prometron	C <sub>10</sub> H <sub>19</sub> N <sub>5</sub> O	225.3	2.9	620	2.4	5.7 (H)
Prometryn	C <sub>10</sub> H <sub>19</sub> N <sub>5</sub> S	241.4	3.3	33	2.6	0.6 (L)
Propazine	C <sub>9</sub> H <sub>16</sub> ClN <sub>5</sub>	229.7	3.9	8.6	2.3	3.8 (H)
Propyzamide	C <sub>12</sub> H <sub>11</sub> Cl <sub>2</sub> NO	256.1	1.3	9.0	2.6	1.8 (L)
Simazine	C <sub>7</sub> H <sub>12</sub> ClN <sub>5</sub>	201.7	2.3	5.0	1.9	2.0 (M)
Simetryn	C <sub>8</sub> H <sub>15</sub> N <sub>5</sub> S	213.3	2.8	450	2.3	3.0 (H)
Terbutylazine	C <sub>9</sub> H <sub>16</sub> ClN <sub>5</sub>	229.7	3.4	6.6	2.4	3.1 (H)
Terbutryn	C <sub>10</sub> H <sub>19</sub> N <sub>5</sub> S	241.4	3.6	25	2.8	2.4 (M)

<sup>a</sup> Water solubility (mg/L). <sup>b</sup> Log  $K_{oc}$  estimated from log  $K_{ow}$ . <sup>c</sup> Groundwater ubiquity score (GUS) index. Leachability in parenthesis (L, low; M, medium; H, high).

**Table 2.** Characteristics of the soils used in this study (mean  $\pm$  % relative standard deviation).

Parameter	Soil A	Soil B	Soil C
Clay (%)	27 $\pm$ 2.1	32 $\pm$ 2.7	33 $\pm$ 3.0
Silt (%)	32 $\pm$ 3.5	47 $\pm$ 3.2	30 $\pm$ 2.8
Sand (%)	40 $\pm$ 2.2	21 $\pm$ 4.3	37 $\pm$ 3.9
Bulk density (g/cm <sup>3</sup> )	1.36	1.30	1.33
Total nitrogen (%)	0.3 $\pm$ 4.2	0.8 $\pm$ 5.1	0.5 $\pm$ 5.3
Total organic carbon (%)	0.7 $\pm$ 2.2	1.2 $\pm$ 4.8	1.8 $\pm$ 3.5
pH (H <sub>2</sub> O 1:1)	7.7 $\pm$ 1.9	8.2 $\pm$ 1.8	7.3 $\pm$ 1.5
Electric conductivity (dS/m)	0.9 $\pm$ 2.1	0.4 $\pm$ 2.8	7.3 $\pm$ 2.2
Alkalinity (mg CaCO <sub>3</sub> /kg)	516 $\pm$ 4.2	601 $\pm$ 4.9	398 $\pm$ 6.2
<i>Clay content (% weight)</i>			
Illite	14 $\pm$ 2.2	16 $\pm$ 3.5	19 $\pm$ 2.2
Vermiculite	14 $\pm$ 3.1	12 $\pm$ 2.9	13 $\pm$ 1.8
Kaolinite	7 $\pm$ 2.7	4 $\pm$ 4.2	6 $\pm$ 3.3
Montmorillonite	37 $\pm$ 2.2	37 $\pm$ 1.9	40 $\pm$ 2.5
Interstratified minerals	28 $\pm$ 3.6	31 $\pm$ 3.3	22 $\pm$ 4.0

columns were filled with sea sand and the bottom 3 cm with sea sand plus nylon mesh with an effective pore diameter of 60  $\mu$ m to minimizing the dead-end volume and prevent losses of soil during the experiment. Experiments were performed in triplicate, at room temperature and protected from direct light. Before the

application of the pesticides, columns were conditioned with 0.01 M CaCl<sub>2</sub> in distilled water to their maximal water holding capacity and then allowed to drain for 24 h. The pore volume (PV) of the packed columns was estimated by the weight difference of water-saturated columns versus dry columns. The calculated PVs (mL)

of the soil columns after saturation were  $70.1 \pm 1.9$  (soil A),  $73.6 \pm 2.2$  (soil B), and  $79.3 \pm 1.6$  (soil C). After this, 1.0 mL of methanol/water solution (10+90, v/v) containing 20  $\mu\text{g}$  of every compound were added to the top of each column. Twenty four hours after pesticide application, the compounds were leached by adding 800 mL of 0.01 M  $\text{CaCl}_2$  during 16 days with a peristaltic pump.  $\text{CaCl}_2$  instead of water was used in order to minimize soil mineral balance disruption. The leachates (50 mL/day) were quantitatively collected at the bottom of the columns, and then filtered through nylon membrane filter (0.45  $\mu\text{m}$ ). After this time, the columns were opened and the soil separated in two segments of approximately 10 cm each.

