

Effect of Undesalted Dissolved Organic Matter from Composts on Persistence, Adsorption, and Mobility of Cyhalofop Herbicide in Soils

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The effect of undesalted dissolved organic matter (DOM) extracted from composts on the degradation, adsorption, and mobility of cyhalofop herbicide in soils was studied. A paddy-field sediment poor in organic matter (OM), an OM-rich forest soil, and DOM from agroindustrial or municipal waste compost were used. DOM increased the cyhalofop-acid but not the cyhalofop-butyl solubility in water. The degradation of cyhalofop-butyl in the sediment was slow, giving cyhalofop-acid as the only metabolite, whereas in forest soil, the process was faster, and three byproducts were detected. Soil pretreatment with DOM did not modify the degradation pattern but only reduced the adsorption of cyhalofop-butyl by soil, whereas it increased the adsorption of cyhalofop-acid. Among the cationic components of DOM solutions, the potassium ion seems to be related to the increased adsorption of the cyhalofop-acid in both OM-poor and OM-rich soils, yielding reversible complexes with the former and favoring hydrophobic interactions with the latter.

KEYWORDS: Pesticide; hydrolysis; leaching; soil columns; cations; metals

INTRODUCTION

Increasing attention has been paid to the adverse impact of pesticides on the environment, human health, and life-support systems. The potential for contamination of water bodies is high in areas where rice is cultivated under flooded conditions (1–6). The agrochemicals applied to aquatic environments such as paddy fields are a matter of concern for potential leaching (7–9) and persistence in soil and water (10). During the draining phase, consisting of a forced movement of paddy water toward other field chambers and finally into surface water courses, agrochemicals can be mobilized and diffused into the environment. Conversely to nonflooded soils, the high volume of paddy water increases significantly the amount of agrochemicals in solution, and their possible adsorption into the paddy-field sediment is not favored.

Generally, the retention and mobility of pesticides in soil are determined by the extent and strength of the interactions with soil surfaces and are governed by the chemical and physical properties of both soil and pesticides. For soils characterized by a low organic matter content, the interaction with pesticides is often related to the active components of the inorganic fraction (i.e., clays and clay

minerals (11)). Usually, an increase in the clay content results in a decreasing mobility of the pesticide. For soils with a higher organic matter content, the retention of pesticides has been related to the total organic content, with the nature of the organic matter having little influence on sorption processes (12, 13). The total soil organic matter includes both soluble and insoluble fractions, although the contribution of soluble organic matter in soil is usually very small.

Many studies performed on the effect of soil dissolved organic matter (DOM) on the behavior of organic pollutants in the absence of soil generally agree upon a solubility enhancement of pesticides (14–18). Usually, these studies deal with nonionizable or neutral chemicals, characterized by high *n*-octanol/water distribution coefficients ($\log K_{ow}$ range of 4–6). The enhanced solubility of pesticides recorded in DOM solutions is not always confirmed when the soil is added to the experimental framework (19). In the presence of soil, contradictory results were obtained in studies concerning the effect of DOM on the behavior of cationic or positively ionizable pesticides in soil and water, probably owing to different experimental conditions (19–22). Despite the negative charge of negatively ionizable pesticides, which constrains them in the soil liquid phase and subsequently in water courses, only a few studies on their behavior in soil in the presence of DOM have been conducted (11, 23, 24).

Although the interactions of pesticides with DOM are affected by the ionic strength of the solutions, DOM is often used in

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Table 1. Summary of Characteristics of Investigated Soils (SD in Parentheses)

soil	pH		texture (%)			TOC ^a (g kg ⁻¹)	CEC ^b (cmol(+) kg ⁻¹)
	H ₂ O	CaCl ₂	clay	loam	sand		
S1	6.00 (±0.29)	5.50 (±0.10)	10	42	48	14.0 (±0.02)	2.00 (±0.01)
S2	7.10 (±0.13)	6.80 (±0.19)	20	54	26	73.0 (±0.27)	9.90 (±0.09)

^a TOC: total organic carbon. ^b CEC: cationic exchange capacity.

laboratory trials, after the removal of salts (i.e., as a purified organic fraction), and sometimes further fractionated in humic and fulvic acids (11, 15). Metals bound to DOM constituents or contained in a free form are lost during the purification procedure, and rarely is purified DOM studied as a function of both ionic strength and saline composition (14).

As many pesticides are found in groundwater (2, 3, 5), it is apparent that there is significant transport of these chemicals through the soil profile. The addition of organic amendments to the soil is an agricultural practice that, introducing a remarkable amount of exogenous soluble organic matter, is considered to potentially affect the pesticide fate in the soil (25, 26). The extent to which the exogenous DOM is involved in the transport process through the soil is far from being understood.

Cyhalofop-butyl (butyl (*R*)-2-[4-(4-cyano-2-fluorophenoxy)phenoxy]propionate, Clincher), applied at rates of up 300 g/ha, is an acetyl CoA carboxylase inhibitor for postemergence control of barnyard grass (*Echinochloa* spp.) and silver top (*Leptochloa fusca*) in rice (27, 28). The esters of aryloxyphenoxyalkanoic acids act as pro-herbicides. The formulation as esters facilitate the uptake through the plant cuticle and, once entered into the plant, they are transformed within a few hours into the acidic form [i.e., the active herbicide (29–31)]. In soils, cyhalofop-butyl is quickly transformed into the more soluble negatively ionizable acidic form (32).

The effect of exogenous DOM from two composts on the behavior of cyhalofop-butyl and -acid was studied in two different soils. Since the behavior of negatively ionizable pesticides is greatly affected by the soil pH, we decided to study the adsorption–degradation of cyhalofop-butyl and -acid in two soils with a similar pH value but differently characterized in organic matter content: a sediment from a paddy field and forest soil. To study the effect of the saline component on the herbicide behavior in soils, DOM was used without any desalting treatment or pH modification at concentration levels never exceeding their maximal solubility. The persistence, adsorption, and mobility of cyhalofop in the presence of DOM by means of solubility tests, determination of adsorption–desorption isotherms in soils, and leaching experiments on soil columns were evaluated.

MATERIALS AND METHODS

Soils. Two Italian soils were used: a paddy-field sediment, obtained by collecting the first centimeters of the soil, from Novara (S1), and a Lythic Usthorrents soil, sampled in the first 10 cm of a forest soil, from Bologna (S2). Although compost amendment is not commonly performed for forest soil, this soil was chosen because of the high organic matter content, in contrast to the low organic content of paddy soil (total organic carbon (TOC) 14.0 and 73.0 g kg⁻¹ for S1 and S2, respectively; see Table 1). In addition, the expected high concentration of endogenous DOM in S2 soil allows us to evaluate its effect with respect to herbicide adsorption–desorption in the presence of exogenous DOM.

Soil samples were air-dried, sieved at <2 mm, and stored at room temperature in the dark. The soil pH was determined in water or 0.01 M CaCl₂ solution with a soil/liquid phase ratio of 1:2.5 w/v. Particle

size distributions were performed using a pipet method (33). The TOC was determined according to the modified Walkley–Black method (34). The cation exchange capacity (CEC) was determined according to the procedure of Hendershot and Duquette (35). A summary of characteristics of the soils is reported in Table 1.

For soil experiments under reduced microbial activity, we followed the autoclaving conditions indicated by Alef and Trevors (36, 37) for small amounts of soil. Soil aliquots of 50 g were spread out in thin layer (1–2 cm) in glass beakers and autoclaved at 121 °C and 1.1 atm for 1 h before use. The adopted method for reducing the microbial activity was good enough to leave unchanged the concentration of cyhalofop-butyl or -acid during 1 week experiments in our soils.

DOM. DOM was extracted from two composts collected after the third week of the curing phase at Caviro (Imola, BO, Italy) or Hera (Rimini, RN, Italy) composting plants. The first compost (C_A) was obtained with a blend of winery byproducts (sewage sludge, marcs, and centrifuged winedregs) and urban plant trimmings by a forced aeration system. The second compost (C_M) was obtained with a blend of municipal solid waste from separate collections and lignocellulosic material by a weakly mixed static pile. The composting time for both composts was 28 days.

The suspension formed by a compost/deionized water ratio of 1:4 was shaken in polypropylene copolymer centrifuge tubes on a horizontal shaker for 24 h at room temperature. After centrifugation at 15000g for 40 min, the supernatant was passed through an ashless filter paper (Whatman 42) and subsequently filtered through 5 and 0.45 μm Durapore membrane filters. The extracts of C_A or C_M compost, called DOM_A and DOM_M solutions from hereon, were finally freeze-dried and stored in a desiccator without any additional treatment.

