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Transformation of Plant Cuticles in Soil: Effect on their Sorptive Capabilities

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ABSTRACT

Plant cuticular materials play an important role in sorption of polar and nonpolar pollutants in soils. The objective of this study was to examine the effect of decomposition and transformation of plant cuticles on their sorption behavior with triazine herbicides and polycyclic aromatic hydrocarbons (PAHs). Sorption–desorption behavior was studied during 12 mo of incubation of cuticles isolated from tomato (*Lycopersicon esculentum* Mill.) fruits and pummelo [*Citrus maxima* (Burm.) Merr.] leaves in sandy soil. Sorption and desorption experiments and spectroscopic and chemical analyses were performed on the samples after 0, 1, 3, 6, and 12 mo of incubation. The decomposition of the cuticles (46–49% after 12 mo) did not affect the organic-C-normalized Freundlich capacity coefficient (K_FOC) for the PAHs. In addition, throughout the incubation period, the two PAHs exhibited linear and reversible sorption isotherms with both cuticles. The isotherms of the triazines were significantly affected by the decomposition of the cuticles from pummelo leaves, whereas only minor changes were recorded for the tomato cuticle samples. For the microcosm with cuticles from the pummelo leaves, the K_FOC values of the triazines increased with increasing decomposition. Preferential degradation of pectin and cutin probably facilitated the interaction between the triazines and the residual cutan and more condensed cutin moieties. Our data suggest that both cutin and cutan play important roles in the sorption of polar and highly nonpolar and aromatic compounds in soils; however, with decomposition, the more condensed structure of the cutin and mainly the cutan biopolymer govern sorption of the cuticle residues.

Sorption and desorption are the major processes influencing the fate of hydrophobic organic compounds (HOCs) in soils. Among the natural sorbents in the environment, soil organic matter (SOM) plays a significant role in the overall sorption of many organic compounds, even at very low levels (>0.1%). Not only the quantity, however, but also the nature and composition of SOM have been suggested to influence the capacity and rate of sorption and the mechanisms of interaction (Gauthier et al., 1987; Pignatello and Xing, 1996; Iglesias-Jimenez et al., 1997; Chiou et al., 1998; Kleinedman et al., 1999; Johnson et al., 2001).

Recently, several reports have emphasized the role of aliphatic-rich sorbents in the binding of HOCs (Salloum et al., 2002; Chefetz, 2003; Gunasekara et al., 2003; Gunasekara and Xing, 2003; Kang and Xing, 2005). Some sorption studies with pyrene and a set of different sorbents, among them highly aliphatic ones (bio- and synthetic polymers), concluded that the aliphatic chains in cutin and poly(acrylic acid) esters are more effective than aromatic moieties in binding PAHs (Kopinke et al., 2001; Sachleben et al., 2004). Based on the high sorption capabilities reported for natural aliphatic-rich sorbents, it is suggested that aliphatic domains of SOM and aliphatic-rich SOM precursors contribute to the overall sorption and sequestration of HOCs in soil environments.

The aliphatic-rich SOM structures have been reported to show selective preservation in soils with little or no alteration (Xing et al., 1996; Lichtfouse et al., 1998; Molse et al., 1998; Almendros et al., 2000). Therefore, aliphatic moieties of SOM tend to accumulate in soils as humification and decomposition proceed (Nierop, 1998; Hu et al., 2000; Chefetz et al., 2002b; Kögel-Knabner, 2002). These aliphatic moieties of SOM have been reported to make up a significant fraction of the humic substances (humic acid and humin) in soils and marine sediments (Augris et al., 1998; Rice, 2001; Chefetz et al., 2002a).

The main source of aliphatic compounds for SOM is biopolymers derived from above- and belowground plant cuticular matter. The plant cuticle is a thin layer of predominantly lipid material that covers all primary aerial surfaces of vascular plants. Plant cuticular material occurs in considerable amounts in both natural and agricultural areas (180 and 1500 kg ha^{-1}, respectively; Gazzola et al., 2004). The principal components of the cuticular membrane are soluble and polymerized aliphatic lipids (Jeffree, 1996). The polymeric lipids are divided into two major classes: (i) cutin—a high molecular weight, polar, cross-linked polymer, which is constructed of interesterified hydroxy-fatty acids and hydroxyepoxy-fatty acids with chain lengths of C_{16} and C_{18}; and (ii) cutan—an unsaponifiable polymethylene polymer. Since the cutin corresponds to 50 to 70% of the plant cuticle, it is the third most abundant plant biopolymer after cellulose and lignin (Jeffree, 1996).

As previously reported (Chefetz et al., 2000; Chefetz, 2003; Chen et al., 2005), cuticular materials exhibit remarkably high sorption capabilities for nonpolar and polar organic pollutants; however, the effects of decomposition and transformation of plant cuticular materials in soils on their sorptive capabilities are poorly understood. Therefore, the objective of this study was to examine the effect of decomposition of plant cuticles on the sorption–desorption behavior of polar (triazine herbicides) and nonpolar (PAHs) organic compounds. Sorption and desorption behavior was studied as a function

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Abbreviations: HOC, hydrophobic organic compound; K_d, distribution coefficient; K_F, Freundlich capacity coefficient; NMR, nuclear magnetic resonance; PAH, polycyclic aromatic hydrocarbon; SOM, soil organic matter.

of incubation time, and spectroscopic and chemical analyses were performed to follow the structural transformation of the cuticles.

MATERIALS AND METHODS

Samples and Incubation Procedure

The soil selected for the study was a sandy loam soil from Rehovot, Israel. The soil sample was collected from a depth of 0 to 30 cm. It was then air dried and passed through a 2-mm sieve. The dry composition of the soil was 93% sand, 1% silt, 6% clay, and 0.14% organic C content. Plant residues were not apparent in the sieved sample. The pH and electrical conductivity of the soil (measured in saturated paste) were 7.8 and 0.3 dS m^{-1}, respectively.

