Assessment of the Leaching Potential of 12 Substituted Phenylurea Herbicides in Two Agricultural Soils under Laboratory Conditions

Simón Navarro,*[†] Joaquín Hernández-Bastida,[†] Goretti Cazaña,[†] Gabriel Pérez-Lucas,[†] and José Fenoll[‡]

[†]Departamento de Química Agrícola, Geología y Edafología, Facultad de Química, Universidad de Murcia, Campus Universitario de Espinardo, 30100, Murcia, Spain

[‡]Departamento de Calidad y Garantía Alimentaria, Instituto Murciano de Investigación y Desarrollo Agrario y Alimentario (IMIDA), C/Mayor s/n, La Alberca, 30150 Murcia, Spain

ABSTRACT: In this study, the potential groundwater pollution of 12 substituted phenylurea herbicides (chlorbromuron, chlorotoluron, diuron, fenuron, fluometuron, isoproturon, linuron, metobromuron, metoxuron, monolinuron, Monuron, and neburon) was investigated under laboratory conditions. For this purpose, leaching studies were conducted using disturbed soil columns filled with two different agricultural soils, one hypercalcic calcisol (HC) and the other endoleptic phaeozem (EP). In the case of the HC, all of the studied herbicides were found in leachates, while for the EP only, chlorbromuron, chlorotoluron, isoproturon, monolinuron, and, especially, fenuron were recovered. For both soils, the groundwater ubiquity score (GUS) index was calculated for each herbicide on the basis of its persistence (as $t_{1/2}$) and mobility (as K_{OC}). The half-lives obtained were markedly higher in the EP (217−518 days) than in the HC (71−178 days). As a consequence, higher values of GUS indexes were observed for EP. The ratio of the GUS between the EP and the HC was about 1.3.

KEYWORDS: *aqueous/soil environment, herbicide mobility, half-life, soil sorption constant, GUS indexes*

■ INTRODUCTION

The widespread application of herbicides to agricultural soils is a well-established and effective practice to control weed growth but has led to increasing environmental concerns because of their low biodegradability and long-term persistence in soil. Consequently, pesticides may pass to both surface and groundwater through runoff and leaching. Runoff is the physical transport of pesticides and other pollutants over the ground surface by rainwater that does not penetrate the soil, while leaching is the movement of water and dissolved chemicals through the soil with rain or irrigation water.[1]

Under certain conditions, some pesticides may leach into groundwater as a result of normal field applications. The transport of herbicides from agricultural soils to the groundwater bodies occurs through matrix flow, although in many cases large macropores operate as preferential flow pathways, provoking rapid movement of the pollutants through the unsaturated zone.[2] This process is receiving increasing attention in European countries because a high percentage of the drinking water is taken from groundwater reserves. For this reason, the European Union established individual (0.1 μg L^{-1}) and total (0.5 μg L^{-1}) concentrations of pesticides in drinking water to safeguard people from harmful effects.

In the leaching process, the physicochemical properties of the agrochemicals used, as well as soil properties (texture, clay content, organic matter, and permeability) play a decisive role.[3] However, among the soil properties, the organic carbon content (OC) is the single largest factor that influences pesticide adsorption and mobility in the soil. The soil organic adsorption coefficient (K_{OC}) is universally used as a measure of the relative potential mobility of pesticides in soils and in fugacity models describing the partitioning of pesticides in soil/water/atmosphere systems.[4−6]

The mobility of herbicides and other pesticides can be studied at two levels: (i) in the laboratory with disturbed or undistributed soil columns and (ii) in the field by means of suction cup lysimeters, which are mainly used for studying the transport of herbicides from surface soil to groundwater, or soil enclosure lysimeters, for measuring the mass balance of the herbicides in different environmental compartments.[7]

Several methods to evaluate the mobility of pesticides through the soil profile have been proposed in recent decades. The classification of McCall et al., which is based on the K_{OC}, is best suited to nonionic chemicals for which the leaching potential is indicated by a mobility classification of medium to very high.[8] Other factors, besides soil sorption coefficients, such as the compound's persistence, affect its leaching potential. Cohen et al.[9] summarized the various physicochemical, transformation, and mobility characteristics of a chemical that has the potential to leach under standard soil conditions. Gustafson[10] developed a leaching potential index, based on persistence in soil and adsorption, by applying the groundwater ubiquity score (GUS) index. SCI-GROW (screening concentration in ground water) is a screening model[11] frequently used by the EPA to estimate pesticide concentrations in vulnerable groundwaters. This model is based on environmental fate properties of the pesticide (aerobic soil degradation half-life and linear adsorption coefficient normalized for soil OC), the maximum application rate, and existing data from small-scale prospective groundwater monitoring studies.

Table 1. Physical−Chemical Characteristics of the Herbicides Used in This Study

Herbicide	X	Y	Z	Molecular formula	Molecular mass	log K_{OW}	$S_W{}^a$	Aqueous hydrolysis[b]	log $K_{OC}{}^c$ Exp.	MCI	log K_{OW}	GUS index[d]
Chlorbromuron (CB)	Br	Cl	OCH_3	$C_9H_{10}BrClN_2O_2$	293.5	3.1	35	-	2.70	2.53	2.58	2.1 (M)
Chlorotoluron (CT)	CH_3	Cl	CH_3	$C_{10}H_{13}ClN_2O$	212.7	2.5	74	Stable	2.02	2.04	2.18	2.8 (M)
Diuron (DR)	Cl	Cl	CH_3	$C_9H_{10}Cl_2N_2O$	233.1	2.9	36	Stable	2.40	2.04	2.33	1.8 (M)
Fenuron (FN)	H	H	CH_3	$C_9H_{12}N_2O$	164.2	1.0	3850	-	1.40	1.62	1.39	4.2 (H)
Fluometuron (FM)	H	CF_3	CH_3	$C_{10}H_{11}F_3N_2O$	232.2	2.3	111	Stable	1.90	2.46	2.19	3.9 (H)
Isoproturon (IP)	$HC(CH_3)_2$	H	CH_3	$C_{12}H_{18}N_2O$	206.3	2.5	70	1560	2.09	2.30	2.45	2.1 (M)
Linuron (LN)	Cl	Cl	OCH_3	$C_9H_{10}Cl_2N_2O_2$	249.1	3.0	64	1460	2.70	2.53	2.64	2.0 (M)
Metobromuron (MB)	Br	H	OCH_3	$C_9H_{11}BrN_2O_2$	259.1	2.4	330	170	2.10	2.32	2.19	2.5 (M)
Metoxuron (MX)	OCH_3	Cl	CH_3	$C_{10}H_{13}ClN_2O_2$	228.7	1.6	678	24	1.72	1.64	1.81	2.4 (M)
Monolinuron (ML)	Cl	H	OCH_3	$C_9H_{11}ClN_2O_2$	214.6	2.2	735	Stable	2.10	2.32	2.14	3.0 (H)
Monuron (MN)	Cl	H	CH_3	$C_9H_{11}ClN_2O$	198.7	1.8	230	-	1.95	1.82	1.92	4.0 (H)
Neburon (NB)	Cl	Cl	$(CH_2)_3CH_3$	$C_{12}H_{16}Cl_2N_2O$	275.2	3.8	5	Stable	3.40	2.84	3.12	-

