Plant Soil (2007) 298:21–30
DOI 10.1007/s11104-007-9318-1

REGULAR ARTICLE

Decomposition and sorption characterization of plant cuticles in soil

Benny Chefetz

Received: 17 January 2007 / Accepted: 30 May 2007 / Published online: 4 August 2007

Abstract The sorption of organic compounds by plant cuticular matter has been extensively investigated; however, little has been studied regarding the effect of plant cuticle degradation on their role in the sorption of organic compounds in soils. The sorption of phenanthrene was studied in soil samples which had been incubated for up to 9 months with three different types of plant cuticle isolated from tomato fruits, pepper fruits and citrus leaves. The main change in the diffuse reflectance Fourier-transform infrared (DRIFT) spectra during incubation of the cuticles was related to cutin decomposition. The peaks assigned to methyl and ethyl vibration and C=O vibration in ester links decreased with decomposition. In general, with all samples, the phenanthrene sorption coefficients calculated for the whole incubated soils (K_d) decreased with incubation time. In contrast, the carbon-normalized K_d values (K_{oc}) did not exhibit a similar trend for the different cuticles during incubation. The origin of the cuticle also affected the linearity of the sorption isotherms. With the tomato and citrus cuticle samples, the Freundlich *N* values were close to unity and were stable throughout incubation. However with the green pepper cuticle, the *N* values exhibited a significant decrease (from 0.98 to 0.70). This study demonstrates that the structural composition of the plant cuticle affects its biodegradability and therefore its ability to sorb organic compounds in soils. Of the residues originating from plant cuticular matter in soils, the cutan biopolymer and lignin-derived structures appear to play a dominant role in sorption as decomposition progresses.

Keywords Cutan · Cutin · Decomposition · Plant cuticle · Sorption

Abbreviations

DRIFT	diffuse reflectance infrared Fourier transform
HOC	hydrophobic organic compound
K_d	whole soil sorption coefficient
K_F	Freundlich sorption capacity coefficient
K_{oc}	carbon-normalized sorption coefficient
K_{om}	organic matter-normalized sorption coefficient
SOM	soil organic matter

Introduction

The primary source for organic matter in soils is above- and below-ground plant residues. With decomposition, the plant residues are transformed via chemical, biological and physical processes into humus. During these processes, some characteristic signals of structurally identifiable plant materials, such as polysaccharides and proteins, are lost, whereas signals from refractory

Responsible Editor: Alfonso Escudero.

B. Chefetz (✉)
Department of Soil and Water Sciences,
The Hebrew University of Jerusalem,
P.O. Box 12, Rehovot 76100, Israel
e-mail: chefetz@agri.huji.ac.il

compounds, such as aromatic and alkyl structures, are enhanced (Baldock et al. 1997; Kögel-Knabner 1997; Stevenson 1994; Zech et al. 1997). Leaf litter contains various biopolymers, among them cellulose, hemicellulose, pectin, lignin, proteins and cutin. Cutin is the major structural component (30–70%) of the plant cuticle, a thin layer of predominantly lipid material that covers all primary aerial surfaces of vascular plants. The cuticle is synthesized by the epidermal cells and deposited on the outer walls of leaves and fruits to protect and waterproof the plant surface (Riederer 2006). The major structural model of the plant cuticle is a bilayer membrane. The outer region is composed mainly of aliphatic lipids while the inner layer contains large amounts of various cell-wall polysaccharides (mainly pectin). The cutin is a high molecular weight, relatively polar and cross-linked biopolymer, which is constructed of inter-esterified hydroxy-fatty acids and hydroxyepoxy-fatty acids with chain lengths of C_{16} and C_{18} (Holloway 1982; Jeffree 1996, 2006; Stark and Tian 2006). In the cuticle of some plant species (such as *Agave americana*), the cutin biopolymer is associated with the cutan biopolymer. This latter biopolymer is non-saponifiable and non-hydrolyzable and has been found in fossilized cuticles (Gupta et al. 2006). The cutan biopolymer is constructed from long-chain alcohols and *n*-alkanes linked to the aromatic backbone (McKinney et al. 1996; Villena et al. 1999).

Several studies have reported that aliphatic-rich biopolymers are selectively preserved in soils and sediments with little or no alteration (Almendros et al. 1996; Lichtfouse et al. 1997, 1998; Molse et al. 1998). In addition, many studies (Kögel-Knabner 1997; Kögel-Knabner et al. 1992; Zech et al. 1997) have provided evidence for the predominantly aliphatic nature of natural soil organic matter (SOM). It has been suggested that aliphatic-rich precursors of SOM are relatively resistant to microbial degradation and therefore tend to accumulate in soils with humification (Nierop 1998). These materials are incorporated into humus in soil and become an integral part of the soils' humic acid macromolecules (Chefetz et al. 2002a, b). Therefore, aliphatic structures make up a significant fraction of the humic substances (humic acid and humin) in soils (Hu et al. 2000; Rice 2001; Zech et al. 1997).