Cuticle sheets were isolated from tomato fruit and pummelo leaves. Cuticles were removed from the fresh fruits and leaves by manual peeling after boiling the plant materials in water for 60 min. Residual fruit or leaf materials still attached to the cuticle sheets were removed by further soaking the cuticles in an ammonium oxalate (16 g L^{-1}) and oxalic acid (4 g L^{-1}) solution at 90°C for 24 h. Then the materials were treated in an ultrasonic bath for 2 h, washed several times with deionized water, air dried, and finely ground (Kolattukudy, 1981; Chefetz, 2003).

The cuticles (10 g) were mixed with 200 g of soil and placed in 400-mL plastic containers. To ensure sufficient nutrient supply, N, P, and K were added to the soils at a level of 60 mg/kg each. After blending, water was added uniformly to the top of the soil–cuticle mixture. The volume of the water was adjusted so that each microcosm was maintained at a moisture level of 80% of the soils' field water capacity. The containers were incubated at 25 ± 1°C for 12 mo. During the incubation period, the moisture level was maintained constant by wetting the soil on a weekly basis according to weight loss. Sufficient microcosm sets were prepared to allow three replicates from each type of cuticle for five sampling periods. Microcosms were sampled after 0, 1, 3, 6, and 12 mo of incubation. Immediately after sampling, the samples were frozen and freeze-dried before analysis and use in the sorption experiments.

Chemical and Spectroscopic Analyses

Organic C content was measured for each sample in duplicate using an automated elemental analyzer (EA 1108, Fisons Instruments, Milan, Italy). Total organic matter content was measured in triplicate by loss of weight on ignition at 400°C for 8 h. The level of cutin in each sample was estimated by C lost during saponification (1% KOH in methanol for 3 h at 70°C). A preliminary study performed with bulk cuticles mixed with soil samples confirmed the efficiency of this treatment at removing cutin from our studied soil.

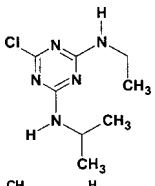
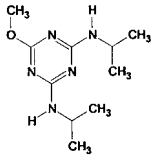
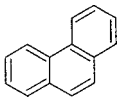
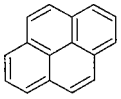
Solid-state cross-polarization magic angle spinning and total-sideband-suppression ^{13}C NMR (nuclear magnetic resonance) spectra were obtained with a Bruker DSX-300 MHz spectrometer (Karlsruhe, Germany) operated at the ^{13}C frequency of 75 MHz. The acquisition parameters were: spinning rate of 5 kHz, contact time of 1.5 ms, 1-s recycle delay, and line broadening of 10 Hz. The number of scans was 100 000. The spectra were integrated into the following chemical-shift regions: paraffinic C (0–50 ppm); alcohols, amines, carbohydrates, ethers, and methoxyl C (96–50 ppm); aromatic and phenolic C (163–96 ppm); and carboxyl, carbonyl and amide C (220–163 ppm).

Sorption–Desorption Experiments

Selected properties of the sorbates are presented in Table 1. The triazine herbicides (98.8% purity) atrazine [6-chloro-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-triazine-2,4-diamine] and prometon [6-methoxy-*N*,*N*′-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine] were kindly supplied by Agan Co. (Ashdod, Israel). Phenanthrene and pyrene were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO) and used without further purification.

All sorption isotherms were obtained using a batch-equilibration technique at 25°C in 35-mL Teflon screw-cap tubes (for the herbicides) or 100-mL Pyrex bottles (for the PAHs). Sorbate solutions were prepared by adding aliquots from concentrated methanol stock solutions to a background solution containing 5 m*M* $CaCl_2$ and 100 mg/L NaN_3 as a biocide. Methanol concentration was maintained at <0.1% (v/v) to avoid cosolvent effects. Atrazine or prometon solutions (15 mL) at initial concentrations ranging from 0.05

Table 1. Selected properties of the solutes used in the sorption experiment (Connell, 1997; Vencill, 2002).

Compound	Structure	Formula	Melting point	Boiling point	Vapor pressure	Log K_{ow}†	Aqueous solubility
			°C		kPa		Mg L^{-1}
Atrazine		$C_8H_{14}ClN_5$	173	200	4.0×10^{-8}	2.70	33
Prometon		$C_{10}H_{19}N_5O$	91.5	125	3.0×10^{-7}	2.99	750
Phenanthrene		$C_{14}H_{10}$	99.2	340	2.6×10^{-5}	4.46	1.15
Pyrene		$C_{16}H_{10}$	151.2	404	8.9×10^{-7}	5.12	0.135

† Octanol–water partition constant.

to 10 mg L^{-1} were added to the soil samples previously weighed into the tubes. The sorbent mass (2 g) was selected to achieve 40 to 70% sorption. The tubes were agitated in the dark at 200 rpm. Preliminary tests indicated apparent equilibrium of atrazine and prometon after 6 and 3 d, respectively. After the desired equilibration time, the tubes were centrifuged (6000 × *g*, 15 min) and 5 mL of the supernatant was removed and replaced with fresh background solution (sorbate free) to perform the desorption step. The tubes were then agitated under similar conditions to obtain a desorption isotherm. A 1-mL aliquot of the removed supernatants (after sorption and desorption steps) was filtered (0.45 μm) and transferred to 1.5-mL vials for HPLC (high-performance liquid chromatography) analysis. For the PAHs, solutions (100 mL) at initial concentrations ranging from 1.5 to 500 μg L^{-1} for phenanthrene and 0.8 to 80 μg L^{-1} for pyrene were added to the microcosm samples previously weighed into the Pyrex bottles. The sorbent mass (125 and 50 mg for phenanthrene and pyrene, respectively) was selected to achieve 40 to 80% sorption. The bottles were agitated in the dark at 200 rpm for 6 d (equilibrium was tested in preliminary experiments). Then, 50 mL of the supernatant was removed and replaced with fresh background solution (sorbate free) to perform the desorption step. The bottles were then agitated under similar conditions to obtain the desorption isotherm. A 0.5-mL aliquot of the collected supernatants (after sorption and desorption steps) was diluted (1:1, v/v) with methanol in 1.5-mL amber HPLC vials. The methanol was added to prevent PAH sorption to the vials.

