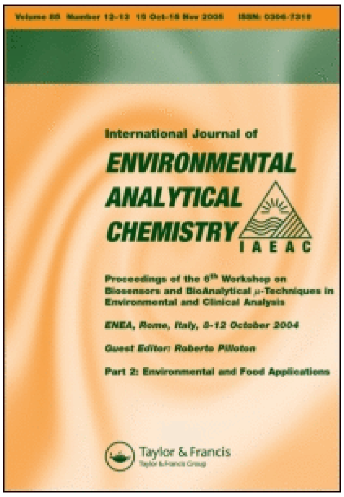

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Leaching potential of several insecticides and fungicides through disturbed clay-loam soil columns

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A laboratory study was conducted in order to determine the leaching potential of five insecticides and six fungicides commonly used during pepper cultivation by use of disturbed soil columns. The tested compounds were pyridaben, pyriproxyfen, tebufenpyrad, buprofezin and pirimicarb (insecticides/acaricides) and azoxyxtrobin, kresoxim-methyl, hexaconazole, tebuconazole, triadimenol, and pyrimethanil (fungicides). For this purpose, 100 µg of each pesticide were added to columns ($n = 5$) filled with 150 g of a clay loam soil and leached with 600 mL of 0.01 M $CaCl_2$ during 10 days. Finally, leachates and soil fractions were analysed for pesticide residues. For insecticides only pirimicarb was found in leachates (48% of the initial amount) while 55% was recovered from the soil layers. For the other studied insecticides, the percentage remaining in the top soil fraction was nearly the total amount added and therefore showing 'non-leaching' behaviour. In the case of fungicides 41% of triadimenol and 6% of pyrimethanil were found in leachates. The amount recovered in leachates for the other fungicides was lower than 2%, hexaconazole and tebuconazole exhibiting the higher retention on the upper layer of soil. Therefore, is extremely important to propose methods and conduct to avoid the potential adverse effect of pesticides behaving as 'leacher' compounds.

Keywords: aqueous/soil environment; pepper protection; pesticide mobility; soil sorption constant

1. Introduction

Spain was the EU's biggest pepper (*Capsicum annuum* L.) producer in 2007, accounting for 1.1 tonnes, of which 65% were produced in the southeast, Almería and Murcia [1]. Because of the specific climatic conditions of this area, some diseases and insect pests threaten efficient pepper production by lowering yield, reducing fruit quality and making harvests unreliable. Although new management practices, as integrated crop management (ICM), have evolved in the last years as response to the need to reduce dependence on pesticides, the use of insecticides and fungicides is still very important in this area.

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All the used pesticides are subject to an approval procedure under EU legislation, and also under national legislation. However, risks are inevitable, and it is not possible to remove these entirely through the approval process. In particular, the use of pesticides has an impact on the natural environment through spray drift, wash-off, leaching or run-off into water, or effects on non-target organisms.

The potential risk involved when a pesticide is incorporated into the soil depends on many factors, especially, its mobility and persistence. Adsorption, degradation and transfer processes determine the ultimate fate of the pesticides in the soil [2–4]. The environmental fate of pesticides depends a lot on their mobility in soils and their tendency to partition into other environmental compartments, such as air and water. Concretely, leaching (the movement of water and dissolved chemicals through the soil) of pesticides through the soil profile from agricultural practices is of special interest in environmental research. Under certain conditions, some pesticides may leach to groundwater from normal field applications [5].

Europe confronts enormous groundwater pollution problems, agriculture being the biggest polluter [6]. The majority of Europeans (about 60–65%) rely on groundwater for drinking water purposes and its use is threatened by the leaching of pesticides and nitrates from agriculture. Many groundwater supplies in EU countries exceed the drinking water directive 98/83/EC maximum of $0.1\,\mu g\,L^{-1}$ for a single pesticide [7]. For the assessment of the leaching risk, the EU-directive 91/414 suggests the performance of simulation studies [8]. Although there is large literature concerning groundwater pollution, predicting pesticide behaviour in subsurface geosystems remains a complex scientific and practical problem [9].