In addition to the importance of plant cuticular matter as possible precursors for SOM, these and other natural aliphatic-rich materials have been recently reported as highly efficient natural sorbents for hydrophobic and polar organic compounds (Boyd et al. 1990; Chefetz 2003; Chefetz et al. 2000; Chen et al. 2005; Gunasekara et al. 2003; Gunasekara and Xing 2003; Kang and Xing 2005; Salloum et al. 2002; Shechter et al. 2006; Stimler et al. 2006). In most cases, sorption of hydrophobic organic compounds (HOCs) by these sorbents, including plant cuticular materials, is in the same range or even higher than the sorption affinity values reported for aromatic-rich natural sorbents. Nevertheless, the role of these aliphatic-rich materials as natural sorbents in soils and sediments has been generally ignored in the past due to the frequently stated assumption that binding of hydrophobic and aromatic organic pollutants is predominantly ruled by the level of aromatic domains in the sorbents (Chin et al. 1997; Chiou et al. 1998; Huang and Weber 1997; Johnson et al. 2001; Xing 1997).

Cuticular materials are relatively biologically and chemically stable in soils and therefore may contribute significantly to SOM, particularly where leaf litter is a significant source (e.g., in forest soils) and in arable soils where crop materials are plowed into the soil on an annual basis. Based on their high sorption capabilities, these materials are expected to contribute significantly to the overall sorption processes of HOCs in soil. However, very little is known about the effects of decomposition and transformation of plant cuticular matter in soils on their sorption capabilities for HOCs. The objective of this study was to elucidate the effects of decomposition of three plant cuticles on their ability to bind phenanthrene.

Materials and methods

Isolation of cuticles

Cuticles were isolated from fruits of green pepper (*Capsicum annuum*, Farm 107) and tomato (*Lycopersicon esculentum* Mill.) and leaves of sweet orange (*Citrus sinensis*). Freshly picked leaves and fruits were washed several times in deionized water and then boiled in water for 60 min, after which the cuticle sheets were manually peeled. These sheets were further treated in ammonium oxalate (16 g/l) and oxalic acid (4 g/l) solution at 90°C for 24 h to remove residual fruit and leaf materials (Chefetz 2003; Kögel-Knabner et al. 1994). This treatment was followed by sonication in an ultrasonic bath for 2 h. The isolated cuticles were washed in deionized water to remove excess of ammonium oxalate and oxalic acid and allowed to dry at room temperature. The dried cuticles were finely ground (<0.1 mm) before use in the incubation experiment.

Incubation

About 1.5 g of the isolated cuticle sheets were mixed with 50 g of sandy soil in 125-ml containers. The soil-cuticle mixtures and a control soil (bulk soil without cuticle) were incubated at 25±1°C for 9 months. During this period, the moisture level of the soil was maintained at 85% of its field water capacity by wetting the soil according to weight loss. Sufficient sets of samples were prepared to allow three replicates from each type of cuticle-soil mixture and the control soil for five sampling periods (0, 1, 3, 6 and 9 months of incubation). Immediately after sampling, all samples were frozen and freeze-dried. The dry composition of the soil was sand, 93%; silt, 1%; clay, 6%, and organic carbon content, 0.17%.

Elemental and spectroscopic analyses

Elemental (C, H, N) composition and SOM content were determined for all samples over the course of the incubation. Total SOM content was measured by loss of weight on ignition at 400°C for 8 h and elemental analysis was conducted in triplicate using an automated elemental analyzer (EA 1108, Fisons Instruments, Milan, Italy). The diffuse reflectance infrared Fourier transform (DRIFT) spectra of the soil samples during incubation were obtained for a wavenumber range of 4,000 to 400 cm^{-1} in a Nicolet 550 Magna-IR™ spectrometer (Nicolet Instruments Corporation, Madison, WI). Dried soil samples (50 mg) were mixed with KBr (IR-grade) for a total sample weight of 300 mg. The samples were transferred to a macro-sample holder and smoothed with a glass slide. To obtain DRIFT spectra, 400 scans were collected. Spectra were compared after a linear baseline correction at 4,000, 2,000, 860 and 400 cm^{-1} as zero absorbance points. To monitor the changes in the organic matter (i.e. cuticular matter) of the samples during incubation, the spectrum of the organic matter was obtained by subtracting the control soil spectrum from the corresponding soil spectrum. The control soil spectrum was obtained for the soil used in the incubation experiment without input of cuticular matter. Using this technique, we were able to reduce the signals originating from the soil's minerals and organic matter and to enhance signals related to the added cuticular matter (Chefetz et al. 1996).

Batch sorption–desorption experiments

All sorption isotherms were obtained using a batch-equilibration technique at 25°C in 30-ml glass tubes. Phenanthrene solutions were prepared by adding aliquots from concentrated methanol stock solutions to a background solution containing 5 mM $CaCl_2$ and 200 mg/l NaN_3 as a biocide. Methanol concentration was maintained at less than 0.1% (*v*/*v*) to avoid a co-solvent effect. The tubes were agitated for 96 h (determined as apparent sorption equilibration time in preliminary experiments) in the dark at 200 rpm. After the desired time, the tubes were centrifuged (4,000×*g*, 30 min) and 0.5-ml aliquots of the supernatant were diluted with methanol (1:1, *v*/*v*) into 1.5-ml HPLC vials. The methanol was added to prevent phenanthrene sorption to the HPLC vials (Oren and Chefetz 2005). 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× 4 mm, 5 μm). Phenanthrene was eluted from the column using isocratic conditions of 15/85 water/acetonitrile (1 ml/min) and detected with a fluorescence detector using 244 and 360 nm as excitation and emission wavelengths, respectively. Phenanthrene was quantified using external standards prepared in a background solution. Because of negligible sorption to the vials (<0.5%), minimal loss to the headspace and no biodegradation, sorption was calculated by mass differences.