Quantitative HPLC analyses of the samples were performed using an L-7100 LaChrom HPLC (Merck-Hitachi, Darmstadt, Germany) with a LiChrospher RP-18 column (25 cm by 4 mm, 5 μm). The compounds were eluted using isocratic conditions of 25:75 and 30:70 water/acetonitrile for atrazine and prometon, respectively, and 15:85 for the PAHs. The flow rate was 1.5 and 1 mL/min for the triazines and PAHs, respectively. The triazines were detected by absorbance at 222 nm and the PAHs were detected with a fluorescence detector using 244 and 360 nm for phenanthrene and 345 and 460 nm for pyrene as excitation and emission wavelengths, respectively. All solutes were quantified using external standards prepared in a background solution. Because of negligible sorption to the vials, minimal headspace, and no biodegradation, sorption was calculated by mass differences.

Data Analysis

All sorption data were fitted to the logarithmic form of the Freundlich equation, $q = K_F C_e^N$, where q is the solid-phase concentration (mg kg^{-1}) and C_e is the liquid-phase equilibrium concentration (mg L^{-1}). The parameters K_F, Freundlich sorption capacity coefficient [(mg kg^{-1})/(mg $L^{-1})^N$] and N (isotherm nonlinearity) were determined by linear regression of log-transformed data. The K_F data were normalized to the organic C level of each sorbent to obtain the K_FOC values. Single-point distribution coefficients (K_d) were calculated at reduced concentrations of $C_e/S_w = 0.01$ and 0.2 (S_w is the aqueous solubility). Statistical analysis (All Pairs, Tukey–Kramer, $P = 0.05$) was performed by JMP software (SAS Institute, 2001).

RESULTS AND DISCUSSION

Transformation of Cuticles in Microcosms

Incubation experiments were performed to reveal the effect of degradation and transformation of plant cuticular matter on its ability to sorb HOCs in soils. In both systems (microcosms of tomato and pummelo cuticles), the total SOM content exhibited a sharp decrease during the incubation time, suggesting rapid decomposition of the plant cuticular matter (Fig. 1). The level of SOM decreased by 15 to 20% during the first 3 mo of incubation. During the next 3 mo, the SOM level continued to decline but at a slower rate (10%); a faster rate of degradation was exhibited during the last stage of the experiment. In general, 46 to 49% of the added cuticular matter was mineralized during the incubation period. Although the decomposition of the bulk SOM exhibited a similar profile for the two cuticles, the level of cutin (estimated as the saponifiable organic matter) in the two systems differed. The cutin made up 62, 62, 55, 35, and 37%, and 51, 60, 48, 39, and 26% of the total SOM at 0, 1, 3, 6, and 12 mo of incubation in soil incubated with tomato and pummelo cuticle, respectively. The relative increase of the cutin fraction of the pummelo leaves at the beginning of the incubation (from 51 to 60% of SOM) suggests that this fraction was more resistant to degradation than the cutin in the tomato cuticle. This can be related to the different compositions of the raw cuticles: cutin makes up 46% (by weight) of the pummelo cuticle and 72% of the tomato cuticle. Moreover, the pummelo cuticle contains (7% by weight) the polyethylene-like cutan biopolymer, whereas the tomato cuticle is cutan free. The presence of cutan in the pummelo cuticle probably hindered cutin degradation.

Carbon-13 NMR analysis was performed to profile the organic components of the cuticles during the course of their incubation in soil. The major peaks exhibited in the ^{13}C NMR spectra of the raw cuticles and samples representing five stages in the incubation process (0, 1, 3, 6, and 12 mo; Fig. 2) were at: 25 to 29 and 31 ppm assigned to amorphous and condensed alkyl chain structures, respectively (Hu et al., 2000), 64, 72, and 105 ppm (alkyl-O C), and 172 ppm (carboxyl C) (Chefetz et al., 2000). The relative level of alkyl C in the tomato cuticle microcosm increased from 60 to 73% during the first month of incubation. From this stage, the level of alkyl C decreased to 45% of the total C, and the level of carboxylic function-

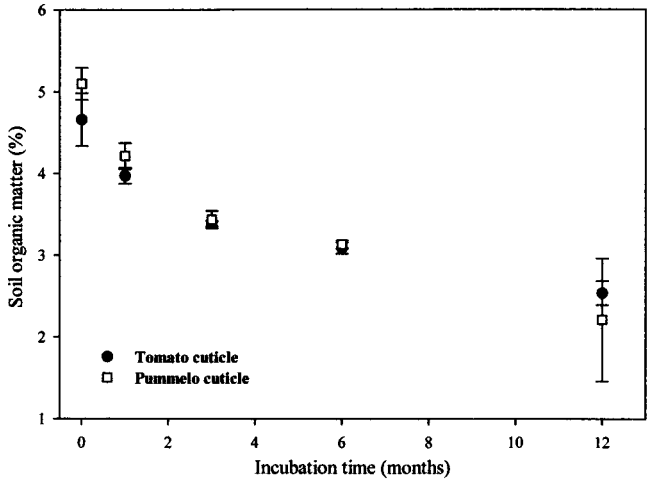


Fig. 1. Soil organic matter content during incubation of tomato and pummelo cuticles in soil.