In the leaching process, the physicochemical properties of the agrochemicals used (the soil organic carbon sorption coefficient (K_{OC}), *n*-octanol/water partition coefficient (K_{OW}), aqueous solubility (S_W), vapour pressure (P), and Henry's law constant (H), as well as soil properties (texture, organic matter content and permeability) play a decisive role [10]. The displacement of pesticides from soil to water mostly depends on the extent to which they are retained in soils. Soil sorption is characterised by the distribution coefficient K_d. This soil sorption constant ($ml\,g^{-1}$) is obtained from:

$$K_d = C_s/C_e$$

where C_s ($\mu g\,g^{-1}$) is the concentration of the pesticide sorbed onto the soil, and C_e ($\mu g\,ml^{-1}$) is the equilibrium solution pesticide concentration, which can be measured through 'batch' or 'slurry' mixing experiment. Values of $K_d > 100$ indicate that a pesticide is strongly sorbed and will be immobile in soil, and also resistant to microbial degradation [11].

It is generally accepted that adsorption of pesticides by soils is more closely related to the soil organic matter content than any other single property [12]. Many papers published in the last four decades have demonstrated a high correlation between the organic matter content and K_d in a variety of soils and compounds. For this, actually it is assumed that soil organic matter, acting as a non-polar surface, is the main sorbent in soils, attracting pesticides because they are typically non-polar organic molecules. However, for more polar solutes, surfaces of other materials in soils, such as clay mineral surfaces, may be preferred sorption sites, particularly in soils where the organic matter fraction is low [13].

The most common and today generally accepted quantitative measure of the sorption of organic pollutants by soils from aqueous solutions is the soil organic adsorption coefficient (K_{OC}). This chemical specific parameter plays a significant role in the fate of pesticides in aqueous/soil environment, like bioaccumulation and leaching ability, and is defined as:

$$K_{OC} = K_d / F_{OC}$$

where F_{OC} is the organic carbon fraction of the soil and K_d is the distribution coefficient.

K_{OC} values are universally used as measures of the relative potential mobility of pesticides in soils and in fugacity models describing the partitioning of pesticides in soil/water/atmosphere systems [14]. In general, compounds with higher $\log K_{OC}$ values will be less mobile than those with lower values. Especially for the hydrophobic pesticides ($K_{OW} \geq 2$), their mobility, and therefore the risk of their leaching into groundwater, has been correlated with weak sorption on the soil, as quantified by K_{OC} [5]. Generally, pesticides with $\log K_{OC} \leq 3$ are potentially leacher compounds although pesticides with $\log K_{OC} \geq 3$ have been found in groundwater and drainage water [15]. Direct measurements for K_{OC} include the soil slurry (batch) equilibrium technique, soil column method and soil thin-layer chromatography. A typical protocol which presents many of the practical considerations is the OECD Guideline of adsorption/desorption, first adopted in 1981 and revised since [16]. However, other indirect methods have been proposed to estimate K_{OC} for predominantly hydrophobic chemicals such as those based on the regression with (S_W), (K_{OW}), or reverse-phase HPLC capacity factor (k') as well as molecular structure parameters [11,17,18].

Several proposals to evaluate the mobility of pesticides through the soil profile have been proposed in the last decades. The classification of McCall *et al.* (1981) is based on the K_{OC}, and is best suited to non-ionic chemicals where leaching potential is indicated by a mobility classification of medium to very high [19]. Other factors, besides soil sorption coefficients, such as the compound's persistence, affect its leaching potential. Cohen *et al.* (1984) summarised the various physicochemical, transformation and mobility characteristics of a chemical that has the potential to leach under standard soil conditions [20]. Gustafson (1989) developed a leaching potential index, based on persistence in soil and adsorption by applying the Groundwater Ubiquity Score (GUS) Index [21].