[a]Water solubility (mg L^{-1}). [b]DT_{50} (days) at 20 °C and pH 7. [c]In parentheses are shown the experimental and estimated values (from molecular connectivity index and log K_{OC}) taken from KOCWIN (EPI Suite v 4.10). [d]GUS index. Leachability in parentheses: L, low; M, medium; and H, high.

Since their discovery shortly after the Second World War, phenylurea herbicides (PUHs) have grown to be one of the most important classes of herbicide used worldwide for pre- and postemergence control of annual broad-leafed weeds and grasses in a wide range of crops.[12] Phenylureas are selective systemic herbicides commonly used in agriculture, alone or in combination. These compounds are a group of pesticides used for general weed control in agricultural and nonagricultural practices (e.g., along railways, utilities' rights-of-way, and in industrial areas). The first PUH, N,N-dimethyl-N'-(4-chlorophenyl)urea, was introduced in 1952 by Du Pont under the common name of Monuron. In subsequent years, many more derivatives of this type of compound have been marketed.[13]

The use of PUHs in agriculture can result in a high risk of these herbicides entering the food chain by means of contaminated water. Progressive increases in the production and application of these kinds of herbicides for plant protection have converted the problem of water quality into an international issue. Several PUHs and their metabolites have been identified as contaminants of groundwater, rivers, lakes, and seawater.[14] The PUHs are relatively involatile compounds and are not ionized in the range of pH conditions normally encountered in the environment. They generally have relatively high water solubilities and low sorbance tendencies, rendering them mobile in soil. The degradation of PUHs in the environment is a relatively slow process that involves biotic and abiotic processes, in which microbially facilitated biodegradation and photodegradation, respectively, are especially important. Moreover, some PUHs have been shown to be endocrine disruptors or have genotoxic or ecotoxic effects.[15,16] Because of their potential toxic risks even at low concentrations and possible carcinogenic properties for humans and wildlife, the control of PUHs in water constitutes a priority objective.

In view of the above, we have studied the mobility of 12 PUHs commonly used in crops to control weed and grasses, by means of disturbed columns loaded with two different agricultural soils under laboratory conditions. Soil columns offer good possibilities to conduct such tests, because they constitute closed systems in which the water leaching through the soil can be monitored.

■ MATERIALS AND METHODS

Chemicals. Pesticide analytical standards (≥98%) 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), aqueous hydrolysis, and GUS index were taken from The Pesticide Properties DataBase[17] and KOCWIN included in the EPI Suite v4.10 program provides by U.S. EPA.[18] Stocks solutions (1000 μg mL^{-1}) of each pesticide standard were prepared in acetonitrile, protected from light, and stored at 5 °C. Different intermediate standard solutions were prepared by dilution in the same solvent. Pesticide grade acetonitrile was supplied by Scharlau (Barcelona, Spain).

Soils. Two different agricultural loam soils were chosen for this study.[19] Soil A [hypercalcic calcisol (HC)] was brought from the Campo de Cartagena, and soil B [endoleptic phaeozem (EP)] was from Calasparra, both located in Murcia (southeastern Spain). Soil samples were collected from the surface (top 20 cm), air-dried, and passed through a 2 mm sieve. The experimental studies began not more than 4 days after soil collection and storage under cool conditions. The composition of the soils is shown in Table 2.

The main characteristics of the soil (organic matter, electric conductivity, pH, alkalinity, texture, field water capacity, and cation exchange capacity) were determined by standard soil analysis techniques.[20] The clay content was determined by means of a powder X-ray diffractometer (XRD) on a Philips PW 1700 using Cu Kα radiation at a scanning speed of 1° (2θ) after washing, disaggregation, and dispersion of the sample.

Determination of the Soil Degradation Half-Lives ($t_{1/2}$) of the Herbicides. The soil degradation experiments were conducted according to the OECD procedure.[21] 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 of the studied pesticides was applied to achieve an initial concentration of about 100 μg kg^{-1} of each, which represents the common agricultural rate of application of these herbicides. All of the flasks were incubated in the dark for 90 days at 21 ± 2 °C with the soil moisture ranging from 40 to 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 2 weeks. The relative humidity was maintained at 70%. After 7, 15, 30, 60, and 90 days of incubation, three pots from each treatment were taken and kept at 4 °C for 2−3 days until analysis.