### Degradation and adsorption experiments of pesticides by soils

The soil degradation experiments were conducted according to the OECD procedure (OECD, 2002). To ascertain pesticide persistence, soil samples (50 g, on a dry weight basis) were placed in incubation flasks ( $n=3$ ). Two milliliters of a methanol/water solution (10+90, v/v) containing all the studied pesticides was applied in order to achieve an initial concentration of 100  $\mu\text{g}/\text{kg}$  of each. All the flasks were incubated in the dark for 120 days at  $21 \pm 2^\circ\text{C}$  with the soil moisture ranging from 40-60% of the water holding capacity. Throughout the incubation period water losses exceeding 10% of the initial values were compensated by the addition of fresh distilled water every two weeks. Relative humidity was maintained at 70%. After 7, 15, 30, 60, and 120 days of incubation, three flasks from each treatment were taken and kept at  $4^\circ\text{C}$  for 2-3 days until analysis.

The dissipation of all pesticides could be described by pseudo first-order kinetics:  $\ln C_t = \ln C_0 - kt$ , where  $C_t$  is the concentration of pesticide in soil;  $C_0$  and  $k$  denote  $y$ -intercept values and the slope of the dissipation lines, respectively; and  $t$  is the post-application time in days. Hence, their half-lives ( $t_{1/2}$ ) were calculated from the equation  $t_{1/2} = \ln 2/k$ . The curve fitting and statistical data were obtained using SigmaPlot v. 12.0 statistical software (Systat, Software Inc., San Jose, CA, USA).

On the other hand, the  $K_d$  (distribution coefficient) value was considered a measure of pesticide adsorption capacity by the soils. The sorption of pesticides was determined using a batch equilibrium method (OECD, 2000). Triplicates 5 g of each soil were equilibrated with 20 mL of an aqueous solution of pesticides at an initial concentration ( $C_i$ ) of 25  $\text{ng}/\text{mL}$  for 24 h at  $22 \pm 1^\circ\text{C}$ . The amount adsorbed ( $C_s$ ) was considered to

be the difference between  $C_i$  and that remaining after equilibration ( $C_e$ ).  $K_d$  values were obtained from the relationship between  $C_s$  and  $C_e$  ( $K_d = C_s/C_e$ ). The organic carbon normalized adsorption coefficient ( $K_{OC}$ ) was calculated as  $(K_d \cdot 100)/\%OC$ .

### Analytical determinations

Water samples (10 mL) were extracted via a liquid-liquid extraction with acetonitrile (10 mL) by sonication, followed by a salting-out step with 2 g NaCl. The samples were shaken and centrifuged for 10 min at 3000xg. Dried soil samples (10 g) were extracted with 20 mL of acetonitrile/water (2/1) by sonication. Then, 20 mL of dichloromethane were added and the mixture was centrifuged for 10 min at 1900xg. Finally, water and soil extracts were filtered quantitatively through a glass funnel with a DP302 filter separation phase paper, 150 mm diameter (Albet, Barcelona). The organic phase was concentrated to dryness by rotary vacuum evaporation. The residue was redissolved in 1 mL of acetonitrile, filtered through 0.45  $\mu\text{m}$  filter and analyzed by liquid chromatography in tandem with mass spectrometry (LC-MS<sup>2</sup>).

The separation, identification and quantification of pesticides studied were carried out by an HPLC system (Agilent Series 1100, Agilent Technologies, Santa Clara, CA, USA) equipped with a reversed phase C8 analytical column of 150 mm  $\times$  4.6 mm and 5  $\mu\text{m}$  particle size (Zorbax Eclipse XDB-C8). The mobile phases A and B were acetonitrile and 0.1% formic acid, respectively. The gradient program started with 10% A, constant for 5 min, followed by a linear gradient to 100% A to 35 min. After this run time, 10 min of post-run time followed using initial 10% of A. The flow-rate was constant (0.6 mL/min) during the whole process. In all cases 5  $\mu\text{L}$  of sample were injected. For the mass spectrometric analysis, an Agilent G6410A triple quadrupole mass spectrometer equipped with an ESI interface operating in positive ion mode, using the following operation parameters: capillary voltage, 3000 V; nebulizer pressure, 40 psi; drying gas, 9 L/min; drying gas temperature,  $350^\circ\text{C}$ . Mass spectra were recorded across the range 50–1000  $m/z$ .