Data analysis

The sorption coefficients (K_d) were calculated from a linear fit of the sorption isotherms. The K_d data were normalized to the carbon and organic matter levels in each sample to obtain the K_{oc} and K_{om} values, respectively. The K_F (Freundlich sorption capacity coefficient) and N parameters were calculated from the Freundlich equation, $q=K_F \times C_e^N$, where q is the phenanthrene solid-phase concentration (mg/kg) and C_e is the phenanthrene liquid-phase equilibrium concentration (mg/l).

Results and discussion

The composition of plant cuticles is known to vary among plant species and plant-organ age; cuticle composition is also affected by exogenous factors (Bargel et al. 2006; Baur et al. 1999; Casado and Heredia 2001; Müller and Riederer 2005; Percy et al. 2002; Riederer and Schonherr 1984). In this study, cuticle (isolated from fruits of green pepper and tomato and leaves of citrus) selection was based on their different structural compositions, as this is assumed to influence their biodegradability and sorptive uptake of HOCs. The tomato cuticle is known as a cutan-free cuticle (Deshmukh et al. 2003), whereas the level of base- and acid-resistant residue (i.e., cutan) in the pepper and citrus cuticles was 9 and 7%, respectively. The level of cutin was 59, 75 and 47% for the pepper, tomato and citrus cuticles, respectively. The highest level of acid-hydrolyzable fraction (i.e., pectin and cellulose) was obtained for the citrus leaf cuticle (40%). The level of this structural fraction in the pepper and tomato cuticles was 30 and 20%, respectively. The level of the epicuticular waxes was similar in the two studied fruit cuticles (2–3%) but was twice as high (6%) in the citrus leaf cuticle.

The total level of organic matter in the incubated cuticle-amended soil samples exhibited a sharp decrease with incubation time (Fig. 1). The degradation level of the added cuticles was 37, 33 and 30% for the tomato, pepper and citrus cuticles, respectively. A higher decomposition level (50%) has been reported by Stimler et al. (2006) for tomato and pummelo cuticles during 12 months of incubation under similar conditions. In this study, the fruit-derived cuticles exhibited a similar decomposition trend. During the first month of incubation, 21 to 23% of the added cuticular organic matter was mineralized, then the organic matter level remained constant (no decomposition) for the following 2 months. From that point (3 months of incubation) on, the cuticles decomposed at a steady rate of about 2.5% per month. In contrast, only 8% of the leaf-derived citrus cuticle decomposed during the first month of incubation and from that point on, the materials decomposed at a steady rate of 2.7% per month. It is important to note that the level of SOM in the control soil was constant at 0.17% during the incubation period. The H/C atomic ratio values of all samples were high (>2), in accordance with the highly aliphatic nature of the cuticles (Chefetz et al. 2000; Chen et al. 2005; Deshmukh et al. 2003, 2005; Holloway 1982). In general, the H/C ratios of the pepper and citrus samples increased gradually with incubation, proba-

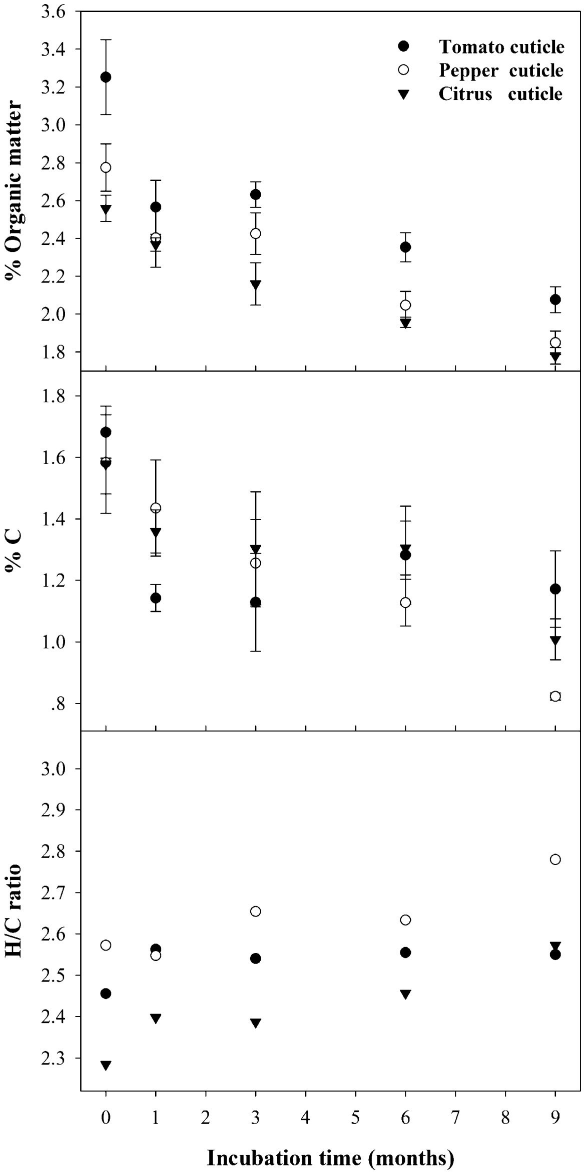

Fig. 1 Change in organic matter, carbon and H/C atomic ratio during incubation of plant cuticles in soil

bly due to relative enrichment of the residual organic matter with the more resistant cuticular matter. These materials include the cutan biopolymer and lignin-like structures (Kögel-Knabner et al. 1994). Since the H/C ratio for aromatic structures such as lignin is low, the obtained increase in H/C ratio was mainly related to enrichment of the organic matter with the cutan fraction. In contrast, the H/C values obtained for the soil samples amended with the tomato cuticle were constant after 1 month of incubation. This cuticle is cutan-free and therefore when cutin (75% of the whole cuticle weight) is decomposed, the H/C ratio remains steady.