Bearing in mind the above, we have studied the mobility of five insecticides and six fungicides commonly used in the growing of peppers in greenhouse in Murcia (Southeast of Spain), using disturbed clay-loam soil columns under laboratory conditions. Soil columns offer good possibilities to conduct such tests, because they constitute closed systems, with the control of water leaching through the soil.

2. Experimental

The soil selected for the study was taken from Campo de Cartagena (Murcia, SE Spain), air dried, ground, sieved through 2 mm mesh sieve and stored at 4°C. Texture was clay loam (33% clay, 30% silt, 37% sand) and the soil had a pH of 7.86, organic matter 1.59%, and electrical conductivity $3.54\,\mathrm{dS\,m^{-1}}$. The characteristics of the soil were determined by standard soil analysis techniques [22].

All active ingredients, insecticides (pyridaben, pyriproxyfen, tebufenpyrad, buprofezin and pirimicarb) and fungicides (azoxystrobin, kresoxim-methyl, hexaconazole, tebuconazole, triadimenol, and pyrimethanil) were supplied by Dr Ehrenstorfer GmbH (Augsburg, Germany). They were higher than 98% pure. Table 1 shows the main physico-chemical properties of the pesticides. Experimental values of octanol/water partition coefficient

Table 1. Main physical-chemical characteristics of the pesticides used.

Pesticides	Mol. formula	Mol. weight	$\log K_{OW}$	$\log K_{OC}$	H $(\mathrm{Pa\,m^{3}\,mol^{-1}})^{a}$	S_W $(\mathrm{mg\,L^{1}})$	GUS Index
Insecticides							
Buprofezin	$C_{16}H_{23}N_3OS$	305.5	4.9	3.4	2.8×10^{-02}	0.46	1.0
Pirimicarb	$C_{11}H_{18}N_4O_2$	238.3	1.7	1.9^{b}	3.3×10^{-05}	3100	4.0
Pyridaben	$C_{19}H_{25}ClN_2OS$	364.9	6.4	4.8	3.0×10^{-01}	0.01	−1.4
Pyriproxifen	$C_{20}H_{19}NO_3$	321.4	5.4	4.3	1.2×10^{-02}	0.37	−0.3
Tebufenpyrad	$C_{18}H_{24}ClN_3O$	333.9	4.9	3.6	1.1×10^{-03}	2.4	0.4
Fungicides							
Azoxystrobin	$C_{22}H_{17}N_3O_5$	403.4	2.5	2.6	7.3×10^{-09}	6.7	2.5
Hexaconazole	$C_{14}H_{17}C_{12}N_3O$	314.2	3.9	3.0	3.3×10^{-04}	18	2.0
Kresoxim-methyl	$C_{18}H_{19}NO_4$	313.4	3.4	2.5	3.6×10^{-07}	2.0	1.8
Pyrimethanil	$C_{12}H_{13}N_3$	199.3	2.8	2.5	3.6×10^{-03}	121	2.6
Tebuconazole	$C_{16}H_{22}ClN_3O$	307.8	3.7	2.9	1.0×10^{-05}	36	2.0
Triadimenol	$C_{14}H_{18}ClN_3O_2$	295.8	3.1	2.4	3.5×10^{-06}	72	3.7

[a] Henry's law constant at 25°C.
[b] Obtained from Sabljic *et al.* [17].

(K_{OW}), soil/organic partition coefficient (K_{OC}), aqueous solubility (S), Henry's law constant (H), dissociation constant (pKa), and GUS Index (Groundwater Ubiquity Score) were taken from The Pesticide Properties DataBase (PPDB) [23]. All the organic solvents were of residue grade (Sharlau, Barcelone, Spain) and their purity degree was higher than 98%.