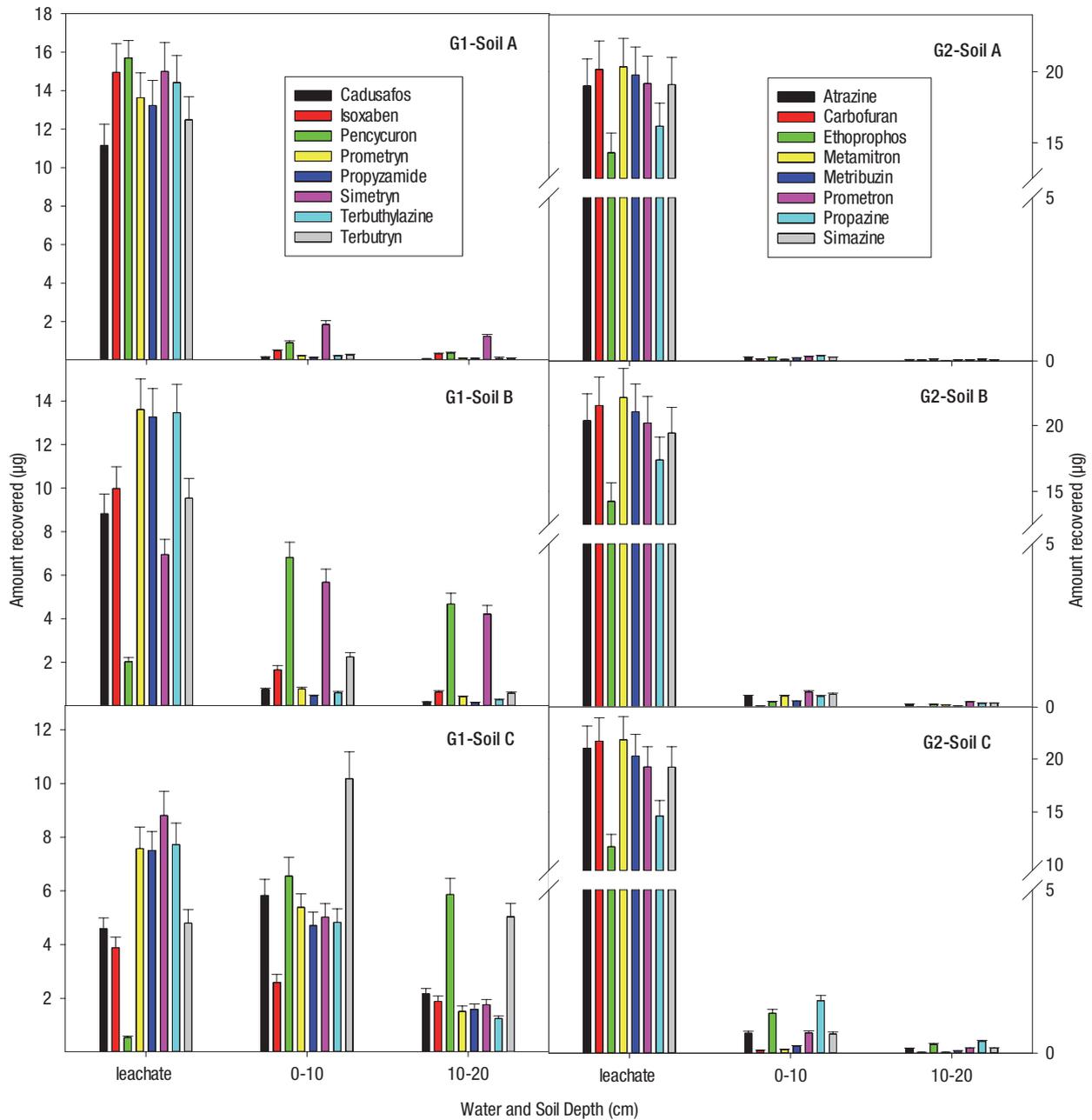
The calibration curves were prepared in soil and water. The calibration samples were analyzed by spiking pesticides at 0.5-200  $\mu\text{g}/\text{L}$  levels into water and soil samples in five replicates. In all cases the correlation coefficients were  $>0.99$ . Limit of detection (LOD, defined as the lowest amount of pesticide in a sample which can be detected but not necessarily quantitated as an exact value) and limit of quantitation (LOQ, as the lowest amount of pesticide in a sample which can