To follow the structural transformation of the cuticular materials during incubation, we analyzed the samples using DRIFT spectroscopy. The spectra of the soil-free samples (i.e., spectra of the organic matter) at three stages of incubation are presented in Fig. 2. These spectra were produced by subtracting the spectrum of the cuticle-free soil (i.e., natural soil) from the spectra of the soil samples taken during incubation. This allowed us to correct for and reduce the contribution of signals from the soil's mineral and natural organic matter components and to monitor the changes in the cuticular-derived organic matter during incubation (Chefetz et al. 1996). All spectra exhibited similar profiles. A peak at 3,620–3,640 cm^{-1} (O–H stretch of alcohols), a broad band at 3,200–3,600 cm^{-1} (H-bonds, OH groups), two distinct peaks at 2,930 and 2,850 cm^{-1} (C–H asymmetric, C–H stretch of –CH), a small peak at 1,846 cm^{-1} (anhydride), a peak at around 1,740 cm^{-1} (C=O in ester bonds), a wide peak at 1,620–1,650 cm^{-1} (carboxylate, C=C in aromatic structures or C=C in vinyl), broad peaks 1,470 and 1,380 cm^{-1} (C–H deformation of CH_2 or CH_3 groups), a peak in the 1,100 cm^{-1} range (C–O stretch of polysaccharide) and a peak at 920 cm^{-1} (Si–O stretch).

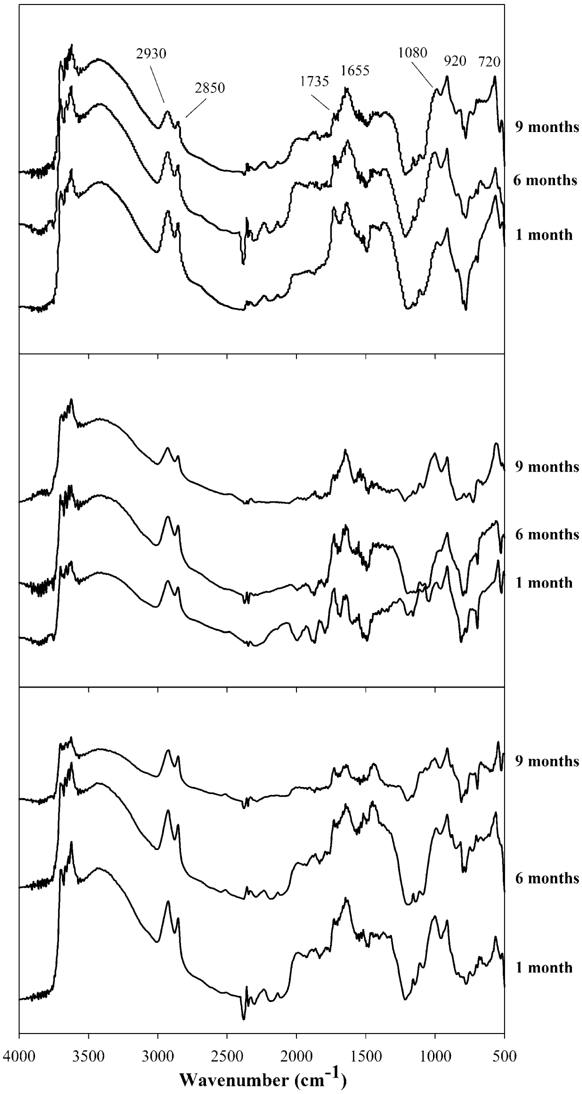

Fig. 2 Diffuse reflectance Fourier-transform infrared (DRIFT) spectra of the incubated cuticle samples (tomato, *top*; pepper, *middle*; citrus, *bottom*)

The main changes in the spectra resulting from cuticle decomposition were a reduction of the methyl and ethyl functionality peaks at 2,930 and 2,850 cm^{-1} and a reduction of the ester-derived peak at 1,730–1,740 cm^{-1}. For all samples during the first 6 months of incubation, reduction of the intensities of these peaks followed a similar trend (i.e., the 2,930:1,730 peak ratio was constant). With the tomato-derived cuticle samples, this peak ratio remained constant till the end of the experiment. These findings suggest that cutin, which is composed of various inter-esterified aliphatic hydroxy acids with chain lengths of C_{16} and C_{18}, was decomposed continuously during incubation. However, during the final stage of the experiment (6 to 9 months of incubation), the 2,930:1,730 peak ratios recorded for the pepper- and citrus-derived cuticular samples increased slightly (from 1.1 to 1.15 and from 1.07 to 1.2, respectively). The increase in the 2,930:1,730 peak ratio was similar to the increasing trend in H/C ratio at the final stage of the incubation. This indicates relative enrichment of the residual organic matter with paraffinic carbons originating from the cutan biopolymer. This biopolymer is present in citrus and pepper cuticles and is known to be slowly degraded. In addition to these changes, the relative intensity of the bands related to C–O of polysaccharides (1,000–1,100 cm^{-1}) decreased significantly with incubation in the samples from the citrus-derived cuticle. This is probably related to the high level of polysaccharides in this sample (40%). In general, our data suggest that cutin was continuously decomposed in the soils, resulting in a relative enrichment of the residual organic matter with the cutan fraction.