The dissipation of all herbicides could be described by a pseudo first-order kinetics: ln C_t = ln C_0 − kt, where C_0 and k denote y-intercept values and the slope of the dissipation lines, respectively, C_t is

Table 2. Characteristics of the Soils Used in This Study (n=3)

	soil	
parameters	HC mean (% RSD)	EP mean (% RSD)
clay (%)	20.2 (2.4)	25.1 (1.6)
silt (%)	39.7 (1.8)	36.8 (3.2)
sand (%)	40.1 (2.0)	38.1 (2.5)
bulk density (g cm^{-3})	1.41 (2.2)	1.37 (2.1)
organic matter (%)	0.76 (3.2)	6.1 (2.9)
total organic carbon (g kg^{-1})	4.4 (4.2)	35.6 (5.1)
pH (H$_2$O 1:1)	8.2 (2.1)	7.7 (1.7)
electric conductivity (dS m^{-1})	0.54 (3.0)	0.99 (2.7)
alkalinity (mg CaCo$_3$ kg^{-1})	626.0 (4.1)	115.8 (3.8)
field water capacity (−0.3 bar) (cm^3 water/cm^3 soil)	0.263 (2.4)	0.281 (3.2)
cation exchange capacity (cmol kg^{1-}) clay content (% weight)	11.8 (3.6)	30.2 (4.2)
illite	67.6 (3.2)	38.2 (3.1)
kaolinite	32.4 (2.8)	20.6 (4.2)
montmorillonite	ND^a	41.2 (2.0)

^{a}Not detected.

the concentration of pesticide in soil, and t is the postapplication time in days. Hence, their half-lives ($t_{1/2}$) were calculated from the equation $(t_{1/2}) = \ln 2/k$.

Estimation of K_{OC} Values and GUS Indexes. The K_{OC} values of the studied herbicides were determined by HPLC according to the OECD guideline.[22] Their capacity factors (k') were calculated after determining retention times by HPLC in triplicate. The logarithms of their capacity factors were plotted versus the log K_{OC} taken from the literature, calculated as the mean values obtained from the experimental data and those estimated from the first order molecular connectivity index and log K_{OC} methods, all of them extracted from KOCWIN.[18]

The leaching potential of the studied herbicides was calculated as GUS, according to Gustafson,[10] applying the following equation:

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

where $t_{1/2}$ is the soil degradation half-life of a pesticide and K_{OC} is the soil adsorption coefficient. The organic compounds whose GUS values are >2.8 are considered potential leachers (L), those whose GUS lies between 1.8 and 2.8 have transient properties (T), and those whose GUS score is <1.8 are considered nonleachers (NL).

Downward Movement of the Pesticides through the Soil Columns. The experiment was performed according to the OECD.[23] The downward movement of the pesticides was studied in polyvinyl chloride (PVC) columns of 40 cm (length) × 4 cm (i.d.) packed with 200 g of soil. The top 3 cm of the columns was filled with sea sand, and the bottom 3 cm was filled with sea sand plus nylon mesh with an effective pore diameter of 60 μm to minimize the dead-end volume and prevent losses of soil during the experiment. Before the application of the compound, columns (three replications at room temperature, avoiding direct light) were conditioned with 0.01 M CaCl$_2$ in distilled water to reach 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 76.4 ± 2.9 (HC) and 99.6 ± 3.1 (EP). Following this, 1 mL of a methanol/water solution (10 + 90, v/v) containing 100 μg of each compound was added to the top of each column. Twenty-four hours after pesticide application, the compounds were leached during 15 days with a peristaltic pump with 1000 mL of 0.01 M CaCl$_2$ to minimize soil mineral balance disruption. The leachates (50 and 100 mL per day during 10 and 5 days, respectively) were quantitatively collected at the bottom of the columns and then filtered through a nylon membrane filter (0.45 μm). After this time, the columns were opened, and the soil was separated into two segments of approximately 10 cm each. Herbicides were extracted from leachates every 2 days to avoid aqueous hydrolysis.

Analytical Determinations. Water samples (10 mL) were added to a centrifuge tube and then extracted with 10 mL of acetonitrile by sonication (15 min at 0.5 cycles and 60% amplitude) using a 200 W sonic dismembrator (Dr. Hielscher GmbH, Stahnsdorf, Germany) followed by a salting-out step with 2 g of NaCl. The tube was shaken and centrifuged for 10 min at 3000g. Dried soil samples (10 g) were extracted with 20 mL of acetonitrile/water (2/1) by sonication. After this, 20 mL of dichloromethane was added and then centrifuged for 10 min at 1900g. Finally, water and soil extracts were filtered quantitatively through a glass funnel containing a DP302 filter separation phase paper, 150 mm diameter (Albet, Barcelona, Spain). The organic phase was concentrated to dryness by rotary vacuum evaporation. The residue was redissolved in 1 mL of acetonitrile, filtered through 0.45 mm filter, and analyzed by LC-MS/MS.

The separation, identification, and quantification of the selected herbicides were carried out using high-performance liquid chromatography (HPLC system) consisting of vacuum degasser, autosampler, and a binary pump (Agilent Series 1100, Agilent Technologies, Santa Clara, CA). This was equipped with a reversed phase C8 analytical column of 150 mm × 4.6 mm and 5 μm 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 postrun time followed using the initial 10% of A. The flow rate was constant (0.6 mL min^{-1}) during the whole process, and 5 μL of sample was injected in every case. For the mass spectrometric analysis, an Agilent G6410A triple quadrupole mass spectrometer in multiple reaction monitoring (MRM) mode,

Table 3. Chromatographic Conditions of the Studied PUHs

herbicide	retention time (min)	transition (m/z) quantifier (qualifier)	fragmentor voltage (V)	collision energy (V)	fragmentor voltage (V)	collision energy (V)
fenuron	16.51	165 →72 (120)	90	20	110	10
metoxuron	19.64	229 →72 (156)	110	20	110	20
Monuron	20.75	199 →72 (126)	110	20	110	30
chlorotoluron	22.71	213 →72 (140)	110	20	110	20
fluometuron	23.27	233 →72 (160)	110	20	110	30
isoproturon	23.52	207 →72 (165)	110	20	110	30
diuron	23.68	233 →72 (160)	110	30	110	20
monolinuron	24.00	215 →126 (148)	90	10	90	10
metobromuron	24.62	259 →148 (170)	90	10	110	20
linuron	26.62	249 →182 (160)	90	10	110	20
chlorbromuron	27.01	295 →182 (206)	110	10	110	20
neburon	29.16	275 →88 (114)	100	10	100	10

using electrospray ionization (ESI), was applied. The ESI source was operated in positive ion mode, using the following operation parameters: capillary voltage, 4000 V; nebulizer pressure, 40 psi; drying gas flow, 9 L min^{-1}; and drying gas temperature, 350 °C. Mass spectra were recorded across the range 50−1000 m/z. MRM transitions, fragmentor voltage, and collision energy were carefully studied and optimized for each target compound individually. Table 3 lists the herbicides, along with their retention times, their optimized SRM transitions, with a dwell time of 15 ms, fragmentor voltage, and collision energy. Nitrogen served as the nebulizer and collision gas. Agilent Mass Hunter Data Acquisition (Qualitative Analysis and Quantitative Analysis) software was used for method development and data acquisition.