be quantitatively determined with suitable precision and accuracy) were evaluated by injecting standard solution into blank matrix at different concentration levels. LOQs were calculated from the signal-to-noise (S/N) ratio of 10. LOQs varied from 0.02-0.3 µg/L and 0.07-0.7 µg/kg in water and soil, respectively.

### Results

The leachability (the state of being leachable) of pesticides as a function of their distribution from soil

and water is shown in Figure 1. The compounds were grouped according their potential leaching. As criteria, the mean concentration of pesticides (MCP) recovered in total leachates obtained from soil A was used. Thus, pesticides showing medium leachability (MCP < 15 µ) were included in group 1 (referred as G1) while those with high leachability (MCP > 15 µ) were termed as G2. As can be seen in graphics G1-A, G1-B and G1-C, the amount recovered in leachates increases in the order: soil A > soil B > soil C while the total amount recovered from the two layer of the soils presents re-

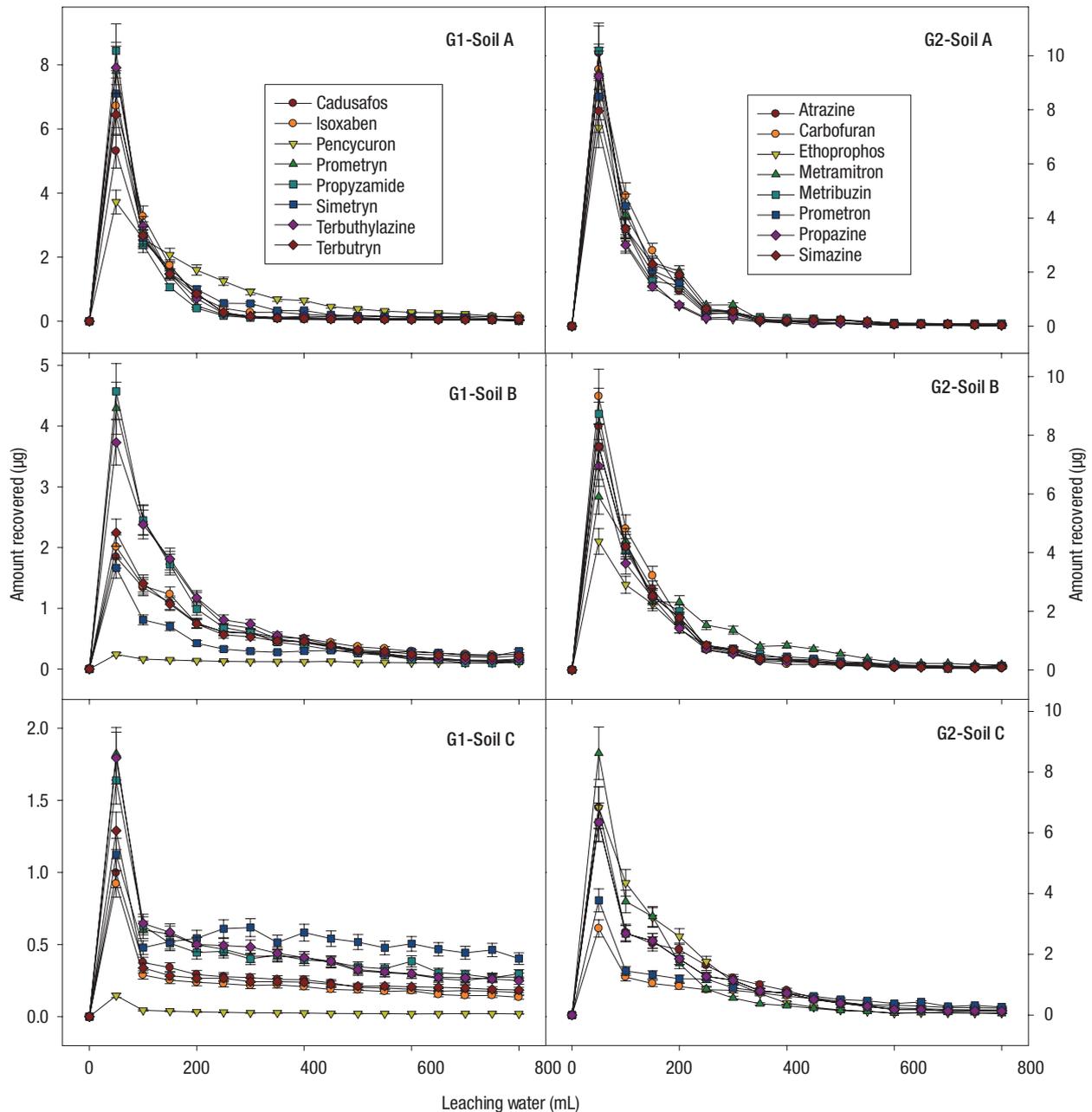