Sorption isotherms of phenanthrene to pepper and tomato fruit cuticles and citrus leaf cuticle at different stages of the incubation are presented in Fig. 3, and sorption coefficients are presented in Table 1. The K_{oc} values calculated for the raw cuticle-soil mixtures (0 month of incubation) were similar to values calculated for phenanthrene sorption by the bulk cuticular matter (74,180±2,010, 75,690±4,250 and 55,140±1,514 l/kg organic carbon for the tomato, pepper and citrus cuticles, respectively). In addition, the phenanthrene K_d value calculated for the soil used in the experiment was negligible (5.53 l/kg) compared with the values calculated for the soil-cuticle systems. This indicates that the changes obtained in sorption parameters during the experiments can be attributed to the added cuticles and their transformation in the system.

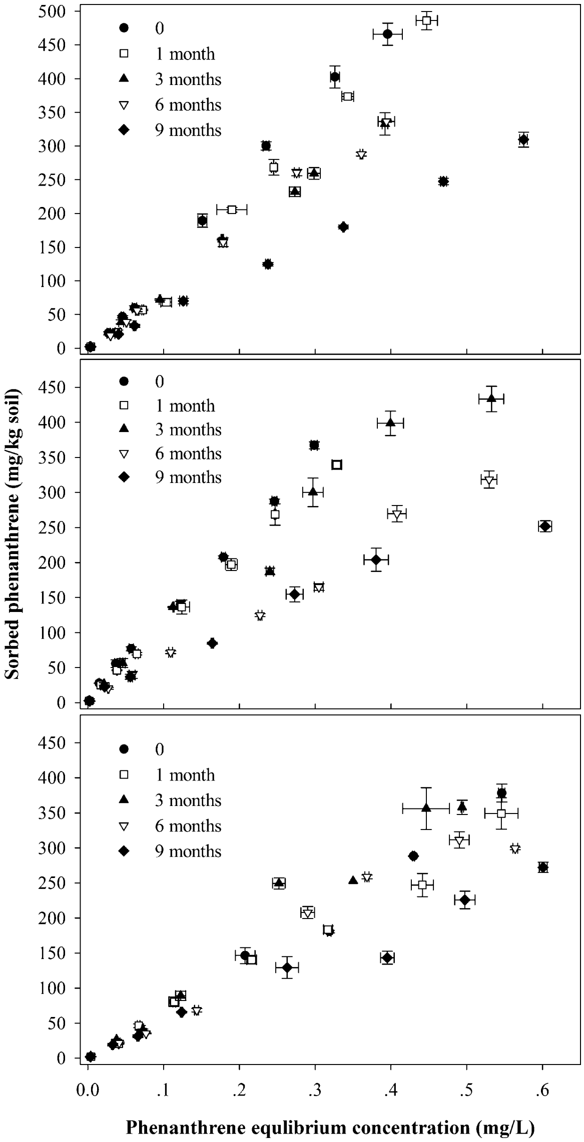

Fig. 3 Sorption isotherms of phenanthrene by tomato (*top*), pepper (*middle*) and citrus (*bottom*) cuticle microcosm samples

In general, the phenanthrene K_d and K_F values, which were calculated for the whole incubated soils, decreased with incubation (degradation). The K_d values decreased by 55, 65 and 37% with incubation for the tomato, pepper and citrus cuticle systems, respectively. During the first month of incubation, the K_d values of the soils were only slightly decreased even though a considerable amount of the added cuticles decomposed during this early stage of incubation. Behavior of K_{oc} was distinct from the K_d trend (Table 1). The K_{oc} and K_{om} values for the tomato cuticle incubation system increased after 1 month of incubation. The relative increase in values recorded for the K_{oc} during the first month of incubation suggests higher sorption capability for the residual cuticular matter. Cuticular matter is composed of readily degradable materials such as pectin and cellulose; these biopolymers are expected to mineralize rapidly at early stages of incubation (Stimler et al. 2006). Since these polymers are highly polar and are therefore not expected to contribute to sorption of highly non-polar sorbates such as phenanthrene, it is suggested that their degradation increased the apparent phenanthrene binding to the remaining residues. From this stage of incubation (after 1 month), the K_{oc} values calculated for the tomato incubation system decreased by up to 47%, similar to the decrease recorded for the K_d values (53%). This can be explained by the continuous decomposition (depolymerization) of the cutin biopolymer to monomers. Cutin biodegradation has been observed by Kögel-Knabner et al. (1989) and Stimler et al. (2006). Though this process (depolymerization) does not significantly affect the amount of organic

Table 1 Phenanthrene sorption coefficients

Incubation time (months)	K_{d}[a]	K_{oc}[b]	K_{om}[c]	K_{F}[d]	N[e]
Tomato cuticle					
0	1220±40	72,480	37,490	1168±83	0.97±0.06
1	1130±32	99,010	44,120	1212±72	1.01±0.05
3	860±24	76,270	32,700	850±53	0.99±0.05
6	850±22	66,590	36,260	813±44	0.96±0.05
9	530±8	52,270	25,610	532±13	0.99±0.03
Pepper cuticle					
0	1,170±24	73,770	42,090	1,159±64	0.98±0.04
1	1,030±32	71,400	42,640	957±69	0.93±0.05
3	850±42	67,530	34,970	762±55	0.82±0.07
6	600±22	53,240	29,330	610±40	0.81±0.07
9	380±20	46,620	20,740	358±13	0.70±0.04
Citrus cuticle					
0	680±20	46,410	26,380	684±25	1.04±0.03
1	600±26	45,310	25,240	588±41	0.97±0.07
3	770±43	59,340	35,820	703±58	0.88±0.08
6	620±30	47,580	31,730	728±25	1.01±0.03
9	430±21	42,580	24,100	425±32	0.96±0.01

The values are means±standard deviations.