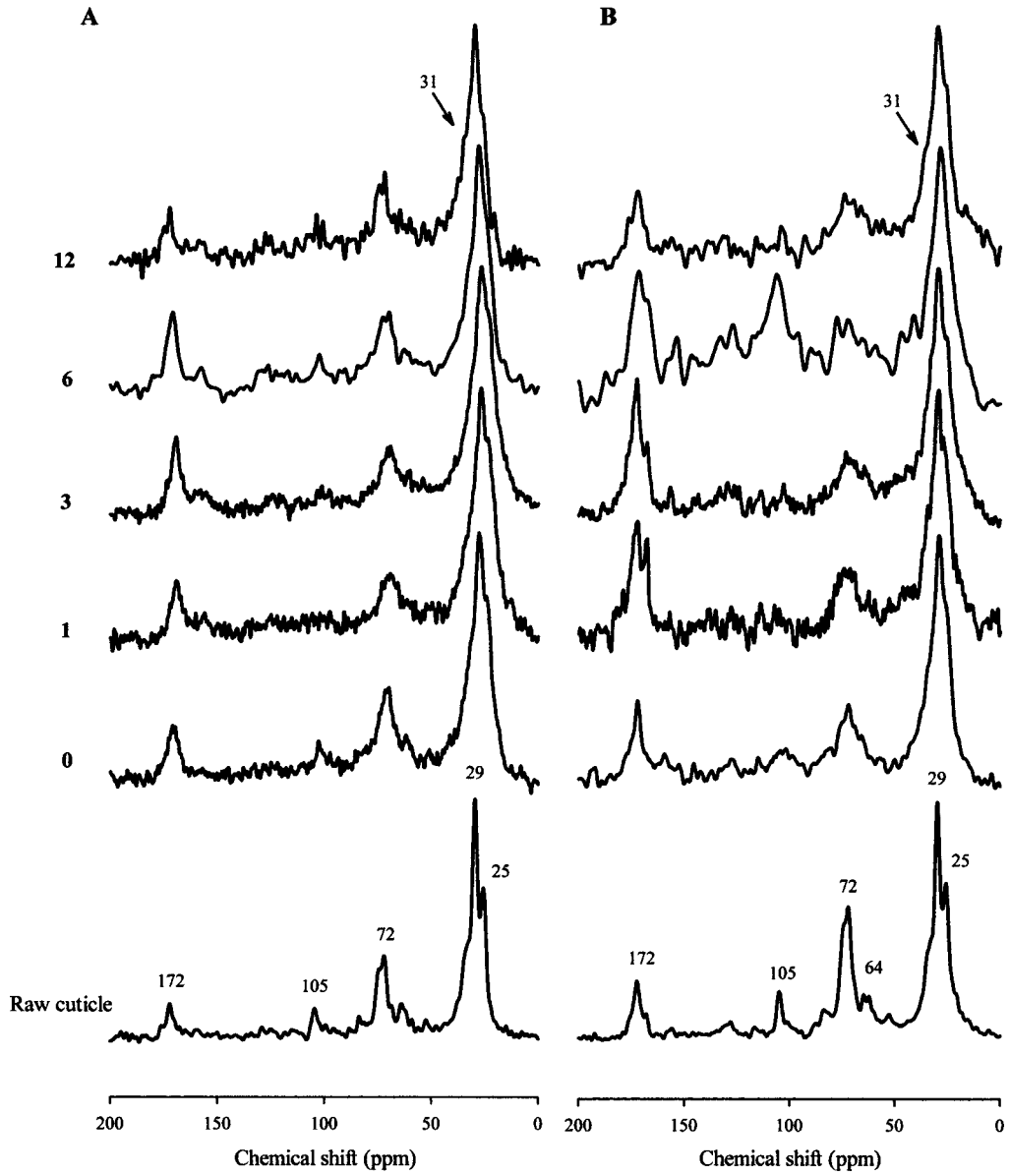


Fig. 2. Carbon-13 NMR (nuclear magnetic resonance) spectra of (A) raw tomato and (B) pummelo cuticles and soil samples after 0, 1, 3, 6, and 12 mo of incubation.

alities increased. In contrast, the ^{13}C NMR spectra of the pummelo-cuticle-amended soil exhibited a stable level of alkyl C (52–56%) during the first 3 mo of incubation, which decreased slightly thereafter to 49% of the total C. These data support those obtained from the saponification analyses suggesting that, at early stages of incubation, the cutin structures originating from the pummelo cuticle are more resistant to degradation than the cutin moieties in the tomato cuticle. The relative decrease of the O-alkyl functionalities was monitored using the ratio of alkyl to O-alkyl. In both microcosms, this ratio increased during the first 3 mo, from 2.1 to 3.4 and 1.8 to 2.8 for tomato and pummelo cuticles, respectively. From this stage, this ratio decreased to 1.4 in the tomato microcosm, whereas only a moderate decrease (to 2.2) was recorded in the pummelo-amended soil. The initial decrease in the carbohydrate content is suggested to result from microbial use of the pectin present in the bulk cuticles. At a later stage of the incubation, the relative decrease of the alkyl-C/alkyl-O ratio is suggested to result from newly formed polysaccharides originating from microbial activity (Nierop, 2001; Rovira and Vallejo, 2002).