The dissolved organic carbon (DOC) of composts C_A and C_M, determined under these extraction conditions, and the TOC of the DOM were measured on freeze-dried DOM samples by a thermo-electron elemental analyzer (Thermo Fisher Scientific). The DOC of composts was 0.9 and 0.2 g kg⁻¹ for C_A and C_M, respectively. The electrical conductivity (EC) of DOM solutions was measured by a type SAT conductimeter (Halosis, Italy) equipped with a 1 cm⁻¹ cell constant platinum electrode (CRISON, 5292). Elemental analysis of DOM was performed by an inductively coupled plasma optical emission spectrometer (Spectro CIR.O.S.CCD) furnished by SPECTRO Analytical Instruments GmbH & Co. (Kleve, Germany) equipped with a plasma source and an optical detector with a charge-coupled device (CCD) able to quantify emission wavelengths of elements ranging between 125 and 780 nm. Before elemental analysis, freeze-dried DOM (100 mg) was dissolved by hot digestion with acids of spectroscopic grade (5 mL of HNO₃ (65% v/v) and 10 mL of 98% H₂SO₄). The DOM also was analyzed by ¹H NMR spectroscopy. Before NMR analysis, freeze-dried DOM samples were resuspended in distilled water. The excess metal ions were removed by sequentially passing the DOM solutions over two IR-120 H cation-exchange resins. After adjusting the leachate pH to a neutral value by the addition of a 0.1 N NaOH solution, the leachate was freeze-dried, and the DOM was desiccated over P₂O₅ at room temperature for 24 h to reduce the water signal in the ¹H NMR spectra. Finally, DOM samples were dissolved, each at its maximum solubility value (*S*_w 3.4 and 1.4 g L⁻¹ for DOM_A and DOM_M, respectively) in 0.75 mL of D₂O. ¹H NMR data were acquired with 3 s of recycle time, 256 transients, and a 90° pulse using a 400 MHz Mercury Plus Varian NMR spectrometer (Varian, Inc.). According to Kaiser and co-workers (38), the proton distribution of DOMs in the region of 0–2.5, 2.5–4.0, and 4.0–9.0 ppm was assigned to aliphatic, carbohydrate (amino acids, sugars, CH₂ adjacent to ester and ether/hydroxyl), and aromatic portions, respectively. The amount of car-

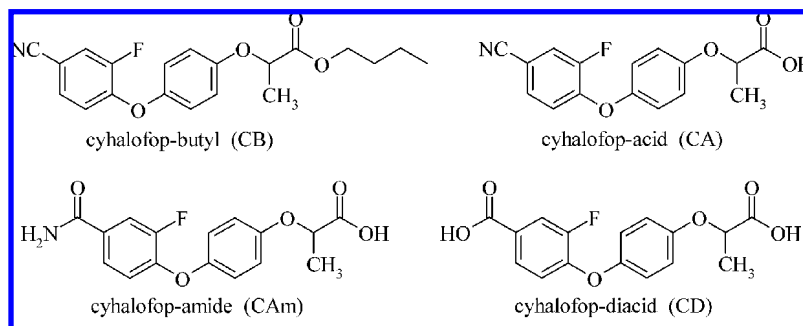


Figure 1. Structures of cyhalofop-butyl and its byproducts.

boxylic protons was determined by titration of acidic moieties with a 0.05 M NaOH solution in the pH range between 3.0 and 10.5. Samples of freeze-dried DOM (60 mg) were dissolved in 100 mL of distilled water, and the pH of the solutions was adjusted at 3.0 by the addition of a 0.05 M HCl solution. The titration curve was obtained by TIM860 Titration Manager (TitraLab, Radiometer Analytical SAS) equipped with a glass pH electrode.

In this study, freeze-dried DOM was redissolved in distilled water at a concentration never exceeding its maximal solubility before use. In the experiments in autoclaved soils pretreated with DOM, freeze-dried DOM samples were also autoclaved at 121 °C and 1.1 atm for 1 h before addition to soil.

Chemicals. Cyhalofop-butyl (butyl (*R*)-2-[4-(4-cyano-2-fluorophenoxy)phenoxy]propionate, CB, purity 99.9%), cyhalofop-acid ((*R*)-2-[4-(4-cyano-2-fluorophenoxy)phenoxy]propionic acid, CA, 99.4%), cyhalofop-amide (2-[4-(4-carbamoyl-2-fluorophenoxy)phenoxy]propionic acid, CAm, 99%), and cyhalofop-diacid ((*R*)-2-[4-(4-carboxyl-2-fluorophenoxy)phenoxy]propionic acid, CD, 98%) were kindly supplied as analytical standards by Dow Agrosciences (Bologna, Italy). Chemical structures of CB and its degradation products are shown in **Figure 1** (32). Because of the low solubility of CB either in water (1.2 μM at pH 7.0 (32)) or in 1% methanol solution (1.9 μM), a 1% acetonitrile aqueous standard solution of CB was prepared (4.0 μM). A 1% acetonitrile standard aqueous solution of CA (500 μM) was prepared and used in the range of 0–500 μM after dilution with distilled water (1% acetonitrile).

Solubility Tests. We followed the solubility enhancement technique proposed by Chiou and co-workers (15) with small modifications to study the effect of exogenous DOM on CB or CA solubility. Sterile DOM solutions were adjusted at pH 6.0 (i.e., similar to the soil pH) and added to a CB or CA amount exceeding that required to saturate the solution. The solutions were sonicated for 10 min and then left to equilibrate on a horizontal shaker at room temperature for 24 h to facilitate the solubilization process. The samples were subsequently centrifuged at 15000g for 40 min to separate the excess solute. After aspiration of undissolved solute particles adhering to the meniscus, an aliquot of the supernatant was withdrawn and directly analyzed by HPLC. The solubilities of CB or CA obtained in an aqueous solution (pH 6.0) were used as controls. The experiments were run five times.

Degradation Kinetics. To simulate the rice cultivation environment where CB is applied, the experiment was conducted in a soil/water suspension. The degradation kinetics of CB was conducted in soils in the presence of DOM, after pre-equilibration of 10 g of soil for 16 h with 5 mL of DOM_A or DOM_M solutions, each at its maximal solubility. An aqueous solution of CB (15 mL, 4.0 μM, 1% in acetonitrile) was then added to the slurry, yielding a 3 μM final concentration. The herbicidal dose used in the experimental design (280 g ha⁻¹) was of the same order of magnitude of the field application dose (300 g ha⁻¹) when considering a distribution in the first centimeter of depth, whereas the DOM amounts corresponded to a compost dose (c.a. 2 t ha⁻¹) lower than the compost amendment dose of paddy fields in the north of Italy (25–30 t ha⁻¹). At different times, the supernatants were separated from the solid phase by centrifugation at 15000g for 40 min and directly analyzed by HPLC. To desorb any chemicals eventually adsorbed on the soil solid phase, each pellet was shaken for 20 min with 20 mL of acetonitrile. Then, the organic phase was again centrifuged and analyzed

by HPLC. As a control, the same procedure was repeated without DOM. All the experiments were run in duplicate. The total recovery of CB and its degradation products from the aqueous solution and the desorbing organic solvent, calculated on a molar basis, was 86.2 ± 2.1 and 78.7 ± 3.1% for S1 and S2 soil, respectively.

To evaluate the effect of the microbial activity on the overall degradation, the CB degradation kinetics was run also in autoclaved soils. A separate study on the CA degradation was run under the same experimental conditions. The recovery of CA and its degradation products from the aqueous solution and the desorbing organic solvent, calculated on a molar basis, was 85.7 ± 0.9 and 80.1 ± 2.8% for S1 and S2 soil, respectively.

Adsorption on Soil. In a preliminary experiment, the adsorption kinetics of CB in autoclaved soils was studied. Since after 24 h the adsorption of CB in soil was complete, the same period was chosen as a contact time for adsorption experiments. Because of the low solubility, the soil adsorption of CB was studied for one point of concentration (3.0 μM, 1% in acetonitrile). The adsorption experiments were conducted in batch in 50 mL centrifuge tubes at 20 ± 2 °C. The adsorption was conducted after pre-equilibrating the soil (10 g) for 16 h with DOM solutions (5 mL) at the maximal solubility. Fifteen milliliters of CB standard solution (4.0 μM, 1% in acetonitrile) was then added to the slurry, giving a 3.0 μM final concentration. Samples were shaken on a horizontal shaker for 24 h. Finally, the suspension was centrifuged, and an aliquot of the supernatant was withdrawn and analyzed by HPLC. The amount of chemicals adsorbed by soils was calculated from the difference between initial and final concentrations both based on a 20 mL total volume. Controls were run after pre-equilibrating soil samples with distilled water. All the experiments were run in duplicate.