[a] Whole soil sorption coefficient (l/kg)

[b] Carbon-normalized sorption coefficient (l/kg)

[c] Organic matter-normalized sorption coefficient (l/kg)

[d] Freundlich sorption capacity coefficient [(mg/kg)/(mg/l)^{N}]

[e] Freundlich correction factor

matter, the sorption capability of the system is drastically decreased due to the high sorptive capacity of the cutin (Chamel and Vitton 1996; Chefetz 2003; Chen et al. 2005; Shechter et al. 2006).

For the pepper cuticle system, the decrease in K_{oc} values was much smaller than the decrease recorded for the K_{d} values (35 and 63%, respectively). Similar to the tomato system, the decrease in K_{oc} values probably resulted from the depolymerization of cutin. The lower decrease in K_{oc} as compared to the tomato system was due to the presence of the non-degradable cutan in this system (7–9%). Hence, the different structural composition of the tomato and pepper cuticles affected the sorption behavior of phenanthrene during the incubation period. For the citrus cuticle system, the K_{oc} values increased by 27% after 3 months. This behavior is similar to the K_{oc} trend in tomato cuticle, and can be explained by the mineralization of pectin, which takes more time (3 months) than in the tomato system (1 month) due to the larger amount of pectin in the citrus cuticle. After 3 months, the K_{oc} values had decreased by 28% due to cutin depolymerization. The K_{d} values in this system decreased by 37% during the period of incubation (similar to the tomato system).

We suggest that in all cases, the decrease in phenanthrene K_{oc} values during incubation resulted from the decomposition of cutin. When this biopolymer is decomposed to monomers, the sorption of phenanthrene decreases dramatically as well. The most drastic decrease in sorption capability of phenanthrene was recorded for the tomato and pepper cuticles, which contain 75 and 60% cutin, respectively. This was confirmed by the results of the DRIFT analysis (i.e., reduction of the 1,735 cm^{-1} peak; Fig. 2). In some cases, the reduction of the C=O ester vibration was followed by an increase in the 1,720 cm^{-1} peak which is assigned to C=O vibrations of the carboxylic acids that are typical for cutin monomers. With all cuticular matter, pectin degradation facilitated the apparent phenanthrene sorption. Because of the high polarity of the pectin, it is a more unfavorable partition medium for phenanthrene. Moreover, Chefetz (2003) has suggested that the polymeric materials pectin and cutin can best be considered an intermediate between physical and chemical mixtures. In the mixture, cutin dominates the sorption potential and the polar component (pectin) has a significant decreasing sorption effect. The ratio of these two processes (sorption by cutin and decreasing sorption ability due to the polarity of the pectin) governs the overall sorption capabilities of the residual organic matter.

With the tomato and citrus cuticle samples, the Freundlich *N* values (i.e., linearity of the phenanthrene sorption isotherm; Table 1) were close to unity and were stable throughout the incubation time. Similar behavior (highly linear sorption isotherms) has been reported by Boyd et al. (1990) for benzene, ethylbenzene and trichlorobenzene with tomato cuticle. Those authors suggested that plant cuticles serve as a powerful partitioning medium for HOCs in soils. However, in this study, the linearity of the phenanthrene sorption isotherm was significantly influenced by the decomposition process of the green pepper cuticle. The Freundlich *N* values decreased from 0.98 to 0.70. This suggests that the type of sorbent-sorbate interactions changed with decomposition due to structural changes in the sorbents. The DRIFT data suggest that the residual organic matter after decomposition of citrus leaf cuticle is enriched with lignin-like and cutan materials. These biopolymers are known to contribute to non-linear sorption isotherms (Gunasekara and Xing 2003; Salloum et al. 2002). Non-linear sorption of phenanthrene can results from its dual interactions with the sorbent (partitioning and hole-filling; Xing and Pignatello 1997) or when phenanthrene interacts specifically (via π–π interactions) with aromatic functional groups (Wijnja et al. 2004; Zhu et al. 2004). We believe that with this set of samples (decomposed citrus leaf cuticles), the non-linear sorption of phenanthrene results from its interactions with the cutin and lignin-like structures present in the leaf cuticle (Kögel-Knabner et al. 1994). Interactions with the cutin probably facilitates partitioning (similar to the data recorded for the cutin-rich tomato cuticle), whereas interactions with the lignin are via π-π interactions with aromatic functionalities.

Conclusions

The role of plant cuticular matter in the sorption of HOCs has been investigated to better understand the mechanisms by which agrochemicals and other HOCs interact with important precursors of SOM. However, little has been studied regarding the effect of the degradation of these natural organic materials on their role as partition and sorption domains for HOCs in soils. This study demonstrates that the structural composition of the plant cuticle affects its ability to sorb HOCs. Moreover, its structural composition is shown to significantly influence its biodegradability and the ability to contribute to the overall sorption of HOCs in soils. Therefore, a single plant cuticle cannot be used as a model for plant cuticles in general when studying HOC sorption. Our data suggest that with decomposition of the plant cuticular matter in soils, mainly the cutan biopolymer and lignin-derived structures dominate sorption. This provides strong evidence for the role of aliphatic-rich plant-derived biopolymers as a sorption domain for HOCs in soils.