Our data (total SOM level, saponifiable organic matter, and ^{13}C NMR spectra) suggest that polysaccharides (pectin) were rapidly degraded in both soils. This process provided a loose cuticular structure, facilitating cutin decomposition. Cutin degradation was similar in rate to observations presented by De Vries et al. (1967). We suggest that the differential decomposition of the cutin in the two studied systems could have resulted from different degrees of estherification and density of the cutin polymers, and the presence of unsaponifiable polymer (cutan). The latter unhydrolyzable and unsaponifiable biopolymer makes up 7% of

the pummelo cuticle, whereas tomato cuticle is cutan free. Due to its more condensed structure, cutan is considered to be more resistant to microbial degradation, therefore its relative level in the pummelo microcosm samples is expected to increase with time. In addition, Mösle et al. (1998) suggested that incorporation of cutin monomers via ether bond could engender cutin monomers resistant to degradation. In our study, the transformation and degradation processes of the cutin resulted in the relative enrichment of the more condensed structures of the cutin and cutan in the residual nondecomposable organic matter. This hypothesis is supported by the presence of a shoulder at 31 ppm in the ^{13}C NMR spectra of the samples taken after 12 mo of incubation (Fig. 2). This peak is assigned to condensed and rigid paraffinic domains (Hu et al., 2000; Sachleben et al., 2004).

Sorption

The properties and composition of SOM have been suggested to influence the sorption behavior of HOCs and pesticides (Gauthier et al., 1987; Chiou et al., 1998; Cox et al., 2000; Johnson et al., 2001). Therefore, in this study we investigated the effects of degradation of cuticles in microcosms on their sorption behavior with environmentally important pollutants—triazine herbicides and PAHs. The distribution coefficient (K_d) and Freundlich capacity coefficient (K_F) values of atrazine for the tomato cuticle microcosm samples decreased significantly (50 and 42%, respectively) with incubation time (Table 2; sorption isotherms are presented in Fig. 3). We suggest that the observed decrease in sorption coefficients is related to the decrease in organic matter content during incubation (Fig. 1); however, the calculated K_FOC values were stable. This suggests that the sorptive capability of the tomato cuticle was not affected by the removal of pectin and the partial degradation of cutin. Similar results have been reported by Sluszny et al. (1998), who found that incubation of soils in the presence or absence of organic matter amendments did not affect the organic-C-normalized K_d values.

The opposite trend was exhibited by the pummelo cuticle microcosm samples. With this sorbent, the atrazine K_d values were stable throughout the experiment, although the SOM content decreased by almost 50%. Therefore, the calculated K_FOC values increased significantly during incubation (from 580 to 920). This suggests that the degradation of pectin and cutin and the consequent relative enrichment of the remaining organic matter with the condensed cutin fraction and cutan biopolymer result in residual organic matter with a higher sorption capability for atrazine.

Trends observed for prometon during incubation were generally similar to those observed for atrazine (Table 2). In the tomato cuticle microcosm, the K_d values decreased following a pattern similar to that exhibited for the degradation of the total SOM, whereas the K_FOC values were slightly increased during incubation. In contrast, a significant increase of 38% in the K_FOC value of prometon was observed in the pummelo microcosm samples between 6 and 12 mo of incubation. This increase was correlated with the intensive cutin decomposition that occurred during this stage. These data are supported by our previous observation (Chefetz, 2003) with cuticular matter from green pepper (*Capsicum annuum* L. var. *annuum*), showing a remarkably high sorption affinity of atrazine to the cutan residue after chemical removal of cutin and pectin. We therefore suggest that microbial processes occurring in the pummelo microcosm revealed

Table 2. Atrazine and prometon sorption and desorption parameters (± standard error).

Microcosm and incubation time	K_d†	K_d‡	Sorption			Desorption		
			Log K_F§	K_FOC¶	N	Log K_F	K_FOC	N
	L kg^{-1}							
Atrazine								
Tomato cuticle								
1 mo	4.60	4.60	0.64 ± 0.02	160	1.02 ± 0.04	0.65 ± 0.03	160	0.91 ± 0.04
3 mo	3.80	3.60	0.57 ± 0.01	170	0.98 ± 0.02	0.59 ± 0.03	170	0.90 ± 0.04
6 mo	3.00	2.90	0.47 ± 0.02	170	1.00 ± 0.01	0.48 ± 0.01	170	0.91 ± 0.02
12 mo	2.40	2.30	0.38 ± 0.02	170	0.99 ± 0.04	0.40 ± 0.03	180	0.85 ± 0.06
Pummelo cuticle								
1 mo	12.10	12.40	1.11 ± 0.01	580	0.97 ± 0.02	1.35 ± 0.02	990	0.98 ± 0.03
3 mo	13.40	12.20	1.09 ± 0.01	670	1.00 ± 0.02	1.34 ± 0.01	1240	0.99 ± 0.02
6 mo	12.50	11.40	1.08 ± 0.01	690	0.97 ± 0.02	1.34 ± 0.01	1180	0.96 ± 0.02
12 mo	11.30	12.00	1.06 ± 0.01	920	1.02 ± 0.03	1.31 ± 0.03	1630	0.90 ± 0.04
Prometon								
Tomato cuticle								
1 mo	5.50	5.00	0.58 ± 0.02	140	0.81 ± 0.03	0.69 ± 0.03	220	0.82 ± 0.03
3 mo	3.70	4.10	0.46 ± 0.03	130	0.83 ± 0.02	0.42 ± 0.08	260	0.86 ± 0.05
6 mo	4.00	4.20	0.49 ± 0.03	180	0.82 ± 0.03	0.70 ± 0.03	320	0.89 ± 0.03
12 mo	3.40	3.00	0.35 ± 0.02	160	0.80 ± 0.02	0.65 ± 0.04	300	0.89 ± 0.04
Pummelo cuticle								
1 mo	4.40	6.40	0.65 ± 0.03	200	0.77 ± 0.03	0.67 ± 0.05	210	0.84 ± 0.05
3 mo	4.20	5.80	0.60 ± 0.04	220	0.77 ± 0.04	0.60 ± 0.07	230	0.83 ± 0.07
6 mo	4.00	5.40	0.57 ± 0.04	210	0.77 ± 0.05	0.61 ± 0.04	220	0.81 ± 0.05
12 mo	3.20	5.50	0.56 ± 0.04	290	0.73 ± 0.04	0.60 ± 0.05	320	0.82 ± 0.04

† Distribution coefficient at $C_e/C_w = 0.01$, where C_e and S_w are the aqueous solubility and equilibrium concentration, respectively.
‡ Distribution coefficient at $C_e/C_w = 0.2$.
§ Freundlich capacity coefficient.
¶ Organic-C-normalized K_F.

