

ADSORPTION OF METHABENZTHIAZURON ON SIX ALLOPHANIC AND NONALLOPHANIC SOILS: EFFECT OF ORGANIC MATTER AMENDMENT

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ABSTRACT

This article reports on methabenzthiazuron [1-(1,3-benzothiazol-2-yl)-1,3-dimethylurea] (MBT) adsorption process on six agricultural allophanic and nonallophanic soils. The effect of amendment with exogenous organic matter was also studied. Adsorption kinetic fits an hyperbolic model. MBT adsorption reached an apparent equilibrium within 2 h and followed a second-order reaction. The maximum adsorbed amounts for natural soils ranged from 32 to 145 $\mu\text{g g}^{-1}$. Rate constants were considered relatively low ($0.27-1.5 \times 10^{-4} [\mu\text{g g}^{-1}]^{1-n} \text{ s}^{-1}$); the slow process was attributed to a combined effect of diffusion and adsorption. MBT adsorption fits the Freundlich model with r values ≥ 0.998 at $P \leq 0.001$ significance levels. K_f and Freundlich exponents ($1/n$) ranged from 5.3 to 82.1 $\text{cm}^3 \text{ g}^{-1}$ and from 0.66 to 0.73, respectively. K_f values for soils with a low organic matter content were lower than that obtained from the only typical allophanic soil derived from volcanic ash under study. Lineal regression analysis between K_f and organic matter content of nonallophanic soils gave a correlation coefficient of 0.980 ($P = 0.02$). Dispersion of K_d values together with close values of K_{OM} indicate that organic matter (OM) was the principal component responsible for MBT adsorption in unamended soils. Addition of peat decreased soil pH and increased adsorption capacity for

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allophanic and nonallophanic soils. Kinetic experiments showed enhancements of X_{\max} values and lower rate constants.

Key Words: Methabenzthiazuron; Adsorption; Organic matter; Soil

INTRODUCTION

Methabenzthiazuron [1-(1,3-benzothiazol-2-yl)-1,3 dimethylurea] (MBT) is a selective herbicide used to control various kinds of grass and broad-leaved weeds in cereals, legumes, garlic, peas, and onions (1). Previous studies have shown that MBT is slowly degraded both in the laboratory and in the field (2–5), stability being attributed to its rapid binding to the soil colloidal complex and more specifically through the incorporation into relatively stable humus components (i.e., humic acids and humins) as nonextractable bound residues (4). In soils with low natural organic matter content, organic amendment and soil disturbance result in increased transformation of MBT. A greater mineralization and a decreased recovery of applied MBT in labile components have been reported (4), thus reducing its uptake by nontarget plants and also keeping the herbicide in firmly bound forms. Adsorption experiments in calcareous soils with low organic matter have also demonstrated a relationship with clay and smectite content as well as with surface area. After an incubation period of 42 days, no degradation was observed and leaching experiments with clay and silt loam soil columns revealed that more than 96% of the MBT applied was retained within the upper layer (6).

Chile is a country with an intensive agricultural production. In spite of the broad use of agrochemicals on a great variety of typical soils, information on the pesticides behavior in these soils is scarce. A previous study reported the presence of some pesticides in water samples collected from the Aconcagua river in the V region of Chile (7). MBT levels were higher than the maximum pesticide residue allowed in drinking water according to European Community regulations limits ($0.1 \mu\text{g/L}$). This compound has a low water solubility and it will be specially susceptible to runoff if a strong adsorption by soil particles is produced.

In Chile, as in other countries (New Zealand and Japan), an important agricultural area is constituted by soils derived from volcanic ash (60% of cultivable surface). The most striking characteristics of these soils are a high physical stability, an accumulation of organic matter, and a considerable capacity to adsorb cations and anions; properties that are thought to be due to the presence of allophane, a noncrystalline aluminum silicate mineral that has a high specific surface area ($\approx 800 \text{ m}^2 \text{ g}^{-1}$). A higher adsorption capacity of several pesticides has been reported for allophanic soils (8). The main soil properties that explained the variation in pesticide sorption were organic carbon, pH, and oxalate-extractable aluminium. However, little is known about the mechanisms involved and, specifically, related with the adsorption of substituted urea herbicides on the complex organic matter allophane or on variable-charge soils.