All experiments were performed according to the OECD guidelines [24]. Downward movement of the pesticides was studied in polyvinyl chloride (PVC) columns of 30 cm (length) × 3 cm (i.d.) packed with 150 g of soil (bulk density, $1.32\,\mathrm{g\,cm^{-3}}$). The top 3 cm of the columns were filled with sea sand and the bottom 3 cm with sea sand plus nylon mesh with an effective pore diameter of 60 µm to minimising the dead-end volume and prevent losses of soil during the experiment. Before the application of the compound, columns were conditioned with 0.01M $CaCl_2$ 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 PV of the soil columns after saturation was 56 ± 4 mL. Following this, 5 mL of a methanol/water solution ($10 + 90$, v/v) containing 100 µg of each compound (equivalent to 352 g/Ha) were added to the top of each column. Twenty-four hours after pesticide application, the compounds were leached with 0.01 M $CaCl_2$ in order to minimise soil mineral balance disruption which was applied at a rate of 60 mL daily (equivalent to 21 mm) during 10 days with a peristaltic pump. The leachates (50 ml) were quantitatively collected at the bottom of the columns, filtered through nylon membrane filter (0.45 µm) and extracted with 40 mL of *n*-hexane-dichloromethane 1 : 1 mixture solvent. After this time, the columns were opened and the soil separated in two segments of approximately 10 cm each one. Five replications were run at room temperature (21 ± 2°C) avoiding direct light. Dried soil samples (5 g) were extracted with 30 mL of acetonitrile/water (2/1) by sonication. After sonication, 20 mL of dichloromethane were added and then centrifuged for 10 min at 1900×*g*. Determination of pesticide residues in leachates and soil extracts was accomplished in both cases by GC-NPD and confirmed by GC/MS according to the method described by Fenoll *et al*. [25]. Recoveries from soil and water ranged from 70 to 115% and limits of quantification (LOQ, signal-to noise ratio 10) varied from 0.6 to 24 μg kg^{-1} and 0.01 to 0.4 μg L^{-1} in soil and water, respectively.

3. Results and discussion

The distribution from soil and water for the insecticides applied to soil columns is shown in Figure 1. Total recoveries of insecticides from soil and water were in the range 94–115% for pyriproxyfen and pyridaben, respectively. Only pirimicarb was found in leachates (48% of the total mass fraction applied to the column) while 16 and 39% of its residue level was recovered from the upper and lower soil layers, respectively. For the other studied insecticides, the percentage remaining in the top soil fraction varied from 93–114% for pyriproxyfen and pyridaben, respectively. For those compounds, no more than 1% of the added amount was recovered from the bottom soil fraction. The breakthrough curve (BTC) of pirimicarb leaching begins at about 1 PV (Figure 2). At the end of the experiment when 9 PV were leached the shape of the curve with upward tendency indicates a certain interaction with the organic and inorganic soil colloids. Thus, bearing in mind the total amount found in leachates (45 μg), pirimicarb has an important leaching potential in the used conditions being able to provoke in some cases the pollution of groundwater while pyridaben, pyriproxyfen, tebufenpyrad, and buprofezin behave as '*non-leacher*' pesticides.

For the fungicides, the BTCs and their distribution from soil and water are shown in Figures 2 and 3, respectively. The distribution of fungicides along the soil column indicates that the amount retained ranged from 88% for hexaconazole to 38% to triadimenol, while recoveries in leachates varied from 1 to 41% for hexaconazole and triadimenol, respectively (Figure 3). For triadimenol, the maximum peak was found about 7.5 PV (Figure 2). Only for this fungicide, the highest recovery from soil was in the bottom 10 cm layer while similar amounts of pyrimethanil were recovered from both soil fractions. Some authors [26,27] have pointed that the presence of dissolved organic matter (DOM),