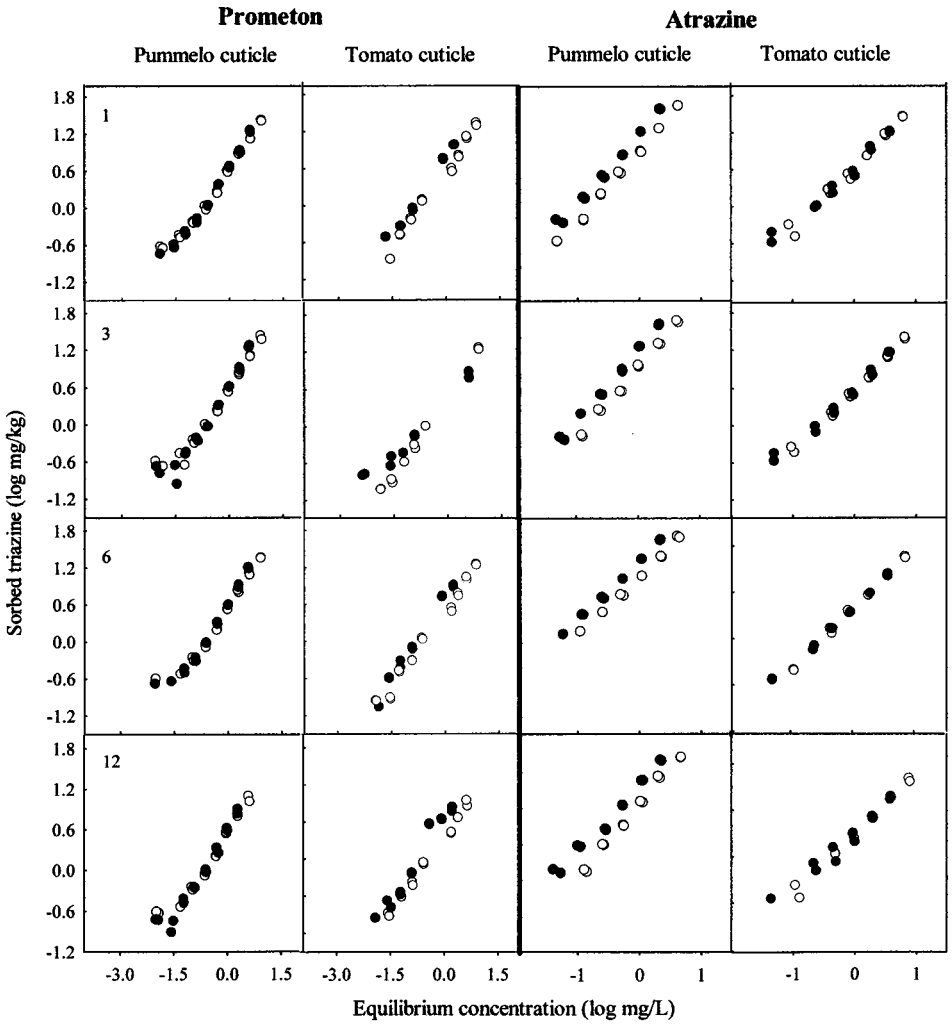


Fig. 3. Sorption–desorption isotherms of prometon and atrazine by soil samples during incubation (open symbols, sorption data; filled symbols, desorption data).

the cutan biopolymer, resulting in the higher sorption capacity of the residual SOM.

It is interesting to note that for atrazine, all sorption isotherms were linear (*N* values of 0.97–1.02) but prometon sorption isotherms exhibited nonlinear behavior (0.73–0.83, Table 2). These differences are probably related to the chemical properties of the two sorbates. Atrazine belongs to the Cl triazine group and prometon is a methoxy triazine. The substituents affect the basicity of the N atoms and the acidity of the N–H bonds of the molecule (pK_a values of 1.7 and 4.3 for atrazine and prometon, respectively), as well as the consequent modes of interaction with the sorbent (Chefetz et al., 2004). This can result in different binding sites for the two solutes, as has previously been reported for different triazines (Xing et al., 1996; Sluszny et al., 1998). The stable *N* values recorded during the incubation suggest that degradation did not significantly affect the heterogeneity of the binding sites of the two triazines.

The sorption isotherms for the PAHs are presented in Fig. 4 and the calculated Freundlich sorption parameters are presented in Table 3. Unlike the triazines, PAHs have no active functional groups to form H-bonding interactions with natural sorbents; however, they can form π–π interactions with aromatic moieties of the sorbent (Pignatello and Xing, 1996). Therefore, in our experiments using sorbents rich in paraffinic moieties (i.e., aromatic-poor sorbents), phenanthrene and pyrene were expected to interact mainly via nonspecific hydrophobic-like interactions with the cuticle residues. In our study, these partition interactions yielded, in most cases, linear sorption isotherms exhibiting *N* values close to unity for both solutes. During the first 3 mo of incubation, phenanthrene exhibited a sharp increase in K_FOC values (from 41 000 to 57 000 and from 45 000 to 66 000 in the tomato and pummelo microcosms, respectively). From this stage, the phenanthrene K_FOC values decreased (in the pummelo cuticle microcosm) or remained stable (in the tomato cuticle microcosm). The phenanthrene K_FOC values obtained for the incubated cuticles were higher than those reported for humic substances, sediments, or soils (Huang and Weber, 1997; Chiou et al., 1998), but were in the range of values reported for the cuticular fraction isolated from pepper fruits (Chefetz, 2003; Chen et al., 2005). For pyrene, a sharp decrease in the K_d and K_FOC values was observed