Acknowledgements This research was supported by a research grant from BARD, the United States-Israeli Binational Agricultural Research and Development Fund. The author wishes to thank Ziva Hochman for her assistance in this study.

References

Almendros G, Guadalix ME, Gonzalez-Vila FJ, Martin F (1996) Preservation of aliphatic macromolecules in soil humin. Org Geochem 24:651–659

Baldock JA, Oades JM, Nelson PN, Skene TM, Golchin A, Clarke P (1997) Assessing the extent of decomposition of natural organic materials using solid-state ^{13}C NMR spectroscopy. Aust J Soil Resour 35:1061–1083

Bargel H, Koch K, Cerman Z, Neinhuis C (2006) Structure-function relationships of the plant cuticle and cuticular waxes – a smart material? Funct Plant Biol 33:893–910

Baur P, Marzouk H, Schonherr J (1999) Estimation of path lengths for diffusion of organic compounds through leaf cuticles. Plant Cell Environ 22:291–299

Boyd SA, Xiangcan J, Lee J-F (1990) Sorption of nonionic organic compounds by corn residues from a no-tillage field. J Environ Qual 19:734–738

Casado CG, Heredia A (2001) Specific heat determination of plant barrier lipophilic components: biological implications. Biochim Biophy Acta Biomembr 1511:291–296

Chamel A, Vitton N (1996) Sorption and diffusion of ^{14}C-atrazine through isolated plant cuticles. Chemosphere 33:995–1003

Chefetz B (2003) Sorption of phenanthrene and atrazine by plant cuticular fractions. Environ Toxicol Chem 22:2492–2498

Chefetz B, Hatcher PG, Hadar Y, Chen Y (1996) Chemical and biological characterization of organic matter during composting of municipal solid waste. J Environ Qual 25:776–785

Chefetz B, Deshmukh PA, Hatcher PG, Guthrie EA (2000) Pyrene sorption by natural organic matter. Environ Sci Technol 34:2925–2930

Chefetz B, Salloum MJ, Deshmukh AP, Hatcher PG (2002a) Structural components of humic acids as determined by chemical modifications and ^{13}C NMR, pyrolysis- and thermochemolysis-GC/MS. Soil Sci Soc Am J 66:1159–1172

Chefetz B, Tarchitzky J, Deshmukh AP, Hatcher PG, Chen Y (2002b) Structural characterization of humic substances in particle-size fraction of an agricultural soil. Soil Sci Soc Am J 66:129–141

Chen B, Johnson E, Chefetz B, Zhu L, Xing B (2005) Sorption of polar and nonpolar aromatic organic contaminants by plant cuticular materials: role of polarity and accessibility. Environ Sci Technol 39:6138–6149

Chin YP, Aiken GR, Danielsen KM (1997) Binding of pyrene to aquatic and commercial humic substances: the role of molecular weight and aromaticity. Environ Sci Technol 31:1630–1635

Chiou CT, McGroddy SE, Kile DE (1998) Partition characteristics of polycyclic aromatic hydrocarbons on soils and sediments. Environ Sci Technol 32:264–269

Deshmukh AP, Simpson AJ, Hatcher PG (2003) Evidence for cross-linking in tomato cutin using HR-MAS NMR spectroscopy. Phytochemistry 64:1163–1170

Deshmukh AP, Simpson AJ, Hadad CM, Hatcher PG (2005) Insights into the structure of cutin and cutan from *Agave americana* leaf cuticle using HRMAS NMR spectroscopy. Org Geochem 36:1072–1085

Gunasekara AS, Xing B (2003) Sorption and desorption of naphthalene by soil organic matter: importance of aromatic and aliphatic components. J Environ Qual 32:240–246

Gunasekara AS, Simpson MJ, Xing B (2003) Identification and characterization of sorption domains in soil organic matter using structurally modified humic acids. Environ Sci Technol 37:852–858

Gupta NS, Collinson ME, Briggs DEG, Evershed RP, Pancost RD (2006) Reinvestigation of the occurrence of cutan in plants: implications for the leaf fossil record. Paleobiology 32:432–449

Holloway PJ (1982) Structure and histochemistry of plant cuticular membranes: an overview. In: Cutler DF, Alvin KL, Price CE (eds) The plant cuticle. Academic, London, pp 1–33

Hu W, Mao J, Xing B, Schmidt-Rohr K (2000) Poly(methylene) crystallites in humic substances detected by nuclear magnetic resonance. Environ Sci Technol 34:530–534

Huang W, Weber WJ Jr (1997) A distributed reactivity model for sorption by soils and sediments. 10. Relationships between desorption, hysteresis, and the chemical characteristics of organic domains. Environ Sci Technol 31:2562–2569

Jeffree CE (1996) Structure and ontogeny of plant cuticles. In: Kerstiens G (ed) Plant cuticles: an integrated functional approach. Bios Scientific Publishers Ltd, Oxford, pp 33–82

Jeffree CE (2006) The fine structure of the plant cuticle. In: Riederer M, Muller C (eds) Biology of the plant cuticle. Blackwell Publishing Ltd, Oxford, pp 11–110

Johnson MD, Huang W, Weber WJ Jr (2001) A distributed reactivity model for sorption by soils and sediments. 13. Simulated digenesis of natural sediment organic matter and its impact on sorption/desorption equilibrium. Environ Sci Technol 35:1680–1687