In this article, the behavior of MBT on six agricultural soils, five nonallophanic from the Aconcagua Valley, and an allophanic one from the IX region of Chile, is described. Rate constants and the order of the adsorption reaction were determined according to the power equation given by Moreale and van Bladel (9) and K_f and $1/n$ from the empirical Freundlich relationship were established. The effect of amendment with exogenous organic matter on all parameters describing the adsorption process is also reported.

MATERIALS AND METHODS

Materials

Chemicals

Pure analytical methabenzthiazuron (Pestanal, chemical purity, >99%), was obtained from Riedel de Häen (Germany). Its solubility in water is $59 \mu\text{g mL}^{-1}$ at 20°C . Acetonitrile, high-performance liquid chromatographic (HPLC) grade, was obtained from J.T. Baker (United States).

Soils

The physical and chemical properties of the soils used in this study are given in Table 1. Pocuro (PCR), Quillota (QLT), Los Hornos (LHS), Cristo Redentor (CTR), and Colunquen (CLQ) are nonallophanic soils from the Aconcagua Valley (V region), and Temuco (TEM) is an allophanic soil from the IX region. Fresh soils

Table 1. Soils Physicochemical Characteristics

Soil	OM (%)	pH	C (%)	N (%)	CEC (mmol kg ⁻¹)	Phyl ^a (%) ^b	Smectite (%) ^b	Surface Area (m ² g ⁻¹)
Pocuro <i>Mollic</i> <i>Fluviaquent</i> (loam)	1.7	7.2	0.80	0.12	180	34	18	55.5
Cristo Redentor <i>Mollic</i> <i>Haploxeralf</i> (silty clay loam)	2.3	6.7	1.04	0.15	140	34	5.5	30.6
Los Hornos <i>Mollic</i> <i>Haploxeralf</i> (clay loam)	3.2	6.7	1.48	0.18	225	37	23	66.8
Colunquen <i>Mollic</i> <i>Haploxeralf</i> (clay loam)	3.7	6.9	1.59	0.19	231	35	8.7	66.8
Quillota <i>Entic Xerumbrept</i> (clay loam)	3.8	7.4	1.78	0.19	228	40	17	66.7
Temuco <i>Medial, mesic</i> , <i>Entic Dystrandept</i> (silt loam)	21.6	6.3	6.64	0.6	555	–	–	198.7

^aPhyl: phyllosilicates.

^bPercent in the total soil.

from the 0- to 20-cm depth were collected, air-dried, and ground to pass a 2-mm sieve before use. The pH was measured on slurries with a 0.01 M soil:CaCl₂ ratio of 1:2, organic matter (OM) was determined by the Walkey and Black (10) method and clay minerals by X-ray diffraction. Nitrogen and carbon total contents were determined with the elemental analyser Vario EL. Cation exchange capacity (CEC) was determined by flame photometric detection of sodium with the Schuhknecht and Schinkel reagent (11). Surface area was determined following the Keeling method (12). The exogen OM used to amend samples was a commercial peat, its OM content being 50%; its pH and CEC were 2.8 and 1190 mmol kg⁻¹, respectively. OM, CEC, and pH were also determined for amended soils.

Kinetic Study

Aliquots of 20 mL of a 20 μg mL⁻¹ aqueous solution of MBT were added to 4 g of air-dried soils into 30-mL sealed tubes. The samples were mechanically shaken (end-over-end) at 30 ± 0.5°C, and test tubes were removed at 5, 15, 30, 60, and 120 min and 4, 7, 14, and 20 h after soil–liquid phase contact. Suspensions were centrifuged at 4000 rpm for 20 min, and the MBT concentration in the supernatant phase was determined by reverse-phase HPLC, as described below. The experiments were repeated twice for each soil type. An additional study was carried out with PCR, QLT, LHS, and TEM soils amended with 10% of peat. A blank sample for every soil was prepared by adding 20 mL of distilled water instead of MBT solution. The standard solution was also run simultaneously, under the same experimental conditions to evaluate MBT stability. No degradation was observed in the absence of soil; a constant concentration of the herbicide was observed throughout the experiment and no new peak appeared on the chromatograms. The amount of MBT adsorbed for each sampling time was calculated from the difference between the initial and equilibrium solution concentrations.