**Figure 1.** Distribution from soil and water of pesticides applied to soil A, B, and C. G1: Group 1; G2: Group 2. The error bars denote standard deviation.

verse order: soil C > soil B > soil A. Regarding the second group of compounds (graphics G2-A, G2-B and G2-C) similar behaviour was noted although in this case the differences were lower because of the high leachability observed for all compounds showing ethoprophos and propazine the lowest leaching potential of this group in all soils. On the other hand, relative breakthrough curves (BTCs) of the pesticides applied to soil columns are shown in Figure 2. The relative BTCs showed that all the pesticides behaved as leacher compounds with rapid leaching (maximum after 50 mL) mainly in the soil A.

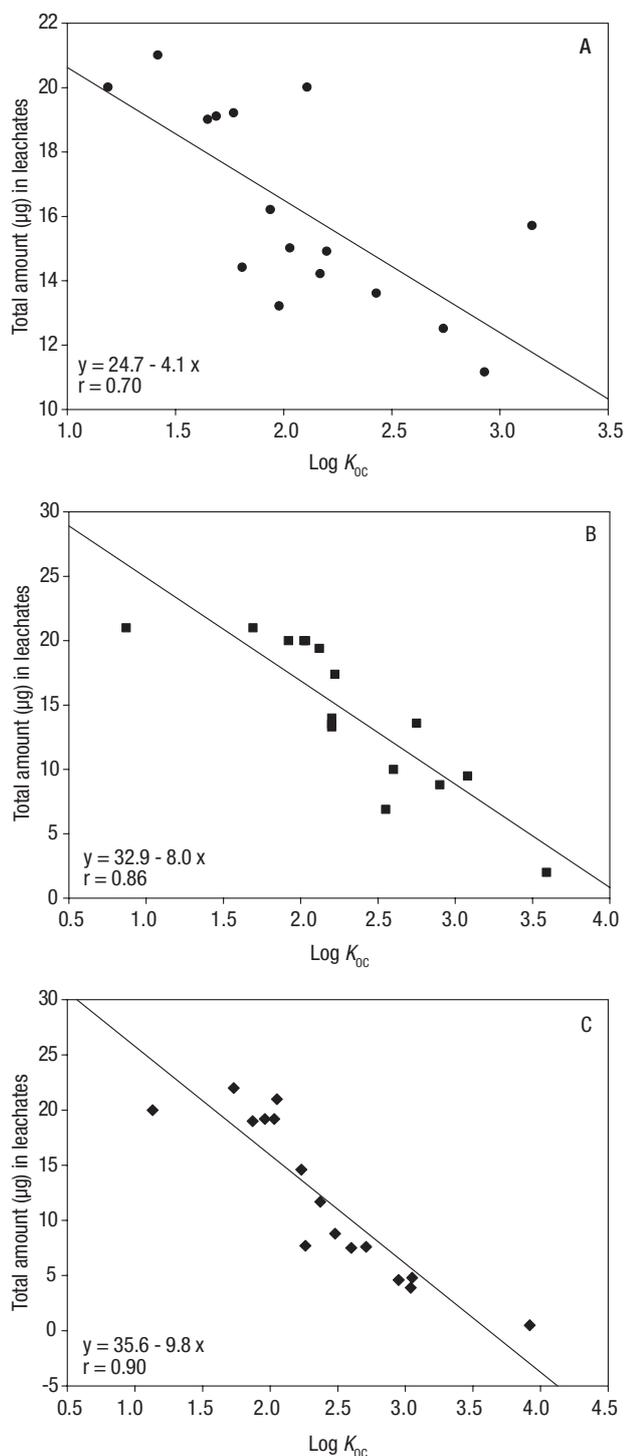
The calculated values of  $K_{OC}$  obtained for the studied pesticides are showed in Table 3. As a general rule,  $K_{OC}$  values are higher in the order: soil C > soil B > soil A, which agrees with the organic carbon content in each soil. As can be seen in Figure 3, where the regression lines obtained between experimental values of  $\log K_{OC}$  and total amount of pesticides recovered from leachates are depicted, better values of the regression coefficient ( $r$ ) were obtained in the order:  $r_{\text{soilC}} > r_{\text{soilB}} > r_{\text{soilA}}$ .