The calibration curves were constructed in soil and water. The calibration samples were analyzed by spiking pesticides at 0.5−200 μg L^{-1} levels into water and soil samples in five replicates. The correlation coefficient was found to be >0.99 in all calibration curves.

Detection limits (LODs) and limits of quantitation (LOQs) were evaluated by injecting standard solution into blank matrix at different concentration levels. Both LODs and LOQs were calculated from the signal-to-noise (S/N) ratio of 3 and 10, respectively. LODs were in the range 0.05−0.5 μg L^{-1}, and LOQs varied from 0.3 to 2.8 μg kg^{-1} and 0.1 to 1.5 μg L^{-1} in soil and water, respectively.

The accuracy of the method was verified by measuring recoveries from spiked blank samples of the different matrices investigated (20 μg L^{-1} and 20 μg kg^{-1} for water and soil, respectively). This fortification level represents the value at the lower part of the linear range. The data evaluation was carried out by comparing the peak areas of the spiked samples to those obtained by matrix-matched standard calibration. The recoveries obtained for all pesticides in water ranged from 83.4 to 107.5% with relative standard deviation (RSD) <6.9%. In the case of soil, the recoveries obtained for all herbicides varied from 87.1 to 106.2% for HC and 76.2 to 109.1% for EP and RSD < 5.8% in the most unfavorable case. In addition, we tested the extractability of the herbicides from saturated aged soil samples to simulate recovery after the leaching process. Spiked soil samples were extracted at different times (10 and 20 days). The results reveal some differences in the extractability of the herbicides studied in these conditions.

■ RESULTS AND DISCUSSION

Distribution of Herbicides from Soil and Water. The distribution between soil and water of the herbicides applied to the soil columns is shown in Figure 1. In the case of the HC, total recoveries of herbicides from soil and water were in the range 24−57% (for neburon and fenuron, respectively), while for the EP, they varied from 41% for linuron and 81% for metoxuron.

In the case of the HC, all of the studied herbicides were found in the leachates although in different proportions. Thus, fenuron, metoxuron, and Monuron were found in percentages higher than 50%, while chlorotoluron, diuron, fluometuron, isoproturon, metobromuron, and monolinuron were recovered at percentages ranging from 30 to 50% of the total mass fraction applied to the column. Finally, for chlorbromuron, linuron, and neburon, the percentage recovered in leachates was lower than 30%. Only chlorbromuron, isoproturon, and neburon were recovered from the upper and lower soil layers, while only linuron was found in the lower layer. For all of these, the percentage recovered from the soil was lower than 10% of the added amount.

In contrast, the behavior of the herbicides in the EP was totally different. All herbicides, with the exception of fenuron, were found in the top fraction of the soil in proportions ranging from 30 to 60%, while the 12 studied herbicides, including fenuron, were recovered in the bottom layer of soil, although the percentage (4−32%) was lower. Only five compounds were
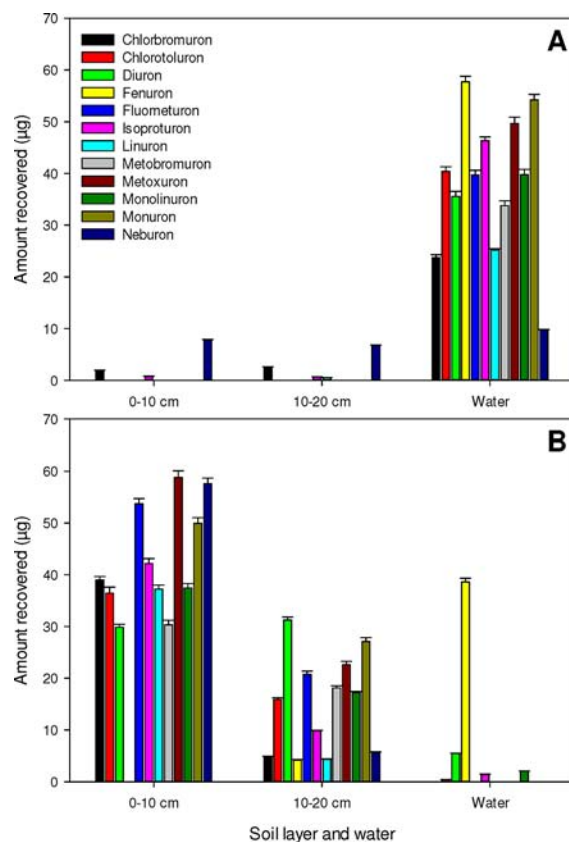

Figure 1. Distribution of the herbicides in the soil columns. (A) HC and (B) EP. The error bars denote standard deviation.

found in the leachates: chlorbromuron, chlorotoluron, isoproturon, and monolinuron in proportions lower than 5% and fenuron (39% of the initial amount). In this case, the total recoveries from soil and water were in the range 42−81% for linuron and metoxuron, respectively. The observed losses may possibly be due to degradation during the experiment. Laboratory experiments carried out with saturated aged soil samples (20 days) confirmed this behavior. The percentage recovered from the soil samples was in the range 65−85%.

Phenylureas have similar pathways of transformation in soils.[24] The first reaction in the transformation pathway of phenylureas in soils is N-demethylation/demethoxylation, which occurs via hydroxymethyl and N-formyl intermediates. Demethoxylatyon is faster, and its intermediates are more difficult to isolate than for demethylation. Hydroxylation of the aromatic rings and aliphatic side chains on these rings can occur simultaneously with the demethylation/demethoxylation reactions to give a wide variety of metabolites. Ureas may subsequently be hydrolyzed to aniline compounds although they would be expected to rapidly form bound residues in the soil.