Adsorption Isotherms

Batch equilibrium isotherms were determined for all soils under study including those amended with peat. Duplicate 4 g of air-dried soil samples were equilibrated with 20 mL of standard solutions (5, 10, 15, 20, and 25 μg mL⁻¹ in distilled water) into 30-mL sealed tubes by shaking mechanically at 30 ± 0.5°C for 14 h. After equilibration (kinetic experiments indicated that adsorption of MBT reached an apparent equilibrium within 2 h) the suspensions were centrifuged, and MBT was determined in the supernatant. As above, the amount of adsorbed herbicide was considered to be the difference between the initially present and that in the equilibrium solution.

Chromatographic Analysis

An HPLC chromatograph equipped with a quaternary gradient pump Waters 600, an autosampler Waters 717 Plus, and a PDA detector Waters 996 was used.

System control, data acquisition, and processing were performed by the Millennium 2010 software. The separation column was a Waters Nova Pack C₁₈ 60 Å, 3.9 × 300 mm, 4-μm particle size; the mobile phase used was CH₃CN:H₂O = 50:50% at a flow rate of 1 mL min⁻¹. Detection wavelength used was 225 nm, and the typical retention time for MBT was 4.9 min at a column temperature of 35°C. No peak from blank samples of soils at the MBT retention time was detected. The minimum detectable amount under the experimental conditions used was 0.005 μg mL⁻¹.

RESULTS AND DISCUSSION

The kinetic of MBT adsorption on natural and amended PCR and TEM soils and CLQ and CTR natural soils are shown in Figure 1. A rapid adsorption was

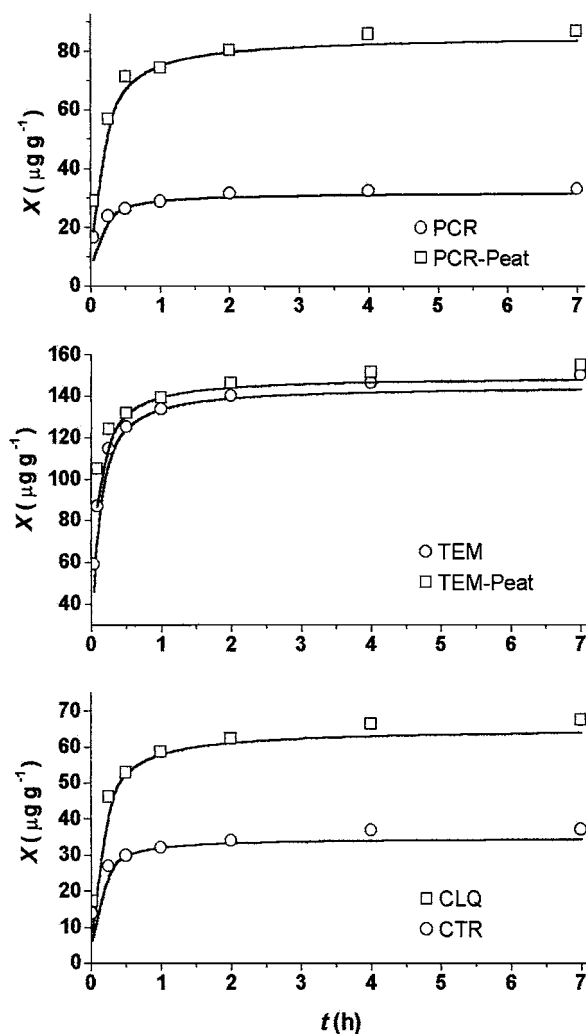


Figure 1. Adsorption kinetic of methabenzthiazuron on natural and peat-amended soils. The symbols represent experimental data and the lines are calculated [see Eq. (1)].

observed during the first few minutes, followed by a slower process that in all cases reached an apparent equilibrium within 2 h. The experimental data follow the hyperbolic model proposed by Biggar et al. (13) for the adsorption of picloram and parathion by soils, which has also been used by Jamet (14) for UKJ-1506 and Dios Cancela et al. (15,16) for cyanazine and carbendazim on peat and montmorillonite surfaces. In the hyperbolic equation:

$$X_t = \frac{X_{\max}t}{B + t} \quad (1)$$

where X_t is the adsorbed quantity at time t ; X_{\max} is the maximum adsorbed; t is the solid-solution contact time; and B is a constant. Values of X_{\max} were calculated by fitting the experimental data to the linear form of Equation (1):

$$1/X_t = \frac{B}{tX_{\max}} + 1/X_{\max} \quad (2)$$

where X_{\max} , B , and the correlation coefficient for the relationship between experimental and calculated X_t data from the hyperbolic equation are given in Table 2.