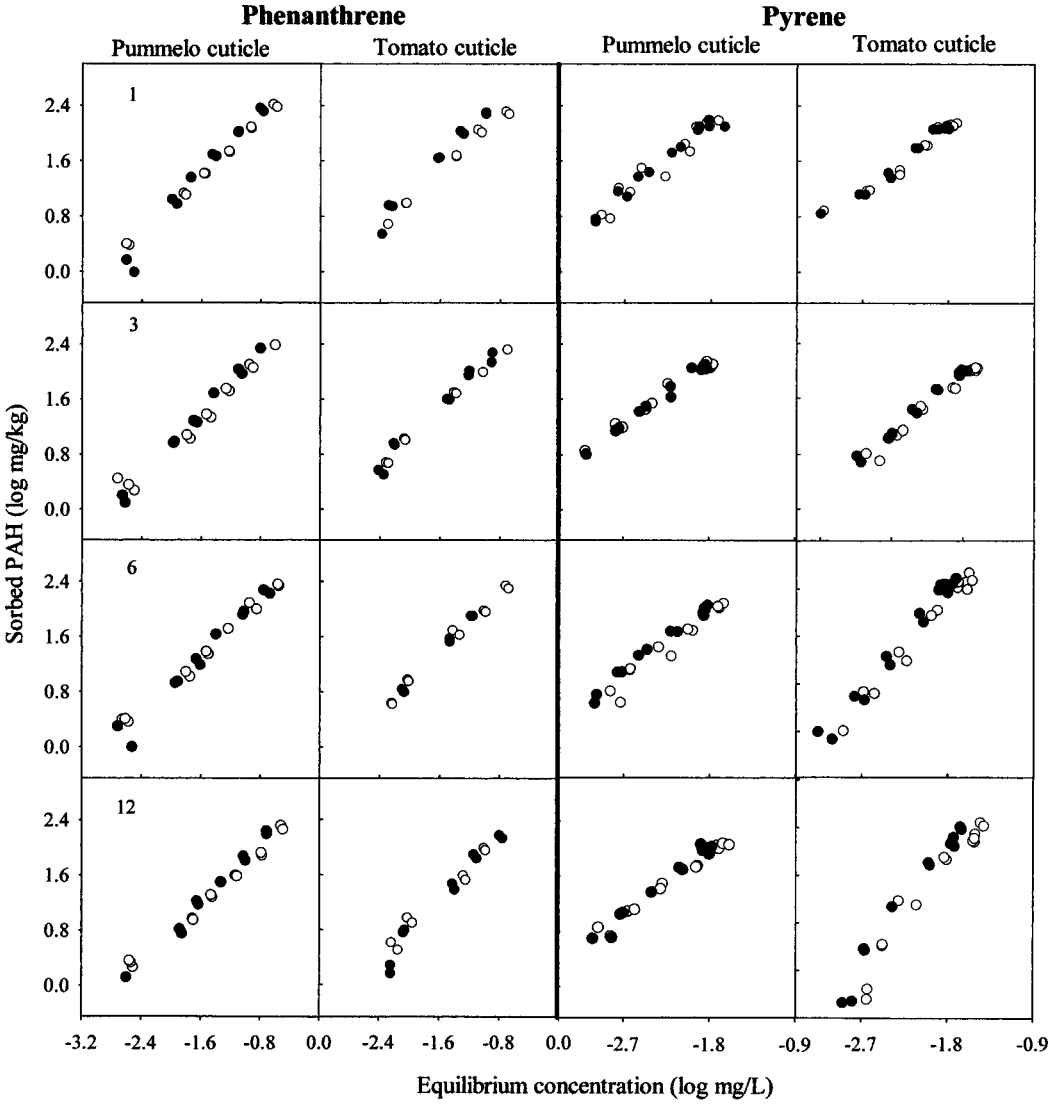


Fig. 4. Sorption–desorption isotherms of phenanthrene and pyrene by soil samples during incubation (open symbols, sorption data; filled symbols, desorption data).

during the first 3 mo of incubation, reaching a steady value thereafter. The increase in the sorption affinity of phenanthrene in both systems was correlated to the intensive degradation of the cuticular polysaccharide fraction. This process increased the hydrophobicity of the sorbents (cuticle residues). Similar observations were recorded by Salloum et al. (2002), who demonstrated increasing hydrophobic interactions of phenanthrene with decreasing content of the polar carbohydrate fraction. The smaller changes in sorption affinities observed for pyrene probably resulted from its higher hydrophobicity relative to phenanthrene. Therefore, its extremely strong tendency to sorption was not significantly affected by the structural changes of the cuticles during the incubation.

Desorption

Desorption isotherms for the triazine herbicides and the PAHs are presented in Fig. 3 and 4, and desorption parameters are presented in Tables 2 and 3, respectively. Pronounced desorption hysteresis was observed for atrazine with the pummelo cuticle microcosm samples. In all samples, the desorption K_FOC values were significantly higher than the sorption K_FOC values. Moreover, as pummelo cuticle degradation proceeded, the desorption hysteresis was more pronounced, especially at low solute concentration. In contrast, atrazine did not exhibit desorption hysteresis with the samples from the tomato cuticle microcosm. The desorption hysteresis behavior of triazine herbicides (mainly atrazine) has been observed in several studies (Lesan and Bhandari, 2003; Drori et al., 2005). Similar to other reports, the desorption of atrazine with the pummelo cuticle microcosm samples increased from low to high solution concentrations (atrazine was readily released at high sorbed-phase concentration), indicating an increase in sorption–desorption hysteresis with lower concentrations. Gunasekara and Xing (2003) have suggested that a limited number of high-energy sorption sites are available and most of them are occupied at low solute concentration. At high solute concentration, more molecules are taken

Table 3. Phenanthrene and pyrene sorption and desorption parameters (± standard error).