Relative and Cumulative Breakthrough Curves (BTCs) of the Herbicides. Relative and cumulative BTCs of the herbicides applied to soil columns are shown in Figures 2 and 3, respectively. In the case of HC, the relative BTCs showed that all of the herbicides behaved as leacher compounds with rapid leaching (maximum about 1.3 PV). In contrast, the maximum leachability in EP was about 6−8 PVs. The shape of the curves, with an upward tendency, indicates a certain interaction with the organic and inorganic soil colloids contrary to the observed behavior in HC. As can be seen in Table 2, EP has a high
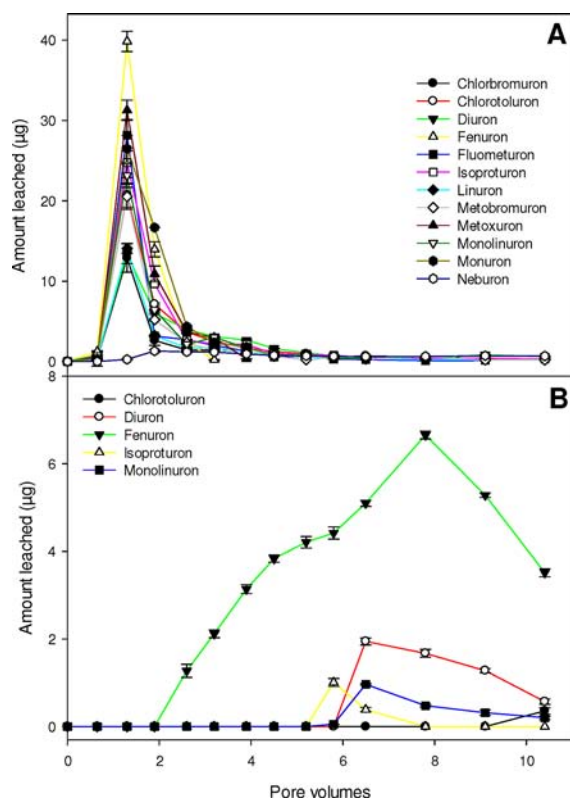
Figure 2. Relative BTCs of the herbicides applied to soil columns. (A) HC and (B) EP. The error bars denote standard deviation.

content of mature organic matter (6.1%) as compared with HC (0.76%). Additionally, EP contains about 42% of montmorillonite, an expanding 2:1 type silicate clay with very high total
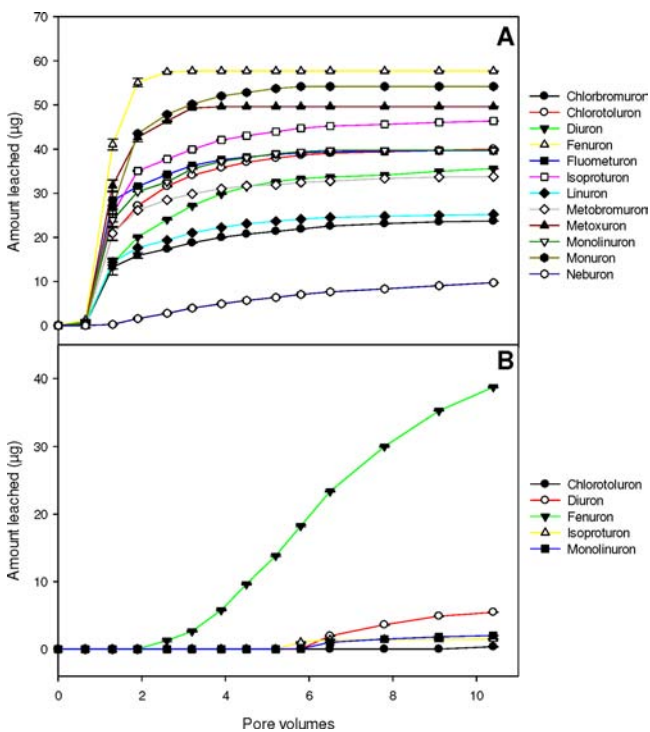

Figure 3. Cumulative BTCs of the herbicides applied to soil columns. (A) HC and (B) EP. The error bars denote standard deviation.

specific surface area (800 m^2 g^{-1}). Although the extent and mechanisms are not yet fully understood, clay–humus interactions undoubtedly contribute to the high organic matter content of clay soils because the organic matter entrapped in the micropores (<1 μm) formed by clay particles is physically inactive to decomposing organisms. Contrary to the traditional hydraulic conductivity measurements that assume uniform soil porosity, dissolved herbicides may be carried downward rapidly by water through large macropores such as cracks and biopores in the HC. This type of nonuniform movement, referred as preferential flow, greatly increases the chances of groundwater pollution, while organic matter improves soil–water retention since it increases both the infiltration rate and the water-holding capacity.[25]

As can be seen in Figure 3, where the cumulative BTCs for both soils are plotted, all of the herbicides show a certain leachability in HC, especially fenuron, chlorbromuron, and metoxuron, because more than 50% of the mass fraction applied to the column was recovered in the leachates after passing four PVs. On the other hand, only fenuron behaved as a leacher compound in EP since about 40% of the initial amount added was found in the leachates after 10 PVs. The difference in the herbicide distribution shows that the leaching is inversely related to their soil adsorption coefficient (as log K_{OC}) neburon having the highest (3.4) and fenuron the lowest (1.4) value.

Some authors have investigated that the presence of dissolved organic matter (DOM), mainly in earlier leachates (amber color), could initially facilitate the leaching of some pesticides by enhancing their water solubility through DOM–pesticide associations.[26] In some cases, competition between pesticides, such as diuron, and DOM molecules for sorption sites rather than interactions in solution contribute to enhanced pesticide leaching.[27] Thevenot et al.[28] investigated DOM–diuron interactions and the possible cotransport of diuron and DOM, finding an increase in diuron leaching as a result of the addition of fresh organic amendments. They concluded that these interactions were related to the aromatic and aliphatic content of the DOM, which determines the formation of hydrogen and noncovalent bonds. Recently, Ding et al.[29] reported that the adsorption of isoproturon in Eutric gleysols was depressed, while desorption and mobility were promoted in the presence of DOM and low molecular weight organic acids, although the opposite results were observed with Hap udic cambisols. This finding suggests that the soil type predominantly affected the physicochemical process. According to Alister et al.,[30] the principal soil property that affects herbicide adsorption is the soil OC, more specifically the fulvic acid–humin fraction relating soil leaching to the inverse of soil adsorption (1/K_d), cation exchange capacity, humic substances content, and herbicide pK_a.