The dissipation of all pesticides follows a pseudo first-order kinetics with  $R^2 \geq 0.9$  in all cases with the exception of prometon in soil A ( $R^2=0.85$ ) and soil C



**Figure 2.** Relative breakthrough curves (BTCs) of pesticides applied to soil columns for soils A, B, and C. The error bars denote standard deviation.

( $R^2=0.80$ ) and isoxaben in soil B ( $R^2=0.84$ ), both showing the highest persistence. For all soils, the standard error of the estimate ( $S_{Y/X}$ ) was lower than 2.34. When the linear estimation fails, other equations, such as those provided in two-phase models, can be used with better results, especially when there is an initial rapid degradation and a subsequent phase in which the com-



**Figure 3.** Correlation between total amounts of each pesticide recovered from leachates and log  $K_{OC}$  for soils A, B, and C.

pound disappears more slowly. In some cases, a modified first-order model proposed by Hoerl (1954) has been used to advantage (Zimdahl *et al.*, 1994; Navarro *et al.*, 2009).

Factors other than  $K_{OC}$ , such as a compound's persistence, affect the leaching potential of pesticides. Thus, bearing in mind the potential leachability of the studied compounds, the evolution of pesticide residues with time was simultaneously assessed in the three soils to evaluate the persistence of each compound in our experimental conditions. The soil half-life is a measure of the persistence of a pesticide in soil. According to Gavrilescu (2005), pesticides can be categorized on the basis of their half-lives as non-persistent, degrading to half the original concentration in less than 30 days; moderately persistent, degrading to half the original concentration in 30-100 days; and persistent, taking longer than 100 days to degrade to half the original concentration. Pesticide persistence is usually characterized in terms of the time it takes for 50% of the pesticide to either degrade ( $t_{1/2}$ ) or dissipate (DT50). As can be seen in Table 4, the calculated half-lives ranged from 4.2 days for carbofuran in soil A to 330 days for prometon in soil C. As a general rule, when higher OC content in the soil the greater persistence of the pesticide was observed. According to the classification above mentioned the studied pesticides can be ordered as a function of their persistence as follows:

**Table 3.** Calculated values of organic carbon-normalized adsorption coefficient as log  $K_{OC}$  ( $K_{OC}$ : the soil organic partition coefficient)

Pesticides	Soil A	Soil B	Soil C
Atrazine	1.65	2.02	2.05
Cadusafos	2.93	2.90	2.95
Carbofuran	2.11	1.69	1.73
Ethoprophos	2.17	2.20	2.37
Isoxaben	2.20	2.60	3.04
Metamitron	1.42	1.92	1.87
Metribuzin	1.19	0.87	1.13
Pencycuron	3.15	3.59	3.92
Prometron	1.77	2.03	2.03
Prometryn	2.43	2.75	2.71
Propazine	1.94	2.22	2.23
Propyzamide	1.98	2.20	2.60
Simazine	1.69	2.12	1.96
Simetryn	2.03	2.55	2.48
Terbutylazine	1.81	2.20	2.26
Terbutryn	2.74	3.08	3.05
<i>Mean value</i>	<i>2.08</i>	<i>2.31</i>	<i>2.40</i>