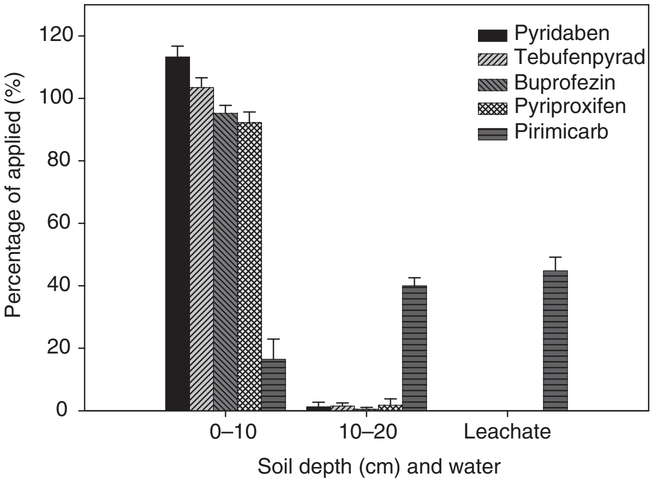

Figure 1. Distribution of insecticides applied to soil columns after leaching. The error bars denote the standard deviation.

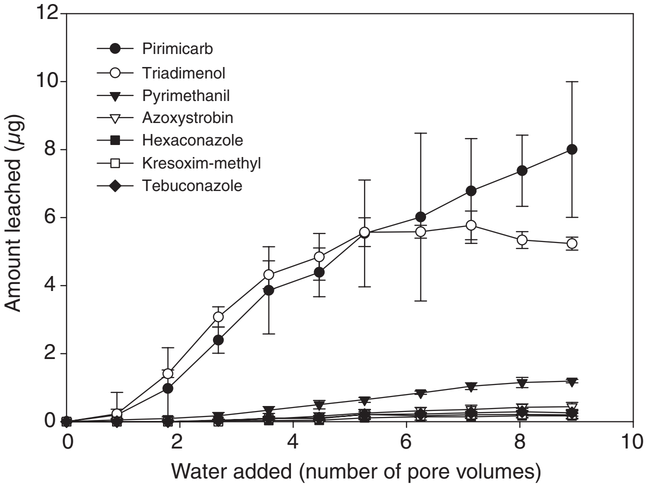

Figure 2. Breakthrough curves (BTCs) for pesticides found in leachates. The error bars denote 95% confidence interval.

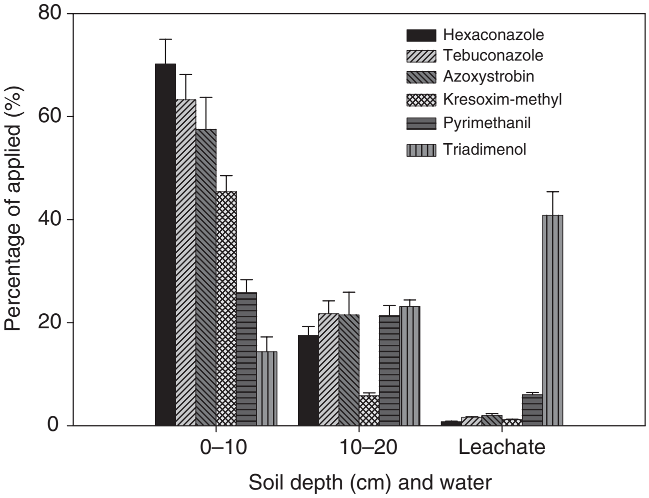

Figure 3. Distribution of fungicides applied to soil columns after leaching. The error bars denote the standard deviation.

mainly in earlier leachates (amber colour), could initially facilitate the leaching of some pesticides by enhancing their water solubilities through DOM-pesticide association. A field lysimeter experiment carried out by Petrovic *et al.* [28] showed that application of the fungicide triadimefon resulted in rapid appearance of the metabolite triadimenol in collected leachates detecting the metabolite in leachates collected several months after the application. No data are available in the open literature about the leaching behaviour of pyrimethanil. In soil leaching studies conducted in laboratory, lysimeter and field azoxystrobin and kresoxim-methyl were shown to be not or moderately mobile [29].