Adsorption isotherms of CA on sterile soils were performed at four concentrations in the range of 0–500 μM following the same procedure described previously for CB. To study the adsorption of the DOM on both soils, adsorption trials were conducted in the absence of herbicides under the experimental conditions described previously. The extent of adsorption was evaluated by measuring the absorbance at 465 nm of soil solutions (39) in the absence or presence of exogenous DOM (Jasco model 7800 spectrophotometer).

Desorption. Desorption was performed for CA in a batch with the dilution technique. After the adsorption process was complete, an aliquot (2 mL) of the supernatant, withdrawn to measure the adsorption as described in Adsorption on Soil, was replaced by the addition of distilled water. The samples were newly shaken for 24 h, and 2 mL aliquots of supernatant were withdrawn and analyzed by HPLC. The process was repeated twice consecutively. The chemicals' concentration in the desorption solution was determined, and the amount remained adsorbed on the soil after each desorption step calculated by the difference. Each level of dilution thus provided one point on the desorption isotherms.

Mobility on Soil Column. Because of the low solubility of CB, the mobility on the soil column was investigated only for CA. Experiments on soil columns were performed at room temperature in glass cylinders (height of 20 cm; i.d. of 3.5 cm) loaded with 150 g of soil at the field capacity (27 and 35% of soil moisture for S1 and S2, respectively) to simulate the rice cultivation environment. The total pore volume of soil columns, calculated by the difference between weights of soil at the saturation capacity and dried at 105 °C, was 390 and 352 cm³ kg⁻¹ for S1 and S2 soil, respectively. A CA solution (5 mL, 500 μM) was

Table 2. Selected Physical and Chemical Properties of Investigated DOMs (SD in Parentheses)

DOM sample	TOC ^b (g kg ⁻¹)	COOH (mmol 100 g ⁻¹ DOM)	¹ H NMR area (%)			pH	S _w ^c (g L ⁻¹)	EC ^d (dS m ⁻¹)	elements ^a (g kg ⁻¹)			
			aliphatics	carbohydrates	aromatics				Ca	K	Mg	Na
DOM _A	262 (±8)	305.0 (±4.8)	64	16	20	5.0 (±0.6)	3.4	0.54 (±0.13)	2.40 (±0.31)	122.0 (±2.7)	105.0 (±0.04)	29.0 (±0.9)
DOM _M	154 (±0.3)	101.0 (±6.1)	51	41	8	10.2 (±0.28)	1.4	0.89 (±0.08)	30.2 (±0.9)	194.0 (±0.35)	9.00 (±0.22)	69.0 (±1.0)

^a Referred to freeze-dried samples. ^b TOC: total organic carbon. ^c S_w: water solubility. ^d EC: electrical conductivity measured on DOM solutions of 1 g L⁻¹.

added to the column top and left to equilibrate for 24 h. Afterward, the column was eluted by adding to the top of the 60 mL of solution of DOM each at its maximal solubility, at a flow of 0.2 mL/min for a period of 5 h equivalent to a rainfall intensity of 32 mm H₂O h⁻¹. Under these experimental conditions, the applied DOM amounts corresponded to a compost dose (16 t ha⁻¹) close to the range of the compost amendment dose of paddy fields in the north of Italy (25–30 t ha⁻¹). After leaching, the soil columns were divided into 4 cm sections, and each section was extracted with 50 mL of acetonitrile. The suspension was shaken for 20 min and centrifuged, and the supernatant was analyzed by HPLC. The same experiment was conducted with a (271 ppm) K⁺ or (42 ppm) Ca²⁺ solution as the eluant. Control soil samples were loaded, left to equilibrate, leached with distilled water, and then treated as described previously. All experiments were run in duplicate. The total recovery of CA and its degradation products, calculated on a molar basis, was 74.1 ± 1.8 and 71.7 ± 3.8% for S1 and S2 soil, respectively.

Chromatographic Analysis. The concentration of CB and its degradation products was determined by HPLC. The system was assembled as follows: a Jasco 880-PU Intelligent pump, a Jasco AS-2055 plus Intelligent Sampler, a Jasco 875-UV Intelligent UV-vis detector at 224 nm, Borwin v 1.2160 chromatography software, a Jones Chromatography model 7971 column heater, and a μ Bondapak C18 analytical column (10 μ m, 3.9 mm × 300 mm) eluted with acetonitrile plus water (50 + 50 by volume, pH 2.75 for H₃PO₄) at a flow of 1 mL min⁻¹ kept at 35 °C in a column oven. Under these chromatographic conditions, the retention times for CB, CA, CD, and CAM were 40.0, 7.0, 4.5, and 3.6 min, respectively. Our HPLC conditions were not able to discriminate free from DOM-adsorbed herbicide. In fact, in a previous experiment (not reported), a complete dissociation of the herbicide DOM or byproduct DOM complexes in the acetonitrile/water mobile phase during HPLC analysis was confirmed by comparing known pesticide or byproduct concentrations in the presence and absence of DOM.

Data Analysis. Adsorption data of CB were expressed as the distribution coefficient: $K_d = C_s/C_e$, where C_s (μ mol kg⁻¹ adsorbent) is the amount of herbicide adsorbed on soil, and C_e (μ M) is the equilibrium concentration in the liquid phase. The data obtained by adsorption or desorption experiments of CA were fitted to the logarithmic form of the Freundlich equation, $\log C_s = \log K_F + 1/n \log C_e$, where $\log K_F$ and $1/n$ are empirical constants representing the intercept and slope of the linear equation, respectively. The hysteresis coefficient, H , for the adsorption–desorption isotherms was calculated according to the formula $H = (1/n_{des})/(1/n_{ads})$, where $1/n_{ads}$ and $1/n_{des}$ are the Freundlich slopes obtained for the adsorption and desorption isotherms, respectively (40).

RESULTS AND DISCUSSION

DOM Characterization. Some physical and chemical characteristics of the DOMs are reported in **Table 2**. The lower solubility of DOM_M in comparison to DOM_A may be due to several reasons. The lower amount of acidic protons (i.e., negatively ionizable carboxylic groups) of DOM_M makes this DOM less soluble than DOM_A. In addition, a higher ionic concentration of the DOM_M solution could allow DOM_M to pass in solution to a smaller extent (salting out effect), albeit to a limited level as suggested by the small conductivity value (EC 0.89 dS m⁻¹, **Table 2**). Likewise other organic polymers (e.g., humic and fulvic acids, pectines, proteins, etc.), the solubility of DOM, mainly constituted by polyanionic structures, is depressed by soluble salts (41). In **Table 2**, the most abundant

Table 3. Solubility Tests of Cyhalofop-Butyl and Cyhalofop-Acid in the Presence of DOMs at pH 6 (Mean of Five Replicates, SD in Parentheses)

solvent medium	CB solubility (μ M)	CA solubility (μ M)
water solution	0.83 (±0.21)	322.0 (±3.9)
DOM _A solution ^a	0.89 (±0.28)	638.0 (±4.7)
DOM _M solution ^a	0.85 (±0.26)	554.0 (±18.1)

^a Solution at the maximal solubility.

metals (Ca, K, Mg, and Na) measured on freeze-dried DOM samples are reported. The higher amounts of base cations of DOM_M together with the lower carboxylic group content justify the lowest observed solubility. The alkaline pH value of DOM_M (pH 10.2, **Table 2**) is the result of the industrial practice to add potassium and calcium carbonate or hydroxide to halt the composting process.

Solubility of Cyhalofop in the Presence of DOMs. In **Table 3**, the solubility of CB and CA in DOM solutions at pH 6.0 is shown. The unchanged solubility of CB in the presence of DOMs indicates that no interaction occurs with the DOMs. This probably results from the high hydrophilicity of the DOM in contrast to a complete hydrophobic character of the CB molecule. On the contrary, the doubled solubility of CA suggests an interaction with the DOM. Since at our working pH (about 6.0) CA, characterized with a pK_a of 3.8 (28), exists mostly in anionic form, a molecular interaction responsible for this increase of solubility must occur despite the repulsion between the negative charges of DOM and CA. Since the carboxyl group is the only molecular moiety differing from the ester CB to the acid CA, this functional group might be reasonably involved in the solubilization of CA in the presence of DOM. Similar to water and cation bridgings formed between the carboxylate groups of humic substances and the soil phases in the presence of base metals (42), polar and/or ionic interactions between metal cation-rich DOM and CA anionic moiety may be assumed to be responsible for the notable increase of CA solubility.