Kang S, Xing B (2005) Phenanthrene sorption to sequentially extracted soil humic acids and humins. Environ Sci Technol 39:134–140

Kögel-Knabner I (1997) ^{13}C and ^{15}N NMR spectroscopy as a tool in soil organic matter studies. Geoderma 80:243–270

Kögel-Knabner I, Ziegler F, Riederer M, Zech W (1989) Distribution and decomposition pattern of cutin and suberin in forest soils. Z pflanzenernahr 152:1–5

Kögel-Knabner I, Hatcher PG, Tegelaar EW, De Leeuw JW (1992) Aliphatic components of forest soil organic matter as determined by solid-state ^{13}C NMR and analytical pyrolysis. Sci Total Environ 113:89–106

Kögel-Knabner I, de Leeuw JW, Tegelaar EW, Hatcher PG, Kerp H (1994) A lignin-like polymer in the cuticle of spruce needles: implications for the humification of spruce litter. Org Geochem 21:1219–1228

Lichtfouse E, Bardoux G, Mariotti A, Balesdent J, Ballentine DC, Macko SA (1997) Molecular ^{13}C and ^{14}C evidence for the allochthonous and ancient origin of C_{16} –C_{18} *n*-alkanes in modern soils. Geochim Cosmochim Acta 9:1891–1898

Lichtfouse E, Chenu C, Baudin F, Leblond C, Silva MD, Behar F, Derenne S, Largeau C, Wehrung P, Albrecht P (1998) A novel pathway of soil organic matter formation by selective preservation of resistance straight-chain biopolymers: chemical and isotope evidence. Org Geochem 28:411–415

McKinney DE, Bortiatynski JM, Carson DM, Clifford DJ, De Leeuw JW, Hatcher PG (1996) Tetramethylammonium hydroxide (TMAH) thermochemolysis of the aliphatic biopolymer cutan: insights into the chemical structure. Org Geochem 24:641–650

Molse B, Collinson ME, Finch P, Stankiewicz BA, Scott AC, Wilson G (1998) Factors influencing the preservation of plant cuticles: a comparison of morphology and chemical composition of modern and fossil examples. Org Geochem 29:1369–1380

Müller C, Riederer M (2005) Plant surface properties in chemical ecology. J Chem Ecol 31:2621–2651

Nierop KGJ (1998) Origin of aliphatic compounds in a forest soil. Org Geochem 29:1009–1016

Oren A, Chefetz B (2005) Sorption-desorption behavior of polycyclic aromatic hydrocarbons in upstream and downstream river sediments. Chemosphere 61:19–29

Percy KE, Awmack CS, Lindroth RL, Kubiske ME, Kopper BJ, Isebrands JG, Pregitzer KS, Hendrey GR, Dickson RE, Zak DR, Oksanen E, Sober J, Harrington R, Karnosky DF (2002) Altered performance of forest pests under atmospheres enriched by CO_2 and O_3. Nature 420:403–407

Rice JA (2001) Humin Soil Sci 166:848–857

Riederer M (2006) Introduction: biology of the plant cuticle. In: Riederer M, Muller C (eds) Biology of the plant cuticle. Blackwell Publishing Ltd, Oxford, pp 1–8

Riederer M, Schonherr J (1984) Accumulation and transport of (2,4-dichlorophenoxy)acetic acid in plant cuticles: I. Sorption in the cuticular membrane and its components. Ecotoxicol Environ Saf 8:236–247

Salloum MJ, Chefetz B, Hatcher PG (2002) Phenanthrene sorption by aliphatic-rich natural organic matter. Environ Sci Technol 36:1953–1958

Shechter M, Xing B, Kopinke FD, Chefetz B (2006) Competitive sorption-desorption behavior of triazine herbicides with plant cuticular fractions. J Agric Food Chem 54:7761–7768

Stark RE, Tian S (2006) The cutin biopolymer matrix. In: Riederer M, Muller C (eds) Biology of the plant cuticle Blackwell Publishing Ltd, Oxford, pp 126–141

Stevenson FJ (1994) Humus chemistry: genesis, composition, reactions. Wiley, New York

Stimler K, Xing B, Chefetz B (2006) Transformation of plant cuticles in soil: effect on their sorptive capabilities. Soil Sci Soc Am J 70:1101–1109

Villena J-F, Dominguez E, Stewart D, Heredia A (1999) Characterization and biosynthesis of non-degradable polymers in plant cuticles. Planta 208:181–187

Wijnja H, Pignatello JJ, Malekani K (2004) Formation of π–π complexes between phenanthrene and model π-acceptor humic subunits. J Environ Qual 33:265–275

Xing B (1997) The effect of the quality of soil organic matter on sorption of naphthalene. Chemosphere 35:633–642

Xing B, Pignatello JJ (1997) Dual-mode sorption of low-polarity compounds in glassy poly(vinyl chloride) and soil organic matter. Environ Sci Technol 31:792–799

Zech W, Senesi N, Guggenberger G, Kaiser K, Lehmann J, Miano TM, Miltner A, Schroth G (1997) Factors controlling humification and mineralization of soil organic matter in the tropics. Geoderma 79:117–161

Zhu D, Hyun S, Pignatello JJ, Lee LS (2004) Evidence for π–π electron donor–acceptor interactions between π-donor aromatic compounds and π-acceptor sites in soil organic matter through pH effects on sorption. Environ Sci Technol 38:4361–4368