Soil Adsorption Coefficient (as log K_{OC}). Figure 4 shows the regression line obtained for the studied herbicides. The K_{OC} obtained for the herbicides indicates their tendency to migrate in soil. Neburon was seen to be the least mobile (log K_{OC} = 2.79) with fenuron presenting the highest leaching potential (log K_{OC} = 1.28).

Herbicide Persistence in the Soils. Other factors besides K_{OC}, such as a compound's persistence, affect its leaching potential. Thus, bearing in mind the potential leachability of the studied compounds, the evolution of pesticide residues with time was simultaneously assessed in both soils to know the GUS index of each compound in our experimental conditions.
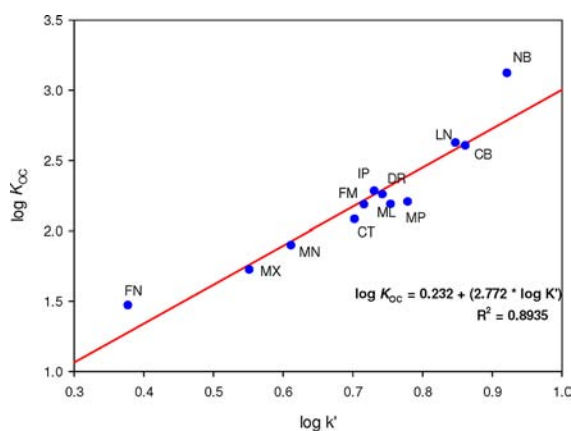
Figure 4. Regression line used for K_{OC} calculation. See Table 1 for compound identification.

The mean initial concentrations recovered for all herbicides were 97 and 87% for HC and EP, respectively. The dissipation of all herbicides follows a pseudo first-order kinetics ($R^2 = 0.95–0.99$) for HC. In the case of EP, the R^2 values obtained are considerably lower (0.66–0.96) as can be seen in Table 4. For both soils, the standard error of the estimate ($S_{y/x}$) was lower than 0.08. However, many authors have reported failures of this model and of the half-life concept to describe degradation data, especially with microbial adaptation or bound residue formation.[31] The first-order equation predicts slower initial and more rapid subsequent dissipation than normally occurs, and these deficiencies are not shared by other equations.

The widely used first-order model is usually valid when the reaction times are short. However, when the reaction is prolonged, it is not appropriate to explain the behavior of pesticides because the results lead to negative concentrations, even though acceptable values of the correlation coefficient (R^2) may be achieved. 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 compound disappears more slowly. In some cases, a modified first-order model proposed by Hoerl[32] has been used to advantage.[33,34]

Degradation in HC pointed to a greater dissipation rate for chlorbromuron, isoproturon, linuron, and neburon ($t_{1/2} < 80$ days), while for the rest of herbicides, $t_{1/2}$ ranged from 80 to 178 days, with percentages remaining at the end of the experiment varying from 41 to 70% for chlorbromuron and fluometuron, respectively. In the case of EP, the half-lives were longer than 200 days for all compounds, diuron being the least persistent ($t_{1/2} = 217$ days) and isoproturon the most persistent ($t_{1/2} = 578$ days). These values were higher than those found in the Pesticide Properties Database[17] where DT_{50} ranged from 20 to 170 days for the studied compounds under laboratory conditions. Fava et al.[35] reported half-lives of 14, 16, 19, and 20 days for linuron, diuron, Monuron, and monolinuron in a soil with a 1.4% OC and 11.5% clay. However, Si et al.[36] demonstrated that the addition of charcoal amendment strongly increases the half-lives of isoproturon in different soils (54−71 days in a paddy soil, 16−136 days in an alfisol, and 15−107 days in a vertisol). Also, significant differences in leaching behavior were observed for isoproturon and linuron as a result of the differences in sorption kinetics obtained with biopurification systems in cow manure, coconut chips, garden waste compost, or sandy loam soil.[37]

Additionally, in our case, the clay type present in the soil was very important. As can be seen in Table 2, EP had an important content of montmorillonite, while HC only contained kaolinite and illite. The most important clay mineral groups in the soils are kaolins, smectites, illites, and chlorites. The sorption capacities of clay minerals are reported to decrease in the following order: smectites > chlorites > illites > kaolins. Kaolinite, the most common kaolin mineral, consists of a single-silica tetrahedral sheet and a single-alumina octahedral sheet. In contrast, montmorillonite (smectite) is composed of units consisting of two silica tetrahedral sheets with a central alumina octahedral sheet. The basic structure of illite is similar to that of montmorillonite but is characterized by a charge deficiency because of which illites are nonexpandable clay minerals.[25] As consequence, the sorption capacity of EP is considerably higher than HC.

Determination of GUS Indexes. Persistence (expressed as $t_{1/2}$) and mobility (expressed as K_{OC}) are key parameters that seem to be particularly representative of the overall leaching potential of nonionic compounds. PUHs are not significantly hydrolyzed at environmental pH values nor are they strongly photodegraded. They are sorbed to soils with intermediate intensity according to their lipophilicity, and they are of