Cyhalofop-Butyl. Degradation Kinetics. The degradation of CB in soils with time is reported in **Figure 2**. The kinetics data for the CB degradation are given in **Table 4**. The CB degradation in nonautoclaved S2 soil follows a simple pseudo-first-order kinetics ($r = 0.952$, **Table 4**), whereas it follows a two-stage trend in nonautoclaved S1 soil as evidenced by **Figure 2**. A two-stage trend of CB degradation already was found by other researchers in European soils (27). In both soils, the CB half-life time ($t_{1/2}$) is about 1 day. This result agrees with the $t_{1/2}$ value found by other researchers in an Italian sandy-loam soil (32). In our soils, a marked difference can be noted between CB degradation trends (**Figure 2**).

In S1 soil, after an initial fast decay during the first 24 h, a slow decrease of the CB level occurs in the remaining period. In S2 soil, CB is completely degraded in about 170 h. Different byproducts are observed in the two soils. In S1 soil, only increasing amounts of the acid CA are formed during the first 24 h; after that, the amounts remain constant with time. In S2 soil, CA is not stable, but it is hydrolyzed to the amide CAM, which in turn is hydrolyzed to the diacid CD (**Figure 1**), the

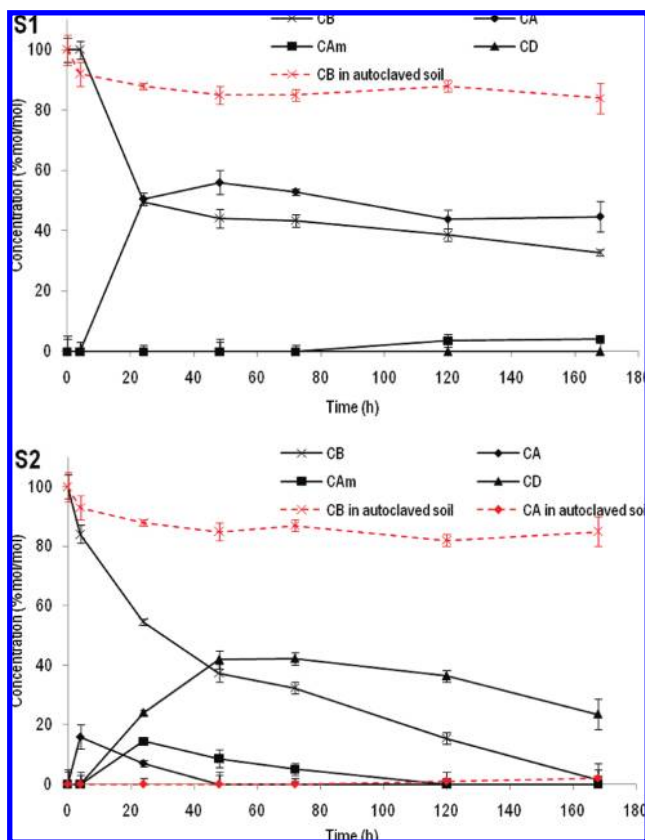


Figure 2. Degradation kinetics of cyhalofop-butyl in autoclaved and nonautoclaved paddy-field sediment (S1) and forest soil (S2) (mean of two replicates, SD as vertical bars).

main degradation product. Generally, in soils, the conversion of esters to carboxylic acids is a common reaction arising through both biotic (43) and abiotic mechanisms (44), whereas the conversion of nitriles to give either amides and subsequently carboxylic acids is mainly due to microbial processes (45). In our soils, the formation of byproduct CA, CA_m, and CD is a process mediated by soil microorganisms as confirmed by the stability of CB in autoclaved soils (Figure 2, $t_{1/2} > 2$ months for both S1 and S2 soils; see Table 4).

In general, the pretreatment with DOM does not modify the pH of our soils and does not affect the degradation trend of CB. Although DOM is an important substrate for microorganisms because it represents a bioavailable carbon source (46, 47), in autoclaved soils, with a reduced microbial activity, these results were expected. Also, in nonautoclaved soils, no significant effect was observed on the CB degradation trend as confirmed by kinetics data (Table 4). Since in S2 soil, the carbon contribution of exogenous DOM is presumably negligible if compared to the endogenous one (S2 soil TOC 73.0 kg g⁻¹), the CB degradation trend, unmodified with respect to the soil without DOMs, is justified. In S1 soil pretreated with DOMs, the unchanged degradation kinetics may be due to its reduced microbial activity as already observed by the slow degradation trend of CB in the nonautoclaved soil shown in Figure 2.

Adsorption. Because of the scarce solubility of CB (0.83 μM, Table 3), only its distribution coefficient, K_d , for adsorption on autoclaved soils was measured (Table 5). The CB adsorption is greater on S2, the soil with the highest clay and TOC content (Table 1). In a study on CB adsorption in European soils, Jackson and Douglas found higher K_d values (32) in comparison to our results. Most likely, our different experimental conditions are responsible for the observed adsorption coefficient. The

pretreatment of our soils with DOM significantly decreases the CB adsorption (Table 5). This finding suggests that DOM addition decreases the sites available to the adsorption of CB on the soil surfaces. Since the DOM does not interact with CB, as shown by the unchanged solubility of CB in its presence (Table 4), the adsorption decrease may be due to the occupation by the DOM of soil sites available for CB. Generally, the DOM from soil or composting processes is smaller in size and more oxygenated than the humified organic structures of soils (48) and, hence, less prone to adsorb the nonpolar CB molecule.

Measurements of the absorption at 465 nm (Abs_{465}) of soil solutions in the absence or presence of exogenous DOM confirm the occupation of soil adsorption sites by DOM. Both DOM_A and DOM_M adsorb on our soils. In fact, for S1 soil treated with DOM_A, in the case that no adsorption of DOM on soil occurs, an absorbance of 0.204, equal to the summation of the absorbance of endogenous DOM (Abs_{465} of 0.168) and exogenous DOM (Abs_{465} of 0.036), is expected. On the contrary, the value recorded on the S1 soil solution after pretreatment with DOM_A is much lower (Abs_{465} of 0.026), indicating that the adsorption of DOM_A on S1 soil occurs. When S1 soil is pretreated with DOM_M, the absorbance of the soil solution is 0.028, lower than the additive absorbance (Abs_{465} of 0.120). In S2 soil pretreated with DOM_A or DOM_M, the Abs_{465} of the soil solution is 0.172 or 0.167, respectively, which is smaller than the additive absorbance (0.349 or 0.265, respectively).

Cyhalofop-Acid. Degradation Kinetics. As CB rapidly hydrolyzed to CA, the main degradation product in the soil and the herbicidal active form, as well as the evaluation of the degradation kinetics of CA in our soils, was evaluated (Figure 3). The degradation of CA in both S1 and S2 soils follows a simple pseudo-first-order kinetics. The kinetics data are given in Table 4. As already reported for CB, the degradation trend of CA presents a marked difference in our soils. In nonautoclaved S1 soil, the degradation kinetics of CA is slow ($t_{1/2}$ of 14 days, Table 4) if compared to the kinetics trend in S2 nonautoclaved soil ($t_{1/2}$ of 15 h, Table 4). In S1 soil, the degradation products CA_m and CD are detected as traces after a 1 week experiment (Figure 3). Conversely, in S2 soil, the diacid CD is almost the only detectable degradation product after a 5 day experiment. In this soil, CD is not stable for a prolonged period as shown by the decrease of its concentration level after the 1 week experiment (Figure 3). The mediation of soil microorganisms to the degradation process is confirmed by the stability of CA in autoclaved soils (Figure 3 and Table 4).

Finally, the soil pretreatment with DOM_A or DOM_M does not affect the degradation trend of CA as shown by the $t_{1/2}$ values in S1 and S2 soils, similar for both pretreated or nonpretreated soils (Table 4). This finding, confirming the results obtained by the study of the degradation of CB in our soils, is supported by the same considerations given under Cyhalofop-Butyl Degradation Kinetics.