The differential dX_t/dt was determined at different times (X_{\max} and B enable to calculate it); the rate constant k and the order of the reaction n were obtained from the logarithmic form of the power equation given by Moreale and van Bladel (9):

$$dX_t/dt = k(X_{\max} - X_t)^n \quad (3)$$

The reaction was second order, and k values for each natural and amended soil are also given in Table 2.

In natural soils, the X_{\max} value increases as the soil OM content increases, being much higher for the allophanic soil (TEM). Enhancements of X_{\max} values were always obtained for amended soils, except for the allophanic one. Adsorption rate constants in general decrease as the soil OM increases, being rather lower for the TEM soil. Nevertheless, these rate constants point to a relatively low rate of reaction. In contrast, values for PCR, LHS, and QLT amended soils were 3.74, 2.17, and 1.97, respectively, times smaller than those of the natural soils. Consequently, the addition of OM not only increases the maximum quantity of MBT adsorbed by the soils, but also decreases the adsorption rate constants. Organic amendment scarcely

Table 2. Kinetic Data for the Methabenzthiazuron Adsorption on Natural and Amended Soils

Soil	Natural Soil				Amended Soil			
	X_{\max} ($\mu\text{g g}^{-1}$)	B	r^a	$k \times 10^4$ ($\mu\text{g g}^{-1}$) ¹⁻ⁿ s ⁻¹	X_{\max} ($\mu\text{g g}^{-1}$)	B	r^a	$k \times 10^4$ ($\mu\text{g g}^{-1}$) ¹⁻ⁿ s ⁻¹
PCR	32	0.086	0.96	1.01	85	0.120	0.99	0.27
CTR	35	0.073	0.97	1.10	—	—	—	—
LHS	51	0.036	0.94	1.50	101	0.040	0.98	0.69
CLQ	65	0.104	0.99	0.42	—	—	—	—
QLT	68	0.061	0.98	0.67	95	0.086	0.97	0.34
TEM	145	0.072	0.99	0.27	149	0.060	0.97	0.31

^aSignificance at $P \leq 0.001$.

modified kinetic parameters for TEM soil. Low rate constants in the adsorption of aniline residues on soils (9) and cyanazine on peat (15) have been attributed to a diffusion-controlled process within the porous organic matter adsorbent, the total rate of reaction being the combined effect of diffusion and adsorption; these facts could be used to explain changes observed in amended soils and the behavior of TEM soil.

Figure 2 shows the adsorption isotherms of MBT on the six soils studied. Sorption data were fit to the linearized form of the Freundlich equation:

$$\log X = \log K_f + 1/n \log C_e \quad (4)$$

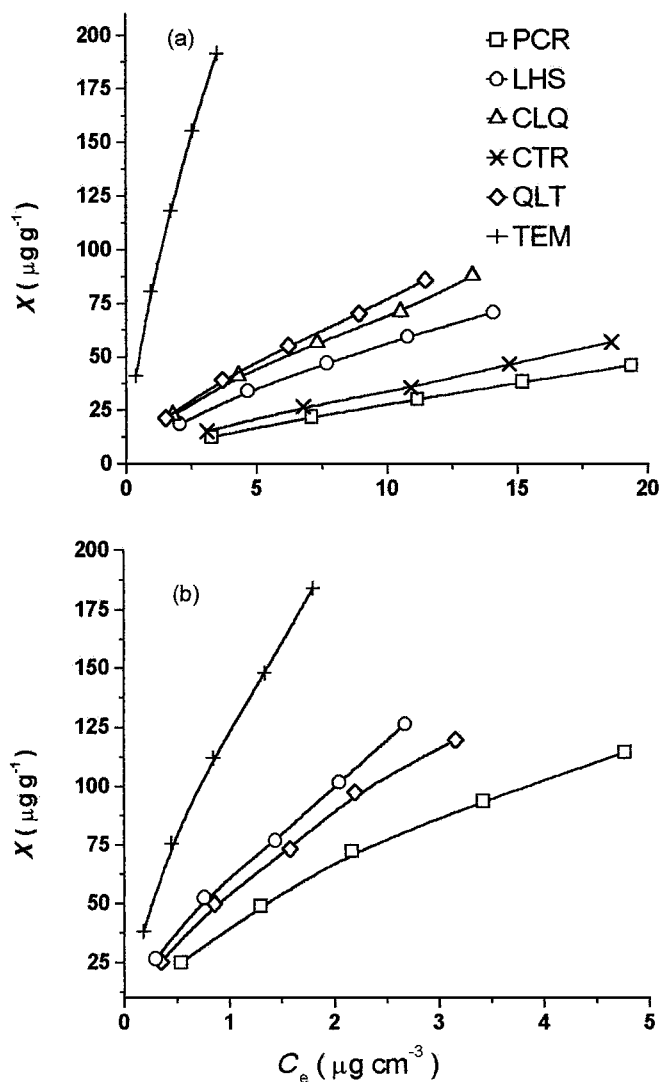


Figure 2. Adsorption isotherms of methabenzthiazuron on natural (a) and peat-amended (b) soils at 30°C.

Table 3. Freundlich Constants (K_f and $1/n$), Correlation Coefficients (r), K_d and K_{OM} for the Adsorption of Methabenzthiazuron

Soil	K_f (cm^3/g)	$1/n$	r^a	K_d^b (cm^3/g)	K_{OM} (cm^3/g)
PCR	5.3	0.73	0.999	3.53	208
CTR	6.5	0.73	0.998	4.36	190
LHS	11.5	0.69	0.999	7.30	228
CLQ	15.4	0.66	0.999	9.36	253
QLT	16.1	0.68	0.999	10.1	267
TEM	82.1	0.68	0.999	51.7	239
PCR + Peat	39.7	0.70	0.998	25.5	369
LHS + Peat	61.9	0.70	0.999	39.8	457
QLT + Peat	54	0.71	0.999	35.3	447
TEM + Peat	124	0.67	0.999	76.5	627

^aSignificance at $P \leq 0.001$.

^bAverage from K_d at $C_e = 2, 5, \text{ and } 10 \mu\text{g cm}^{-3}$.

where X is the amount of pesticide adsorbed ($\mu\text{g g}^{-1}$ of soil), C_e is the pesticide concentration in the solution at equilibrium ($\mu\text{g mL}^{-1}$) and K_f and $1/n$ are the Freundlich coefficients. In Table 3, K_f , $1/n$, and correlation coefficient (r), obtained from Freundlich equation, are given.

The isotherms fit the Freundlich equation with r values ≥ 0.998 . From the K_f values, it is deduced that the MBT adsorption capacity follows the order TEM > QLT > CLQ > LHS > CTR > PCR, the adsorption being markedly higher for the allophanic soil (TEM). An enhancement in the adsorption capacity was also observed for peat-amended soils. Linear regression analysis between K_f and OM content from natural soils gave a correlation coefficient = 0.980 ($P = 0.002$). As expected, N content, C/N ratios and CEC gave also a good correlation ($r = 0.94$, $P < 0.05$; $r = 0.960$, $P < 0.01$, and $r = 0.86$, $P = 0.07$, respectively). Soil surface area, phyllosilicates content, and pH showed a lack of correlation, probably due to the small differences existing between soils. It must be pointed that in all cases, data from TEM soil were not included because of its high weight, compared with those from the other soils.

Adsorption isotherms showed marked curvature, with slopes ($1/n$) significantly less than one in each case, indicating a convex, or L-type isotherm according to Giles et al. (17). No differences for amended soils were obtained. The slope of these kind of isotherm steadily decreases with a rise in solute concentration because vacant sites become less accessible with the progressive covering of the adsorbent surface.

K_f represents adsorption at a low equilibrium concentration of the adsorbate ($1 \mu\text{g mL}^{-1}$) and $1/n$ values ranging 0.66–0.73 will have a remarkable impact on distribution coefficients K_d ($K_d = C_s/C_e$) determined at a single equilibrium concentration. This in turn, will be observed expressing sorption as K_{OM} . Results obtained by Cox et al. (18) for imidacloprid showed that leaching potential according to the GUS index model would be overpredicted if K_d is obtained from high initial concentrations when $1/n$ is < 1 . Otherwise, Romero et al. (6) determined K_d values

for MBT in calcareous soils from the average of isotherm points when Freundlich exponents were lower than 0.8. Taking into account these criteria and comparing the results with those previously reported, K_d values, in addition to the K_f constant, were calculated for $C_e = 2, 5,$ and $10 \mu\text{g cm}^{-3}$ and then averaged. To determine the contribution of OM content on the sorption process K_{OM} values ($K_d/\%OM \times 100$) were obtained for each soil (Tab. 3).