Microcosm and incubation time	K_d†	K_d‡	Sorption		Desorption	
			Log K_FOC§	N¶	Log K_FOC	N
	L kg^{-1}					
Phenanthrene						
Tomato cuticle						
1 mo	1130	1120	4.6 ± 0.18	1.00 ± 0.04	5.0 ± 0.11	1.15 ± 0.06
3 mo	1270	1240	4.8 ± 0.19	1.02 ± 0.09	4.9 ± 0.10	1.08 ± 0.06
6 mo	1100	1070	4.8 ± 0.12	1.06 ± 0.61	5.0 ± 0.29	1.16 ± 0.18
12 mo	900	840	4.8 ± 0.19	1.06 ± 0.10	5.1 ± 0.13	1.24 ± 0.08
Pummelo cuticle						
1 mo	1010	990	4.7 ± 0.03	1.02 ± 0.16	5.7 ± 0.11	1.26 ± 0.06
3 mo	930	900	4.8 ± 0.09	1.01 ± 0.05	5.6 ± 0.06	1.19 ± 0.03
6 mo	820	790	4.6 ± 0.05	0.96 ± 0.31	5.8 ± 0.10	1.10 ± 0.62
12 mo	610	530	4.6 ± 0.05	0.95 ± 0.03	5.9 ± 0.13	1.14 ± 0.08
Pyrene						
Tomato cuticle						
1 mo	13070	14460	5.9 ± 0.23	1.20 ± 0.10	5.7 ± 0.01	1.16 ± 0.05
3 mo	8820	6700	5.4 ± 0.09	0.92 ± 0.04	5.6 ± 0.08	1.01 ± 0.03
6 mo	6270	5160	5.9 ± 0.23	1.01 ± 0.04	5.8 ± 0.10	1.08 ± 0.04
12 mo	6060	4630	5.5 ± 0.10	0.97 ± 0.04	5.9 ± 0.20	1.10 ± 0.05
Pummelo cuticle						
1 mo	8500	7760	5.6 ± 0.12	1.1 ± 0.15	5.6 ± 0.11	1.02 ± 0.05
3 mo	5920	3880	5.3 ± 0.10	0.93 ± 0.05	5.5 ± 0.07	0.98 ± 0.03
6 mo	3480	3720	5.3 ± 0.07	1.01 ± 0.04	5.5 ± 0.09	0.99 ± 0.04
12 mo	3400	3270	5.5 ± 0.14	1.05 ± 0.07	5.8 ± 0.13	1.12 ± 0.06

† Distribution coefficient at $C_e/C_w = 0.01$, where C_e and S_w are the aqueous solubility and equilibrium concentration, respectively.
‡ Distribution coefficient at $C_e/C_w = 0.2$.
§ Organic-C-normalized Freundlich capacity coefficient.
¶ Isotherm nonlinearity.

up by low-energy binding sites and therefore can readily desorb. In our study, the removal of pectin and the partial degradation of the cutin in the pummelo cuticle system resulted in more sites available for stronger sorbate–sorbent interactions. These sites are probably located in the more condensed cutin and cutan-like residues, which are rich in the O moieties that are favored for H-bonding with the triazines.

With prometon, the opposite trend was observed. Desorption hysteresis was more obvious with the samples from the tomato cuticle microcosms, whereas the samples from the pummelo cuticle microcosms did not exhibit any desorption hysteresis (Fig. 3). The pronounced hysteresis observed for atrazine vs. prometon in the pummelo system is suggestive to the ability of Cl triazines to form stronger H-bonding with carboxylic moieties than other classes of less acid triazines, such as ametryn [*N*-ethyl-*N*′-(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine] and prometon (Chefetz et al., 2004). This probably suggests that prometon interacts with the cuticular matter mainly via hydrophobic interactions.

Unlike the triazine herbicides, none of the PAHs exhibited desorption hysteresis in any of the samples (Fig. 4). These data suggest that partitioning is the main sorption mechanism for PAHs with cuticular matter and that flexible hydrophobic domains are the major sorptive sites for PAHs in the cuticular matter (Sachleben et al., 2004). Sorption to the rubbery domains of SOM, and in our study the rubbery moieties of cuticular matter, is supported by the presence of a dominant amorphous paraffinic domain (29 ppm peak in the ^{13}C NMR spectra; Fig. 2). This type of paraffinic domain facilitates linear, noncompetitive, and fully reversible sorption.

CONCLUSIONS

This study examined the effect of the decomposition and transformation of plant cuticular matter on the sorption–desorption behavior of triazine herbicides and PAHs. The rapid decomposition of the cuticular materials during incubation had only a minor effect on the sorption–desorption behavior of the PAHs. These sorbates interacted with the decomposing cuticular matter mainly via a partition-like mechanism. On the other hand, the sorption affinity and desorption hysteresis of the triazines were influenced by the degradation of the cuticles. The preferential degradation of pectin and cutin probably facilitated the triazines' interaction with the residual cutan and the more condensed moieties of the residual cutin. Therefore, sorption affinity and desorption hysteresis increased as decomposition proceeded. Our data suggest that both cutin and cutan play important roles in the sorption of HOCs in soils; however, with decomposition (or humification), the more condensed structure of the cutin and mainly the cutan biopolymer dominated sorption to the cuticle residues.

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