Adsorption and Desorption. Because of the fast soil degradation of CB ester to CA acid, the study was extended to the adsorption-desorption behavior of CA by soils. The Freundlich adsorption parameters of CA on soils are shown in Table 6. Similarly to that observed for CB adsorption, CA is also more adsorbed on organic forest S2 soil than on paddy-field S1 sediment (K_{Fads} of 0.52 and 3.00 μg^(1-1/n) mL^{1/n} g⁻¹ for S1 and S2, respectively). The isotherms are nonlinear with slopes (1/n) smaller than 1, resembling the L-type curves described by Giles et al. (49). The L shape suggests a relatively higher affinity of the herbicide for the adsorption sites at low equilibrium concentrations. The desorption parameters, shown in Table 7,

Table 4. Kinetics Data of Cyhalofop-Butyl and Cyhalofop-Acid Degradation in Paddy-Field (S1) and Forest Soil (S2) Pretreated or Untreated with DOM Solutions (SD in Parentheses)

sample	nonautoclaved soil			autoclaved soil		
	$K_{obs} (\times 10^{-3} \text{ h}^{-1})$	$t_{1/2}$	r	$K_{obs} (\times 10^{-3} \text{ h}^{-1})$	$t_{1/2}$ (days)	r
Cyhalofop-Butyl						
S1		24 h ^a		0.30 (± 0.02)	96.3	0.935 (± 0.030)
S1 + DOM _A		24 h ^a		0.31 (± 0.05)	94.1	0.935 (± 0.020)
S1 + DOM _M		24 h ^a		0.31 (± 0.03)	93.9	0.954 (± 0.070)
S2	21.9 (± 0.9)	31.6 h	0.952 (± 0.030)	0.50 (± 0.01)	57.8	0.931 (± 0.060)
S2 + DOM _A	23.8 (± 0.7)	29.1 h	0.898 (± 0.050)	0.52 (± 0.04)	55.4	0.903 (± 0.050)
S2 + DOM _M	24.0 (± 0.9)	28.9 h	0.905 (± 0.090)	0.52 (± 0.02)	55.0	0.865 (± 0.030)
Cyhalofop-Acid						
S1	2.11 (± 0.20)	13.7 days	0.979 (± 0.020)	0.20 (± 0.08)	144	0.876 (± 0.090)
S1 + DOM _A	2.39 (± 0.10)	12.1 days	0.956 (± 0.040)	0.20 (± 0.07)	143	0.978 (± 0.060)
S1 + DOM _M	2.40 (± 0.20)	12.0 days	0.969 (± 0.060)	0.20 (± 0.04)	143	0.989 (± 0.070)
S2	46.6 (± 1.20)	14.9 h	0.981 (± 0.040)	1.20 (± 0.20)	24.1	0.884 (± 0.080)
S2 + DOM _A	44.7 (± 1.00)	15.5 h	0.909 (± 0.070)	1.22 (± 0.10)	23.7	0.908 (± 0.070)
S2 + DOM _M	46.8 (± 0.90)	14.8 h	0.966 (± 0.050)	1.25 (± 0.20)	23.0	0.950 (± 0.040)

^a Value not calculated by first-order kinetics but experimentally determined.

Table 5. Distribution Coefficient of Cyhalofop-Butyl^a in Soils (Mean of Two Replicates, SD in Parentheses)

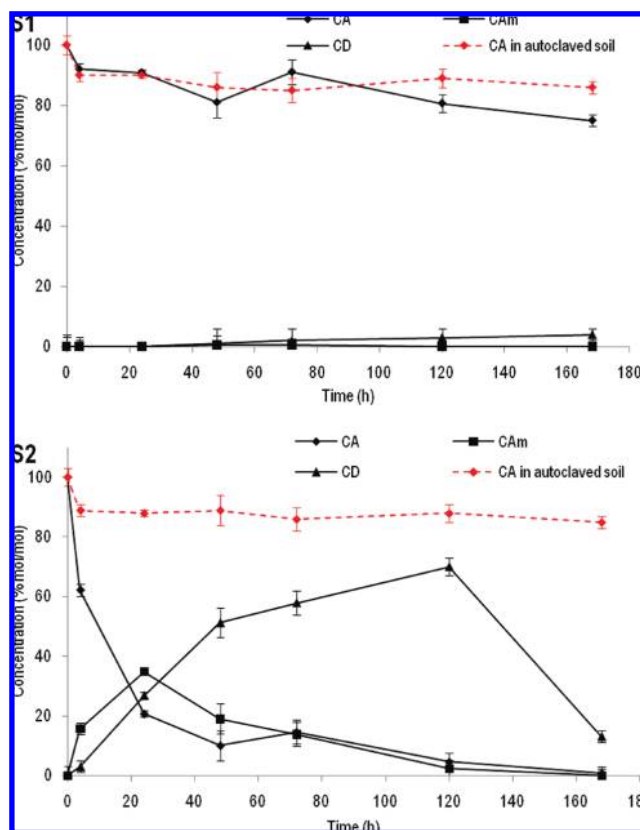
sample	C_e^b (μM)	k_d (L kg ⁻¹)
S1	1.20 (± 0.20)	1.30 (± 0.30)
S1 + DOM _A	2.90 (± 0.10)	n.a. ^c
S1 + DOM _M	3.00 (± 0.20)	n.a.
S2	0.70 (± 0.01)	3.34 (± 0.05)
S2 + DOM _A	1.32 (± 0.02)	0.85 (± 0.07)
S2 + DOM _M	1.43 (± 0.03)	0.61 (± 0.03)

^a Initial concentration: 3.0 μM in 1% acetonitrile. ^b C_e : equilibrium concentration in liquid phase. ^c n.a.: not available because no adsorption was observed.

are indicative of the complete reversibility of the CA adsorption on S1 soil and the complete irreversibility on S2 soil. The hysteresis coefficient, H , for the adsorption and desorption isotherms (Table 7) is a measure of the extent of hysteresis in the desorption. A value of 1 indicates that the desorption proceeds as fast as the adsorption does and that hysteresis does not occur. For all equilibrium points, CA desorption from S1 soil is completely reversible with unitary H coefficients. The opposite behavior of the soil-CA adsorption complex toward the dilution is indicative of a polar-ionic interaction (reversible by dilution) with S1 soil and a hydrophobic interaction (not reversible by dilution) with S2 soil.

Although the contribution of the organic carbon from DOM is negligible as compared to the organic carbon content of our soils (ΔTOC of 0.4 and 0.1 g kg⁻¹ for DOM_A and DOM_M, respectively; see Table 6), the DOM pretreatment increases the CA adsorption. On S1 soil, the addition of DOM notably enhances the CA adsorption, whereas on S2 soil, the increase is lower.

With respect to the control, S1 soil pretreated with DOM shows an enhanced affinity for the adsorption of CA, as indicated by the notable increase of K_{Fads} (ΔK_{Fads} of 904 and 500% in soil treated with DOM_A or DOM_M, respectively; see Table 6) and the lowering of $1/n_{\text{ads}}$ values ($1/n_{\text{ads}}$ of 0.85 for control and 0.43 and 0.55 for soil treated with DOM_A or DOM_M, respectively; see Table 6). Nevertheless, the adsorption still remains completely reversible (H value of ca. 1, Table 7). This finding may be explained by two mechanisms: (i) DOM previously adsorbed on soil surfaces increases the number of organic sites available to interact with CA by a polar-ionic mechanism and (ii) the addition of base cations increases the base metal saturation degree of the sediment, hence linking to a higher extent the CA carboxylate moiety through cation and

**Figure 3.** Degradation kinetics of cyhalofop-acid in autoclaved and nonautoclaved paddy-field sediment (S1) and forest soil (S2) (mean of two replicates, SD are vertical bars).

water bridges (42). The first mechanism is supported by the modification of soil surfaces as a consequence of DOM adsorption (see Cyhalofop-Butyl Adsorption) and by the increased solubility of CA in the presence of DOM (Table 3). The second mechanism is supported by the pH decrease of S1 soil measured in CaCl₂ solution in comparison to distilled water (ΔpH -0.5, Table 1) due to a further release of protons as a consequence of cationic exchange by Ca ions. In a similar manner, the addition to soil of base metals brought by DOM (Table 2) promotes the exchange reactions on organic and mineral phases of soils. In addition, the low content of organic matter present in S1 sediment (TOC 14.0 g kg⁻¹, Table 1) makes its mineral surfaces more available to the interaction with

Table 6. Freundlich Parameters for Cyhalofop-Acid Adsorption in Soils (Mean of Two Replicates, SD in Parentheses)

sample	ΔTOC^a (g kg ⁻¹)	$1/n_{\text{ads}}$	K_{Fads} ($\mu\text{g}^{(1-1/n)} \text{ mL}^{1/n} \text{ g}^{-1}$)	ΔK_{Fads}^b (%)	r
S1		0.85 (± 0.001)	0.52 (± 0.08)		0.985 (± 0.001)
S1 + DOM _A	0.4	0.43 (± 0.06)	4.70 (± 1.70)	904	0.910 (± 0.060)
S1 + DOM _M	0.1	0.55 (± 0.08)	2.60 (± 1.00)	500	0.890 (± 0.040)
S2		0.80 (± 0.10)	3.00 (± 1.00)		0.980 (± 0.010)
S2 + DOM _A	0.4	0.72 (± 0.04)	4.90 (± 0.90)	163	0.990 (± 0.010)
S2 + DOM _M	0.1	0.79 (± 0.04)	3.50 (± 0.40)	117	0.996 (± 0.001)

^a ΔTOC : contribution of DOM organic carbon to soil TOC. ^b ΔK_{Fads} : increase of K_{Fads} owing to DOM pretreatment of soil.