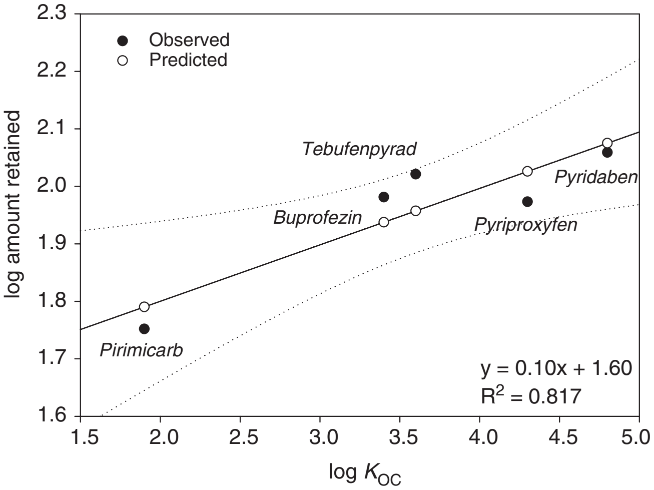

Figure 4. Plot of log K_{OC} *vs.* log of amount (μg) retained into the soil for insecticides. Dotted curves denote 95% confidence interval.

For other fungicides, the higher percentages of initial amount remained in the upper layer. As pointed out by Singh [30] triazole fungicides show great sorption and therefore scarce mobility to soil and only triadimefon leach down to 25–30 cm depth which it is in agreement with our findings.

The difference in the insecticide distribution shows that the leaching is inversely related to their soil adsorption coefficient (as log K_{OC}) having pyridaben and pyriproxyfen the higher (>4.3) and pirimicarb the lower value (1.9). As can be seen in Figure 4, the linear regression model shows that log K_{OC} is significantly intercorrelated with the insecticide amounts retained into the soil ($r^2 = 0.82$) with regression coefficient statistically significant ($p < 0.05$). This model exhibits a low standard error of estimate (<0.06) and residual values show that the amounts retained are slightly overestimated for tebufenpyrad (0.06 log units) and buprofezin (0.04 log units) while an underestimation was found for pririmicarb (0.04 log units), pyriproxyfen (0.05 log units) and pyrydaben (0.02 log units).

Also for fungicides, the leaching potential is inversely related to their organic carbon partition coefficient (K_{OC}). As shown in Figure 5, the variation in the retained amounts can be explained by the linear correlation with K_{OC} values ($r^2 = 0.77$). All compounds show residuals lower than 0.07 log units with the exception of azoxystrobin (overestimation of 0.14 log units). The slope (0.56 ± 0.15) appear to be statistically significant ($p < 0.05$) and standard error of estimate was 0.08.

Other factors besides K_{OC}, such as the compound's persistence, affect its leaching potential. Gustafson [21] developed the following leaching potential index, based on persistence in soil and adsorption:

$$\mathrm{GUS} = \log(t_{1/2}) \times [4 - \log(K_{OC})]$$

where $t_{1/2}$ is the soil degradation half-life of a pesticide.

In accordance with GUS Index, the organic compounds whose GUS are >2.8 are considered potential leachers (L), those whose GUS lie between 1.8 and 2.8 have transient properties (T) and those whose GUS <1.8 are considered non-leachers (NL).