Table 4. Kinetic Parameters of the Fitting

	HC					EP				
herbicides	C_0	$K \times 10^{-3}$ (days^{-1})	R^2	$S_{y/x}$ [a]	$t_{1/2}$ [b]	C_0	$K \times 10^{-3}$ (days^{-1})	R^2	$S_{y/x}$ [a]	$t_{1/2}$ [b]
chlorbromuron	67.0	9.8	0.9811	0.05	71	67.7	2.9	0.6604	0.08	239
chlorotoluron	75.0	7.0	0.9500	0.06	99	84.5	1.6	0.9608	0.02	433
diuron	88.0	7.9	0.9722	0.05	88	80.4	3.2	0.9333	0.03	217
fenuron	84.0	6.2	0.9468	0.06	112	88.9	1.3	0.7986	0.02	533
fluometuron	73.0	3.9	0.9722	0.03	178	73.0	2.0	0.7326	0.05	347
isoproturon	87.0	9.0	0.9992	0.01	77	93.6	1.2	0.8740	0.02	578
linuron	67.0	8.8	0.9967	0.02	79	67.4	2.7	0.7632	0.06	257
metobromuron	68.0	7.6	0.9985	0.01	91	70.8	2.3	0.7560	0.05	301
metoxuron	78.0	5.8	0.9685	0.04	119	94.9	1.8	0.9456	0.02	385
monolinuron	72.0	8.4	0.9977	0.02	82	72.5	2.3	0.7056	0.06	301
Monuron	79.0	5.7	0.9830	0.03	122	88.9	1.8	0.6759	0.05	385
neburon	71.0	9.2	0.9943	0.03	75	66.9	2.8	0.7503	0.06	248

[a]Standard deviation of the fitting (standard error of the estimate). [b]Time in days.

intermediate persistence in aerobic soils not being of short persistence.[38]

According to the results shown in Figure 5, in HC, neburon has low leachability, chlorbromuron and linuron have transient
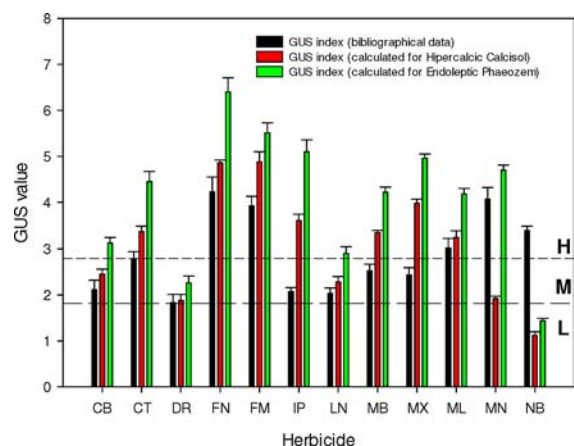

Figure 5. Comparison between calculated and bibliographical GUS indexes for both soils. The error bars denote standard deviation. Leachability: L, low; M, medium; and H, high. See Table 1 for compound identification.

properties, and the other herbicides behave as leacher compounds, while all of the studied herbicides have high leachability in EP. The relation between GUS EP/GUS HC was approximately 1.3.

The dissociation of ionizable compounds in response to the ambient soil pH affects adsorption and, hence, 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 both soils (pH about 8). According to other factors, summarized by Cohen et al.,[9] all of the herbicides with the exception of neburon are potential leacher compounds because they have water solubilities of >30 mg L^{-1}, a Henry's law constant of <10^3 Pa m^3 mol^{-1}, a hydrolysis half-life of >25 weeks, a photolysis half-life of >1 week, and a half-life in soil of >2−3 weeks.

■ AUTHOR INFORMATION

Corresponding Author
*Tel: +34 868 887477. Fax: +34 868 884148. E-mail: snavarro@um.es.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Rao, P. S. C.; Hornsby, A. G. *Behavior of Pesticides in Soil and Water*; Soil Science Fact Sheet SL 40; Institute of Food and Agricultural Sciences, University of Florida: Gainesville, FL, 2001.

(2) Guzzella, L.; Pozzoni, S.; Rullo, S.; Giuliano, G. Mobility of herbicides used for weed control in maize in lysimeter experiments. In *Pesticide Behaviour in Soils and Water*; Walker, A., Ed.; Proc. Int. Conf. Brighton, UK. 13−15 Nov.; British Crop Protection Soc.: Bracknell, United Kingdom, 2001; pp 101−106.

(3) Navarro, S.; Vela, N.; Navarro, G. An overview on the environmental behaviour of pesticide residues in soils. *Span. J. Agric. Res.* **2007**, *5*, 357−375.

(4) Mackay, D.; Paterson, S. Evaluating the multimedia fate of organic-chemicals—A level III- Fugacity model. *Environ. Sci. Technol.* **1991**, *25*, 427−436.

(5) Arias-Estévez, M.; López-Periago, E.; Martínez-Carballo, E.; Simal-Gándara, J.; Mejuto, J. C.; García-Río, L. The mobility and degradation of pesticides in soils and the pollution of groundwater resources. *Agric. Ecosyst. Environ.* **2008**, *123*, 247−260.

(6) Elliott, J. A.; Cessna, A. J.; Best, K. B.; Nicholaichuk, W.; Tollefson, L. C. Leaching rates and preferential flow of selected herbicides through tilled and untilled soil. *J. Environ. Qual.* **2000**, *29*, 1650−1656.

(7) Guzzella, L.; Capri, E.; Di Corcia, A.; Caracciolo, A. B.; Giuliano, G. Fate of diuron and linuron in a field lysimeter experiment. *J. Environ. Qual.* **2006**, *35*, 312−323.

(8) McCall, P. J.; Swann, R. L.; Laskowski, D. A. Partition Models for Equilibrium Distribution of Chemicals in Environmental Compartments. In *Fate of Chemicals in the Environment*; Swann, R. L., Eschenroder, A., Eds.; American Chemical Society: Washington, DC, 1983; pp 105−123.

(9) Cohen, S. Z.; Creeger, S. M.; Carsel, R. F.; Enfield, C. G. Potential for pesticide contamination of groundwater resulting from agricultural uses. In *Treatment and Disposal of Pesticide Wastes*; Krugger, R. F., Seiber, J. N., Eds.; American Chemical Society: Washington, DC, 1984; pp 297−325.

(10) Gustafson, D. I. Groundwater ubiquity score. A simple method for assessing pesticide leachability. *Environ. Toxicol. Chem.* **1989**, *8*, 339−357.

(11) USEPA Pesticides: Science and Policy. SCI-GROW Description; http://www.epa.gov/oppefed1/models/water/scigrow_description.htm, 2012.