Table 7. Freundlich Parameters for Cyhalofop-Acid Desorption (Mean of Two Replicates, SD in Parentheses)

sample	C_i^a (μM)	$1/n_{\text{des}}$	k_{des} ($\mu\text{g}^{(1-1/n)} \text{ mL}^{1/n} \text{ g}^{-1}$)	r	H^b
S1	89.0 (± 2.0)	0.87 (± 0.002)	1.10 (± 0.07)	0.979 (± 0.030)	1.02
	180.0 (± 4.0)	0.86 (± 0.001)	1.16 (± 0.20)	0.989 (± 0.050)	1.01
S1 + DOM _A	275.0 (± 3.0)	0.86 (± 0.01)	2.70 (± 0.70)	0.989 (± 0.060)	1.01
	99.0 (± 1.0)	0.46 (± 0.004)	1.48 (± 0.02)	0.989 (± 0.020)	1.07
	206.0 (± 3.0)	0.48 (± 0.01)	2.40 (± 0.30)	0.989 (± 0.070)	1.12
	311.0 (± 0.5)	0.44 (± 0.04)	15.10 (± 1.20)	0.977 (± 0.003)	1.02
S1 + DOM _M	100.0 (± 0.5)	0.55 (± 0.05)	5.60 (± 0.40)	0.989 (± 0.09)	1.00
	203.0 (± 2.0)	0.61 (± 0.03)	6.23 (± 0.09)	0.989 (± 0.070)	1.11
	307.0 (± 3.0)	0.56 (± 0.02)	14.90 (± 1.30)	0.975 (± 0.100)	1.02
S2	60–300	n.a. ^c	n.a.	n.a.	n.a.
S2 + DOM _A	60–300	n.a.	n.a.	n.a.	n.a.
S2 + DOM _M	60–300	n.a.	n.a.	n.a.	n.a.

^a C_i : initial concentration. ^b H : hysteresis coefficient ($1/n_{\text{des}}/1/n_{\text{ads}}$). ^c n.a.: not available because no desorption was observed.

CA. Both mechanisms may be involved in the increase of CA adsorption on S1 soil.

The scenario in S2 soil is different; the CA adsorption still remains irreversible after DOM treatment (**Table 7**) that, hence, does not modify the interaction mechanism. Very likely, the amount of adsorption sites available to a hydrophobic interaction with CA does not vary as a consequence of the adsorption of DOM on the soil. This is reasonably supported by the very high content of organic matter of S2 soil (TOC of 73.0 g kg⁻¹, **Table 1**). The adsorption of DOM on the soil surfaces does not modify the hysteresis in the desorption of CA (**Table 7**). The increases of the adsorption extent after pretreatment of S2 soil with DOM (ΔK_{Fads} of 163 and 117% in soil treated with DOM_A or DOM_M, respectively, **Table 6**) may be due to the ionic content of DOM solutions whose cationic component, complexing the negatively charged groups, lowers the negative charges of both soil organic matter and CA. At our working pHs, the decrease of the electrostatic repulsion between soil organic matter— $\text{p}K_{\text{a}}$ values of ~ 5 according to Stevenson (50)—and CA would allow CA to come to a shorter distance from soil surfaces and hence to favor the hydrophobic interactions without modifying the adsorption mechanisms as confirmed by the similar values of CA affinity for untreated and treated soil ($1/n_{\text{ads}}$ of 0.80 for control and 0.72 and 0.79 for soil treated with DOM_A or DOM_M, respectively; see **Table 6**).

Mobility on Soil Column. In the study of CA mobility on soil columns, the top soil was previously treated with the herbicide, left to equilibrate, and then eluted with DOM solutions. All aliquots of leachate collected from the soil columns did not contain detectable levels of herbicide or its degradation products. In agreement with the CA stability recorded in S1 soil and its degradation in S2 soil (**Figure 3**), in the column experiments, CA was recovered unchanged at the end of the experiment in S1 and partially degraded to CAM and CD in S2 soil (**Figure 4**). In both soils, the presence of DOM influences the mobility of the chemicals along the soil profile but does not affect their persistence in comparison to control soils. In fact, their molar balance is similar in soils eluted with distilled water or DOM solutions.

The presence of the DOMs in the eluting solution reduces the CA mobility along both S1 and S2 soil profiles in comparison to soils eluted with distilled water (controls). In both soils, DOM_M, with the highest content of base metals and the lowest content of organic matter and carboxylic groups (**Table 2**), is more active than DOM_A in decreasing the CA mobility. In addition, in S2 soil, the mobility of the metabolites CAM and CD, both containing carboxylate moieties (**Figure 1**), is reduced (**Figure 4**).

Although the adsorption of DOM on soil surfaces during the elution time (5 h) cannot be stated, it seems reasonable to assume that this time period is enough for the base cations contained in the DOM solutions to modify the soil surfaces by cation exchange and, in adsorbed form, increase the retention of CA along the soil profile by interactions with the carboxylic moiety.

The same mechanisms suggested to explain the increased adsorption of CA in S1 and S2 soil in the presence of DOM can be adopted to explain the reduced mobility of CA along the soil column. In fact, in the leaching experiment on the column filled with the soil poorer in organic matter (S1), the cationic exchange by base metals brought by DOM on soil surfaces can be responsible for the higher extent of cation and water bridges with the carboxylate moiety of CA. In the soil with the highest organic matter content (S2), the base metals contained in the DOM solutions, decreasing the repulsive forces between the negative charges of both soil organic matter and carboxylate groups of CA, CAM, and CD, reduces their movement along the soil profile (**Figure 4**).

In **Figure 4**, the CA mobility in the soils eluted with solutions of K⁺ and Ca²⁺ also is reported—the most representative monovalent and divalent cations found in the DOM_M solution; see **Table 2**—to analyze the contribution of the cationic component to the retention process of CA. The concentration of K⁺ or Ca²⁺ in the leaching solutions is the same as the DOM_M solution (271 and 42 ppm for K and Ca, respectively). Since the speciation of metals contained in the DOM was beyond the purpose of this study, we roughly considered the total metal amount contained in DOM_M as free metals to highlight their effect on the CA mobility in soils. In both soil