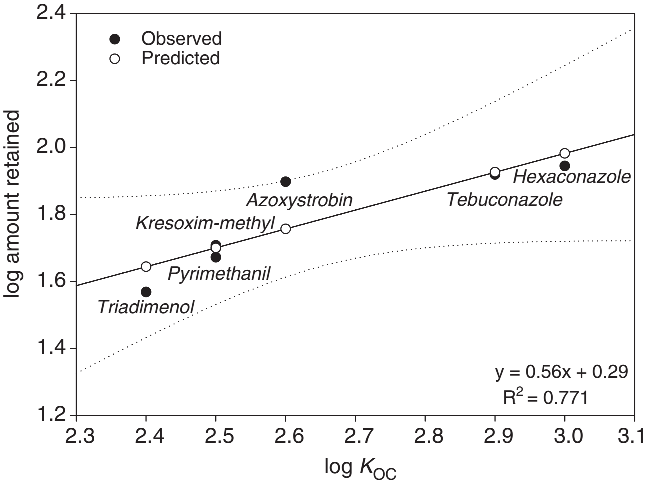

Figure 5. Plot of log K_{OC} *vs.* log of amount (μg) retained into the soil for fungicides. Dotted curves denote 95% confidence interval.

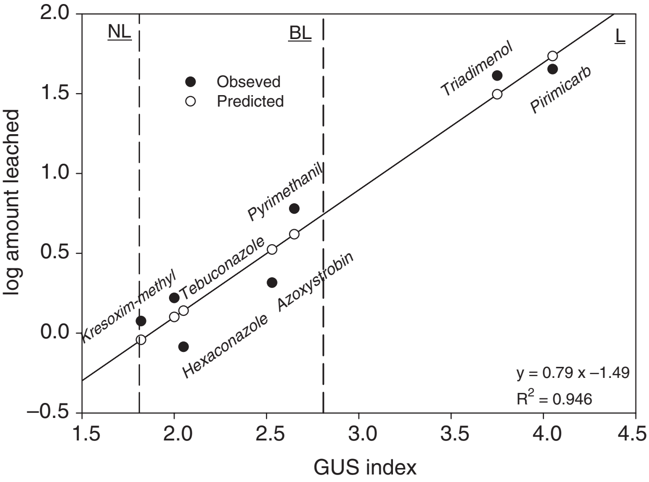

Figure 6. Plot of GUS index *vs.* log of amount (μg) leached for pesticides found in leachates (NL: Non-leacher; BL: Borderline leacher; L: Leacher behaviour).

According to this index, the leaching behaviour for the pesticides found in leachates was evaluated using linear regression ($r^2 = 0.95$) between the amount of pesticides leached and GUS index obtained from the database used [23]. According to the obtained results shown in Figure 6, triadimenol and pirimicarb can be considered as leacher compound in the used conditions, while azoxyxtrobin, kresoxim-methyl, hexaconazole, tebuconazole, and pyrimethanil have transient properties.

Dissociation of ionisable compounds in response to the ambient soil pH affects adsorption and, therefore, mobility in soil. Anionic species are likely to have a very high leaching potential. Bearing in mind the pK_a of the compounds studied the dissociation is null or minimum in the soil (pH = 7.8). According to other factors, summarised by Cohen *et al.* [20], triadimenol and pirimicarb are potential 'leacher' compounds because they have water solubilities $>30\,\mathrm{mg\,L^{-1}}$, Henry's law constant $<10^3\,\mathrm{Pa\,m^3\,mol^{-1}}$, hydrolysis half-life >25 wk, photolysis half-life >1 wk, and half-life in soil >2–3 wk.

4. Conclusions

As a consequence of phytosanitary protection during pepper crop, an important fraction of pesticides, mainly insecticides and fungicides, can be deposited on soil surface. Some compounds used to control pest and fungal diseases with scarce capacity of soil adsorption and high solubility in water such as pirimicarb, triadimenol and pyrimethanil can be leached along the clay-loam soil profile. This behaviour could provoke in some cases the pollution of groundwater, which not only affects the health of humans being as it is being used for drinking purpose, but also can act as a source of contamination for food chain, when used for irrigation. Although field studies are required, the need to safeguard the quality of the subsurface groundwater body against the potential adverse effect of those pesticides is extremely important, especially in the case of triadimenol, endocrine disrupter with negative effects on reproduction and development. For this purpose, the use of organoclays and organic amendments should be an effective method to decrease pesticide leaching.

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