K_{OM} values present the same order of magnitude than those obtained for calcareous soils by Romero et al. (6) (ranging between 140 and 619); however, according to the dispersion corresponding to those data, they concluded that OM does not influence the MBT adsorption at the content present in soils (1.64–2.17%). In this study K_{OM} values are very close for all natural soils (from 190 to 267), so it can be concluded that OM is the principal component responsible for MBT adsorption. Nevertheless, a greater dispersion is obtained when K_{OM} values from peat-amended soils (from 369 to 627) are included. After organic amendment pH of soils decreased to 4.4–5.3. Taking into account the pH values of natural soils (6.3–7.4), the MBT molecules would be mainly in a neutral form. Interactions will be predominantly by physical bonding such as van der Waals' forces or hydrogen bonding between the amino hydrogen of the herbicide and hydroxyl groups of humic acids (19), or through the carbonyl group, which could act as a strong donor to hydrogens of the alcoholic and phenolic groups on the humic acid (20). The significantly higher K_f values found for amended soils, including TEM soil, suggest that an additional or a different bonding mechanism could be present at lower pH. Protonation of weakly basic herbicides as *S*-triazines, simultaneous ionization of humic acid acidic groups (pH-depending reactions), and ionic bonding leading to adsorption have been frequently mentioned as additional adsorption mechanisms (20,21). These types of interactions could be present for MBT through the benzothiazol-*N* or the secondary amino group of the molecule. Further studies would be required to explain sorption behavior of MBT in these conditions.

K_f values obtained by Romero et al. (6) for calcareous soils are in good agreement with those expected in soils with a low OM content. Data from this type of soil showed a lack of correlation with this parameter; in turn, the soil clay and smectite contents were considered the most important factors governing the adsorption process. In the present study, despite the differences between soils for smectite contents, no significant correlation was obtained. However, the contribution of the mineral constituents to the global process must not be discarded. The relationship between K_f and OM% calculated through the linear least squares method from natural soils data is $K_f = 5.344 \text{ OM}\% - 4.75$ ($r = 0.984, P \leq 0.001$); when amended soils are included in this analysis, the equation is $K_f = 8.290 \text{ OM}\% - 13.28$ ($r = 0.991, P \leq 0.001$) (as above, in both cases TEM data were not included). As it can be observed, a slope change is produced and, in both cases, the intercept does not equal zero; these facts suggest that, especially at low OM content, interaction of soil components may account for MBT adsorption.

The clay mineral analysis of TEM soil also gave a 26% of maghemite, a crystalline iron oxide. Its high MBT adsorption capacity could also be associated with the presence of this mineral in addition to the prominent presence of allophane.

Taking into account that MBT solubility in water is 59 mg L^{-1} ($>30 \text{ mg L}^{-1}$), the half-life in soils is >1 year, direct photolysis half-life is also >1 year (1), and K_{OC} values ($K_{OM} \times 1.724$) are >300 for natural soils and >600 for amended soils, it is possible to estimate, according to Cohen et al. (22), that the leaching potential for MBT in these soils is low. Thus, accumulation in the soil and/or transportation by runoff to surface waters could be important processes associated with the fate of MBT.

CONCLUSIONS

MBT adsorption behavior is strongly associated with the OM content of soils. The order of the kinetic reaction is two. The slow process may be attributed to the diffusion of MBT molecules within the porous of the soil matrix. On the adsorption kinetic for nonallophanic soils, organic matter amendment increases the X_{\max} values and decreases the rate constant pointing out a higher porosity of the soil matrix. This amendment does not change the kinetic data obtained for the allophanic soil. Peat amendment considerably increases soil retention of this herbicide in all soils under study; thus, a lower leaching potential for this compound could be expected in this situation. The strong adsorption by soils with medium to high OM content, avoiding leaching, and the low susceptibility to degradation reported previously could explain the presence of this herbicide in surface waters in Chile, produced by losses from the sediment-adsorbed pesticide through runoff process.

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