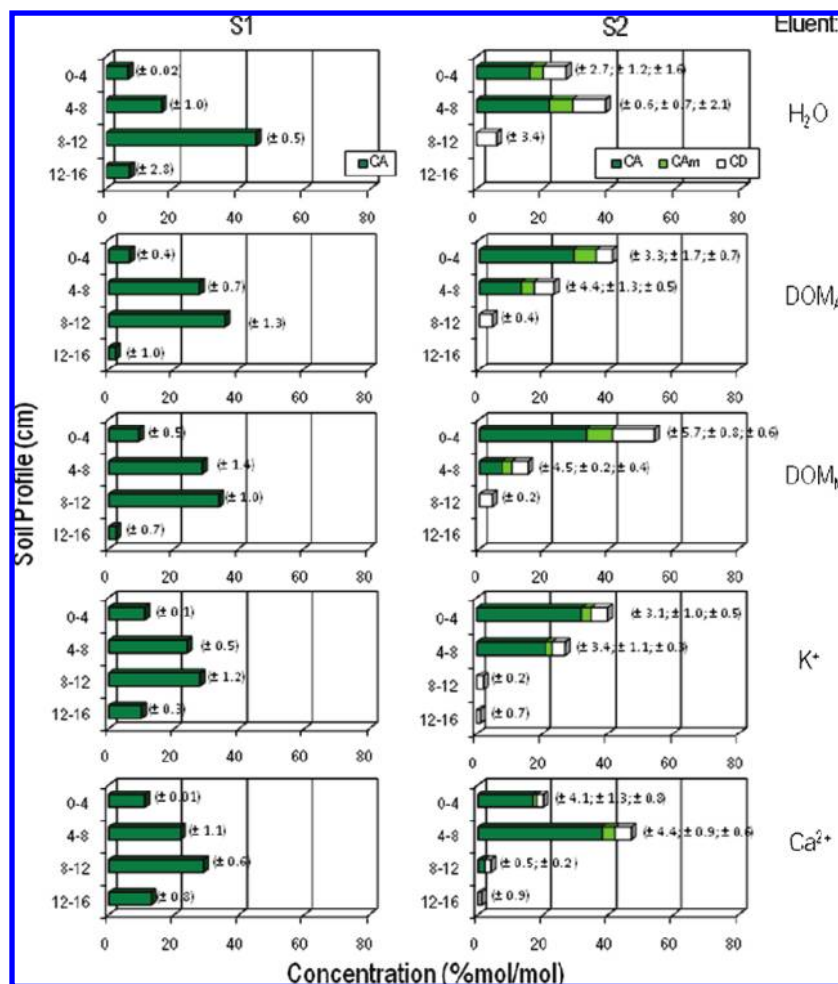


Figure 4. Mobility of cyhalofop-acid and byproducts along the profile of S1 and S2 soil columns leached with exogenous dissolved organic matter (DOM_M or DOM_H) or metal (K⁺ or Ca²⁺) solutions (mean of two replicates, SD of CA, CA_m, and CD, respectively, are in parentheses).

columns, with respect to controls, the presence of K ions decreased the CA mobility along the soil profile, partially reproducing the CA distribution in the presence of DOM_M. Therefore, the K ion seems to be involved in the decreased mobility of CA in our soils eluted with DOM solutions. The Ca ion shows a different behavior, mobilizing a lower and higher amount of CA along the profile of S1 and S2 soils, respectively, with respect to controls. The difference in the binding activity of the two cations in the adsorbed form toward the carboxylates can be explained. In fact, while in the adsorbed form K⁺ may give rise to a cation bridge with carboxylates due to the formation of an inner-sphere complex, Ca²⁺ forms a water bridge, a weaker outer-sphere complex mediated by water molecules (42, 51). The different strength between K and Ca complexes may be responsible for the best CA retention in soils eluted with K ions with respect to Ca ions.

In studies on the effect of the binding ability of Ca ions adsorbed on soil and clay matrices toward the adsorption of acifluorfen, a herbicide containing a carboxylic moiety, the formation of an insoluble complex with Ca ions was found to simulate an increase of adsorption (52, 53). In our work, although the chemical structures for CA and acifluorfen are similar, the precipitation of an insoluble Ca–CA complex can be excluded by an increase in the CA solubility in the highly saline DOM solutions (Table 3).

Conclusion. This study indicates that the presence of undesalted exogenous DOM in a paddy-field sediment and a forest soil does not affect the degradation, mediated by soil microor-

ganisms, of cyhalofop-butyl and cyhalofop-acid, whereas it influences their retention in the soils under study. In DOM solutions, the solubility is unmodified for CB and increased for CA. The carboxylic group arising from the hydrolysis of ester CB to the acid CA is involved in the solubilization process. Ionic interactions such as water and cation bridges between DOM and CA anionic moieties may be responsible for the increase of CA solubility in the presence of DOM. Owing to the adsorption of polar DOM molecules to the soils, the adsorption of the nonpolar CB decreased, whereas the adsorption of the anionic CA increased. In the poorly organic paddy-field sediment, the adsorption of CA is reversible. After DOM treatment, the soil adsorption notably increases, but it still remains reversible. This enhancement is ascribed to the interaction of CA with DOM or cations, both in the adsorbed form onto soil surfaces. In the highly organic forest soil, the adsorption of CA is nonreversible, indicative of hydrophobic interactions, and so remains after the DOM pretreatment. The increase of adsorption recorded in the presence of DOM is ascribed to the high cationic content of DOM that, by its complexing activity, lowering the electrostatic forces between the negative charges of both soil organic matter and the CA carboxylate, favors the hydrophobic interaction. The increased adsorption of CA to soils is confirmed by its decreased mobility along the soil profile in soil columns eluted with DOM solutions. The K ions, contained in the largest amount in the DOM solutions, known to form an adsorbed form reversible inner-sphere complex with carboxylates, decrease the mobility of CA

along the soil profile. The saline component of compost extracts seems to account for a large extent of the increased adsorption of the anionic herbicide cyhalofop-acid in both paddy field and forest soils, generating highly reversible complexes with the former and nonreversible complexes with the latter, both involving the CA carboxylate group.