(12) Tomlin, C. D. S., Ed. *The Pesticide Manual*, 15th ed.; British Crop Protection Council: Surrey, United Kingdom, 2009.

(13) Liu, J. Phenylurea herbicides. In *Handbook of Pesticide Toxicology: Principles*, Krieger, R., Ed.; Academic Press: San Diego, CA, 2001; Vol. *II*, pp 1521−1528.

(14) Sorensen, S. R.; Bending, G. D.; Jacobsen, C. S.; Walker, A.; Aamand, J. Microbial degradation of isoproturon and related phenylurea herbicides in and below agricultural fields. *FEMS Microbiol. Ecol.* **2003**, *45*, 1−11.

(15) Lintelmann, J.; Katayama, A.; Kurihara, N.; Shore, L.; Wenzel, A. Endocrine disruptors in the environment. IUPAC Technical Report. *Pure Appl. Chem.* **2003**, *75*, 631−681.

(16) Mnif, W.; Hassine, A. I. H.; Bouaziz, A.; Bartegi, A.; Thomas, O.; Roig, B. Effect of endocrine disruptor pesticides: A Review. *Int. J. Environ. Res. Public Health* **2011**, *8*, 2265−2303.

(17) Agriculture & Environment Research Unit (AERU) at the University of Hertfordshire, The Pesticide Properties DataBase (PPDB); http://www.herts.ac.uk/aeru/footprint, 2012.

(18) U.S. EPA. *Estimation Programs Interface Suite for Microsoft Windows*, v 4.10. U.S. Environmental Protection Agency: Washington, DC, 2012.

(19) ISSS-ISRIC-FAO. *World Reference Base for Soil Resources*; World Soil Resources Report 84; FAO: UN, Rome. 1998.

(20) Reeuwijk, L. P., Ed. *Procedures for Soil Analysis*; International Soil Reference and Information Centre: Wageningen, The Netherlands, 2002.

(21) OECD, Organization for Economic Cooperation and Development. Guidelines for Testing of Chemicals, No. 307. *Aerobic and Anaerobic Transformation in Soil*; OECD: Paris, France, 2002.

(22) OECD, Organization for Economic Cooperation and Development. Guidelines for Testing of Chemicals, No. 121. *Estimation of the Adsorption Coefficient (K_{OC}) on soil and on Sewage Sludge Using High Performance Liquid Chromatography (HPLC)*; OECD: Paris, France, 2001.

(23) OECD, Organization for Economic Cooperation and Development. Guidelines for Testing of Chemicals, No. 312. *Leaching in Soil Columns*; OECD: Paris, France, 2007.

(24) Roberts, T. R.; Hutson, D., Eds. *Metabolic Pathways of Agrochemicals. Part one: Herbicides and Plant Growth Regulators*; The Royal Society of Chemistry: Cambridge, United Kingdom, 1998.

(25) Brady, N. C.; Weil, R. R. *Elements of the Nature and Properties of Soils*; Pearson Education Inc.: New York, 2010.

(26) Rao, P. S. C.; Hornsby, A.G..; Kilcrease, D. P.; Nkedi-Kizza, P. Sorption and transport of hydrophobic organic chemicals in aqueous and mixed solvent systems: Model development and preliminary evaluation. *J. Environ. Qual.* **1985**, *14*, 376−381.

(27) Cox, L.; Velarde, P.; Cabrera, A.; Hermosín, M. C.; Cornejo, J. Dissolved organic carbon interactions with sorption and leaching of diuron in organic-emended soils. *Eur. J. Soil Sci.* **2007**, *58*, 714−721.

(28) Thevenot, M.; Dousset, S.; Hertkorn, N.; Schmitt-Kopplin, P.; Andreux, F. Interactions of diuron with dissolved organic matter from organic amendments. *Sci. Total Environ.* **2009**, *407*, 4297−4302.

(29) Ding, Q.; Wu, H. L.; Guo, L. J.; Liu, K.; Gao, H. M.; Yang, H. Impact of low molecular weight organic acids and dissolved organic matter on sorption and mobility of isoproturon in two soils. *J. Hazard. Mater.* **2011**, *190*, 823−832.

(30) Alister, C.; Araya, M.; Kogan, M. Effects of physicochemical soil properties of five agricultural soils on herbicide soil adsorption and leaching. *Cienc. Invest. Agrar.* **2011**, *38*, 243−251.

(31) Martins, J. M.; Mermoud, A. Sorption and degradation of four nitroaromatic herbicides in mono and multi-solute saturated/unsaturated soil batch systems. *J. Contam. Hydrol.* **1998**, *33*, 187−210.

(32) Hoerl, A. E. Fitting curves to data. In *Chemical Business Handbook*; Perry, J. H., Ed. McGraw-Hill: New York, 1954; pp 55−57.

(33) Zimdahl, R.; Cranmer, B. K.; Stroup, W. Use of empirical equations to describe dissipation of metribuzin and pendimethalin. *Weed Sci.* **1994**, *42*, 241−248.

(34) Navarro, S.; Bermejo, S.; Vela, N.; Hernández, J. Rate of loss of simazine, terbuthylazine, isoproturon and methabenzthiazuron during soil solarization. *J. Agric. Food Chem.* **2009**, *57*, 6375−6382.

(35) Fava, L.; Orrú, M. A.; Businelli, D.; Scardala, S.; Funari, E. Leaching potential of some phenylurea and their main metabolites through laboratory studies. *Environ. Sci. Pollut. Res.* **2006**, *13*, 386−391.

(36) Si, Y.; Wang, M.; Tian, C.; Zhou, J.; Zhou, D. Effect of charcoal amendment on adsorption, leaching and degradation of isoproturon in soils. *J. Contam. Hydrol.* **2011**, *123*, 75−81.

(37) De Wilde, T.; Mertens, J.; Spanoghe, P.; Ryckeboer, J.; Jaeken, P.; Springael, D. Sorption kinetics and its effects on retention and leaching. *Chemosphere* **2008**, *72*, 509−516.

(38) Briggs, G. G. Adsorption of pesticides by some Australian soils. *Aust. J. Soil Res.* **1981**, *19*, 61−68.