**Table 4.** Kinetic parameters of pesticides in three types of soil.

Pesticides	Soil A			Soil B			Soil C		
	$R^2$	$K$	$t_{1/2}$	$R^2$	$K$	$t_{1/2}$	$R^2$	$K$	$t_{1/2}$
Atrazine	0.962	0.0143	48.3	0.991	0.0132	52.5	0.974	0.0082	84.5
Cadusafos	0.962	0.0186	37.3	0.959	0.0114	60.8	0.957	0.0134	51.7
Carbofuran	0.988	0.0679	10.2	0.996	0.0513	13.5	0.952	0.0456	15.2
Ethoprophos	0.997	0.0326	21.3	0.996	0.0343	20.2	0.989	0.0328	21.1
Isoxaben	0.967	0.0073	95.0	0.837	0.0051	135.9	0.929	0.0045	154.0
Metamitron	0.992	0.0253	27.4	0.991	0.0275	25.2	0.987	0.0169	41.0
Metribuzin	0.990	0.0216	32.1	0.997	0.0340	20.4	0.988	0.0148	46.8
Pencycuron	0.985	0.0277	25.0	0.976	0.0229	30.2	0.990	0.0159	43.6
Prometon	0.849	0.0027	252.3	0.899	0.0026	266.6	0.798	0.0021	330.1
Prometryn	0.975	0.0188	36.9	0.997	0.0268	25.9	0.925	0.0130	53.3
Propazine	0.951	0.0132	52.6	0.989	0.0107	64.8	0.955	0.0083	83.5
Propyzamide	0.998	0.0753	9.2	0.981	0.0305	22.7	0.988	0.0232	29.9
Simazine	0.963	0.0182	38.1	0.979	0.0165	42.0	0.976	0.0070	99.0
Simetryn	0.995	0.0300	23.1	0.998	0.0216	32.1	0.979	0.0174	39.8
Terbuthylazine	0.979	0.0103	67.3	0.985	0.0098	70.7	0.955	0.0084	82.5
Terbutryn	0.967	0.0249	27.8	0.991	0.0213	32.5	0.902	0.0120	57.8

$K$ : rate constant ( $\text{days}^{-1}$ );  $t_{1/2}$ : half-life time (days).

- *Non persistent*: Carbofuran < Ethoprophos < Propyzamide
- *Moderately persistent*: Pencycuron < Metamitron  $\approx$  Metribuzin  $\approx$  Simetryn < Prometryn  $\approx$  Terbutryn < Cadusafos < Simazine  $\approx$  Atrazine < Propazine < Terbuthylazine
- *Persistent*: Isoxaben < Prometon

## Discussion

### Leaching of pesticides through disturbed soil columns

The shape of the curves for soils B and C (Fig. 2) indicates a certain interaction with the organic and inorganic soil colloids unlike soil A. Clay-humus interactions contribute to the high organic matter content of clay soils because the organic matter entrapped in the micropores (<1  $\mu\text{m}$ ) formed by clay particles is physically inactive to decomposing organisms. Dissolved pesticides may be carried downward rapidly by water through large macropores. This type of non-uniform movement, referred as preferential flow, greatly increases the chances of groundwater pollution, while organic matter improve soil water retention since it increases both infiltration rate and water-holding capacity (Brady & Weil, 2010).

It is generally accepted that the leaching of a compound depends mainly on its degradation and sorption to the soil (Moorman *et al.*, 2001). Adsorption is the binding of pesticides to mineral or organic matter. Sorption retards movement, and may also increase persistence because the pesticide is protected from degradation. Among various soil properties, OC content is the single largest factor that has maximum influence on pesticide degradation, adsorption and mobility in soil (Wauchope *et al.*, 2002). In our case, the three soils have similar clay content (29-33%). Moreover, the percentage of weight of montmorillonite, an expanding 2:1-type silicate clay with a very high total specific surface area (800  $\text{m}^2/\text{g}$ ) is also similar (37-40%) in the three studied soils. Therefore, the differences observed in the leachability can be attributed to the different organic carbon content in the soils (0.7-1.8%), mainly for the soil C.

The coefficient  $K_{\text{OC}}$  describes the tendency of a pesticide to bind to soil. At higher values of the  $K_{\text{OC}}$ , the greater the sorption potential. Results showed in Table 3 are consistent with the organic carbon content in the soil. Recently, Navarro *et al.* (2012) pointed the strong decrease of the leachability of 12 substituted phenylurea herbicides through an Endoleptic phaeozon (OC=6.1%) as compared with a Hypercalcic calcisol (OC=0.7%). As a consequence, a strategy to reduce the movement of the pesticides through the soil profile is the addition of organic wastes (Fenoll *et al.*, 2014a,b; 2015).