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LITERATURE CITED

- Celis, R.; Barriuso, E.; Houot, S. Sorption and desorption of atrazine by sludge-amended soil: Dissolved organic matter effects. *J. Environ. Qual.* **1998**, *27*, 1348–1356.
- Capri, E.; Cavanna, S.; Trevisan, M. Ground and surface water bodies contamination by pesticide use in a paddy field. In *Environmental Risk Parameters for Use of Plant Protection Products in Rice*; Capri, E., Cervelli, S., Arnold, G., Eds.; Tipolitografia: Piacenza, Italy, 1999; pp 48–71.
- Charizopoulos, E.; Papadopoulou-Mourkidou, E. Occurrence of pesticide in rain of the Axio stream basin, Greece. *J. Environ. Sci. Technol.* **1999**, *33*, 2363–2368.
- Gomez de Barreda, C. Rice scenario, ecology of the paddy field, and monitoring studies in Spain. In *Environmental Risk Parameters for Use of Plant Protection Products in Rice*; Capri, Cervelli, Arnold, Eds.; Tipolitografia: Piacenza, Italy, 1999; pp 23–28.
- Cerejra, M. Simazine, metribuzine, and nitrates in ground water of agricultural areas of Portugal. *Toxicol. Environ. Chem.* **2000**, *75*, 245–253.
- Miao, Z.; Padovani, L.; Riparbelli, C.; Ritter, A. M.; Trevisan, M. Prediction of the environmental concentration of pesticides in a paddy field and surrounding surface water bodies. *Paddy Water Environ.* **2003**, *1*, 121–132.
- Boesten, J. J. T. I.; van der Linden, A. M. A. Modeling the influence of sorption and transformation on pesticide leaching and persistence. *J. Environ. Qual.* **1991**, *20*, 425–435.
- Flori, P.; Pancaldi, D.; Braschi, I.; Gessa, C. Behavior of Four Herbicides in a Paddy Field: Simulation by a Laboratory Microcosm. *XII Symposium on Pesticide Chemistry*, Piacenza, Italy, June 4–6, 2003, pp 223–232.
- Müller, K.; Magesan, G. N.; Bolan, N. S. A critical review of the influence of effluent irrigation on the fate of pesticides in soil. *Agric. Ecosys. Environ.* **2007**, *120*, 93–116.
- Braschi, I.; Pusino, A.; Gessa, C. Adsorption–Desorption of Pretilachlor and Cinosulfuron on Paddy Field Sediment. *XII Symposium on Pesticide Chemistry*, Piacenza, Italy, June 4–6, 2003, pp 161–167.
- Spark, K. M.; Swift, R. S. Effect of soil composition and dissolved organic matter on pesticide sorption. *Sci. Total Environ.* **2002**, *298*, 147–161.
- Jenks, B. M.; Roeth, F. W.; Martin, A. R.; McCallister, D. L. Influence of surface and subsurface soil properties on atrazine sorption and degradation. *Weed Sci.* **1998**, *46*, 132–138.
- Beckbolet, M.; Yenigum, O.; Yucel, I. Sorption studies of 2,4-D on selected soils. *Water, Air, Soil Pollut.* **1999**, *111*, 75–88.
- Carter, C. W.; Suffet, I. H. Binding of DDT to dissolved humic materials. *Environ. Sci. Technol.* **1982**, *16*, 735–740.
- Chiou, C. T.; Malcolm, R. L.; Brinton, T. I.; Kile, D. E. Water solubility enhancement of some organic pollutants and pesticides by dissolved humic and fulvic acids. *Environ. Sci. Technol.* **1986**, *20*, 502–508.
- Döring, U. M.; Marschner, B. Water solubility enhancement of benzo(a)pyrene and 2,2',5,5'-terachlorobiphenyl by dissolved organic matter (DOM). *Phys. Chem. Earth* **1998**, *23*, 193–197.
- Salloum, M. J.; Dudas, M. J.; McGill, W. B. Variation of 1-naphthol sorption with organic matter fractionation: The role of physical conformation. *Org. Geochem.* **2001**, *32*, 709–719.
- Lee, S.; Gan, J.; Liu, W. P.; Anderson, M. A. Evaluation of K_d underestimation using solid phase microextraction. *Environ. Sci. Technol.* **2003**, *37*, 5597–5602.
- Pennington, K. L.; Harper, S. S.; Koskinen, W. C. Interactions of herbicides with water-soluble soil organic matter. *Weed Sci.* **1991**, *39*, 667–672.
- Barriuso, E.; Baer, U.; Calvet, R. Dissolved organic matter and adsorption–desorption of dimefuron, atrazine, and carbetamide by soils. *J. Environ. Qual.* **1992**, *21*, 359–367.
- Klaus, U.; Mohamed, S.; Volk, M.; Spittler, M. Interaction of aquatic humic substances with anilazine and its derivatives: The nature of the bound residues. *Chemosphere* **1998**, *37*, 341–361.
- Seol, Y.; Lee, L. S. Effect of dissolved organic matter in treated effluents on sorption of atrazine and prometryn by soils. *Soil Sci. Soc. Am. J.* **2000**, *64*, 1976–1983.
- Xing, B. Potential Movement of Pesticides Related with Dissolved Organic Matter from Organic Fertilizer Application on Turf; Massachusetts Water Resources Research Center Publication No. 180, 2006, pp 1–21.
- Said-Pullicino, D.; Gigliotti, G.; Vella, A. J. *Environmental fate of triasulfuron in soils amended with municipal waste compost.* *J. Environ. Qual.* **2004**, *33*, 1743–1751.
- Cox, L.; Cecchi, A.; Celis, R.; Hermosín, M. C.; Koskinen, W. C.; Cornejo, J. Effect of exogenous carbon on movement of simazine and 2,4-D in soils. *Soil Sci. Soc. Am. J.* **2001**, *65*, 1688–1695.
- Hesketh, N.; Brookes, P. C.; Addiscott, T. M. Effect of suspended soil material and pig slurry on the facilitated transport of pesticides, phosphate and bromide in sandy soil. *Eur. J. Soil Sci.* **2001**, *52*, 287–296.
- Buendía, J.; Barotti, R.; Fullick, K.; Thompson, A.; Velilla, J. Cyhalofop, a New Postemergence Herbicide for Grass Control in Rice. *6th EWRS Mediterranean Symposium*, Montpellier, France, 1998.
- APVMA. Evaluation of the New Active Cyhalofop-Butyl in the Product Barnstorm Herbicide. *Australian Pesticide and Veterinary Medicines Authority*, Canberra, Australia, July 2005, pp 1–39.
- Hendly, P.; Dicks, J. W.; Monaco, T. J.; Slyfield, S. M.; Tummon, O. J.; Barret, J. C. Translocation and metabolism of pyridinyloxyphenoxypionate herbicides in rhizomatous quackgrass (*Agropyron repens*). *Weed Sci.* **1985**, *33*, 11–24.
- Duke, S. O.; Kenyon, W. H. Polycyclic alkanolic acids. In *Herbicides: Chemistry, Degradation, and Mode of Action*; Kearney, P. C., Kaufman, D. D., Eds.; Marcel Dekker: New York, 1988; pp 71–116.
- Ferreira, K. L.; Burton, J. D.; Coble, H. D. Physiological basis for antagonism of fluzafop-P by DPX-PE350. *Weed Sci.* **1995**, *43*, 184–191.
- Jackson, R.; Douglas, M. An Aquatic Risk Assessment for Cyhalofop-Butyl: A New Herbicide for Control of Barnyard Grass in Rice. *XI Symposium on Pesticide Chemistry, Human and Environmental Exposure to Xenobiotics*, Cremona, Italy, 1999, pp 345–354.
- Indorante, S. J.; Follmer, L. R.; Hammer, R. D.; Koenig, P. G. Particle-size analysis by a modified pipette procedure. *Soil Sci. Soc. Am. J.* **1990**, *54*, 560–563.
- Jackson, M. L. Organic matter determination for soils. In *Soil Chemical Analysis*; Prentice Hall: Englewood Cliffs, NJ, 1958; pp 219–222.
- Hendershot, W. H.; Duquette, M. A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Sci. Soc. Am. J.* **1986**, *50*, 605–608.
- Alef, K. Sterilization of soil and inhibition of microbial activity. In *Methods in Applied Soil Microbiology and Biochemistry*; Alef, K., Nannipieri, P., Eds.; Academic Press: San Diego, 1995; pp 52–54.
- Trevors, J. T. Sterilization and inhibition of microbial activity in soil. *J. Microbiol. Methods* **1996**, *26*, 53–59.

- (38) Kaiser, E.; Simpson, A. J.; Dria, K. J.; Sulzberger, B.; Hatcher, P. G. Solid-state and multidimensional solution-state NMR of solid phase extracted and ultrafiltered riverine dissolved organic matter. *Environ. Sci. Technol.* **2003**, *37*, 2929–2935.
- (39) Stevenson, F. J. *Humus Chemistry. Genesis, Composition, Reactions*; John Wiley and Sons: New York, 1994; pp 303–307.
- (40) Barriuso, E.; Laird, D. A.; Koskinen, W. C.; Dowdy, R. H. Atrazine desorption from smectites. *Soil Sci. Soc. Am. J.* **1994**, *58*, 1632–1638.
- (41) Kalbitz, K.; Solinger, S.; Park, J.-H.; Michalzik, B.; Matzner, E. Controls on the dynamics of dissolved organic matter in soils: A review. *Soil Sci.* **2000**, *165*, 277–304.
- (42) Sposito, G. *The Surface Chemistry of Soils*; Oxford University Press: New York, 1984; pp 143–147.
- (43) Smith-Greenier, L. L.; Adkins, A. Degradation of dichlofop-methyl by pure cultures of bacteria isolated from Manitoban soils. *Can. J. Microbiol.* **1996**, *42*, 227–233.
- (44) Pusino, A.; Gessa, C. Catalytic hydrolysis of diclofop-methyl on Ca-, Na-, and K-montmorillonites. *Pestic. Sci.* **1990**, *30*, 211–216.
- (45) Kobayashi, M.; Shimizu, S. Versatile nitrilases: Nitrile-hydrolysing enzymes. *FEMS Microbiol. Lett.* **1994**, *120*, 217–224.
- (46) Marschner, B.; Kalbitz, K. Controls of bioavailability and biodegradability of dissolved organic matter in soils. *Geoderma* **2003**, *113*, 211–235.
- (47) Kalbitz, K.; Schmerwitz, J.; Schwesig, D.; Matzner, E. Biodegradation of soil-derived dissolved organic matter as related to its properties. *Geoderma* **2003**, *113*, 273–291.
- (48) Wershaw, R. L. Evaluation of Conceptual Models of Natural Organic Matter (Humus) from a Consideration of the Chemical and Biochemical Processes of Humification, *Scientific Investigations Report, USGS Series, Report 2004-5121*, **2004**, <http://pubs.er.usgs.gov/usgspubs/sir/sir20045121>.
- (49) Giles, C. H.; MacEwan, T. H.; Nakhwa, S. N.; Smith, D. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *J. Chem. Soc.* **1960**, *111*, 3973–3993.
- (50) Stevenson, F. J. Organic matter reactions involving herbicides in soil. *J. Environ. Qual.* **1972**, *1*, 333–339.
- (51) Theng, B. G. K. Clay polymer interactions: Summary and perspectives. *Clays Clay Miner.* **1982**, *30*, 1–10.
- (52) Pusino, A.; Micera, G.; Gessa, C. Interaction of the herbicide acifluorfen with montmorillonite: Formation of insoluble Fe^{3+} , Al^{3+} , Cu^{2+} , and Ca^{2+} complexes. *Clays Clay Miner.* **1991**, *39*, 50–53.
- (53) Pusino, A.; Weiping, L.; Fang, Z.; Gessa, C. Effect of metal-binding ability on the adsorption of acifluorfen on soil. *J. Agric. Food Chem.* **1993**, *41*, 502–505.

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