Chemical reactions between unaltered pesticides and/or their metabolites often lead to the formation of strong bonds (chemisorption), resulting in an increase in the persistence of the residues in the soil, while causing it to lose its chemical identity. From a toxicological point of view, binding of pesticides to humus lead to a decrease of material available to interact with biota, a reduction in the toxicity of the compound, and immobilising the pesticide, thereby reducing its leaching and transport properties (Navarro *et al.*, 2007).

### Persistence of pesticides in the soils

The calculated half-lives (as mean value for the three soils) showed in Table 4 are consistent with those included as typical DT50 in the Pesticide Properties Database (AERU, 2015). According to GUS index (Gustafson, 1989), carbofuran and ethoprophos behave as leacher compounds while propyzamide has transient properties (*i.e.*, borderline leacher). As a consequence, their permanence in the soil is lower. In addition to pencycuron (phenylurea fungicide) and cadusafos (organophosphate insecticide) the triazine compounds with the exception of prometon (methoxy-triazine) show moderate persistence in the order triazinones < methylthio-triazines < chloro-triazines. Typical values of  $t_{1/2}$  or DT50 for triazine compounds range from 14 to 102 days, with a mean  $t_{1/2}$  or DT50 of  $36 \pm 25$  days (Koskinen & Banks, 2008). Triazine retention in soil is influenced primarily by OC content, soil clay content and type, and pH. Other important factors influencing retention include the amount applied, the amount of dissolved OC in soil solution, soil water content and soil contact time (aging). Isoxaben and prometon were the compounds with higher persistence ( $t_{1/2} > 100$  days).

Pesticide residues can be found in the soil as free and bound residues. Such terms were coined to indicate that the former can be readily extracted from soil without altering their chemical structures, whereas the latter are resistant to such extraction. However, the distinction between these two fractions is not always clear, because while they are in the soil, even the extractable residues are not entirely free from any form of binding because they may be sorbed to the soil solid phases and, therefore, show reduced bioavailability and degradation. The environmental significance of a bound residue depends not on its nonextractability under laboratory conditions, but on its bioavailability. Depending on the nature of binding, immobilised pesticides may be released back to the soil solution or mineralized as a result of chang-

ing environmental conditions in the soil (Khan, 1982).

To conclude, the results obtained in this work on texturally similar agricultural soils, soil A (Hipercalcic calcisol), soil B (Calcáric regosol), and soil C (Haplic calcisol) show that all the studied pesticides behave as leacher compounds although in different proportions. Cadusafos, isoxaben, pencycuron, prometryn, propyzamide, simetryn, terbuthylazine, and terbutryn (G1) show medium leachability while atrazine, carbofuran, ethoprophos, metamitron, metribuzin, prometon, propazine, and simazine (G2) show high leachability through the soil columns. As a general rule,  $K_{OC}$  (the tendency of a pesticide to bind to soil) values are higher in the order: soil C > soil B > soil A, which agrees with the OC content in each soil. As a consequence, at higher values of the  $K_{OC}$ , the greater the sorption potential and lower the leaching.

On the basis of the half-lives obtained, carbofuran, ethoprophos and propyzamide can be categorized as non-persistent pesticides ( $t_{1/2} < 30$  days) while isoxaben and prometon can be classified as persistent pesticides ( $t_{1/2} > 100$  days) showing the rest of the studied pesticides moderate persistence ( $t_{1/2} = 30-100$  days). As it can be observed, when higher OC content in the soil the greater persistence of the pesticide was observed. Disappearance of the pesticides follows first order degradation kinetics although for the most persistent compounds (isoxaben and prometon) bi-phasic models could be more appropriate because there is an initial rapid degradation and a subsequent phase in which the compounds disappear more slowly.

Bearing in mind that these residues can reach water bodies by leaching and runoff, and as they are inherently toxic molecules, they can adversely affect aquatic environment and non-targeted organism. Moreover, presence of these pesticides in groundwater is extremely hazardous as groundwater is major source of drinking water. Therefore, the results obtained point to the interest in the use of organic wastes such as agro-industrial, composted manure, sewage sludge, etc., by-products available at low- or no-cost in reducing the pollution of groundwater by pesticide drainage, mainly in arid and semiarid regions, as Mediterranean area where soils generally have low organic matter contents.

### Acknowledgements

We wish to thank to I Garrido, J Cava and MV Molina for technical assistance.

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