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Phenanthrene Sorption by Fruit Cuticles and Potato Periderm with Different Compositional Characteristics

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Phenanthrene sorption by fruit cuticles (tomato, apple, and grape), potato tuber periderm, and their fractions were investigated to elucidate effects of compositional characteristics on affinity of plant cuticle (above-ground) and periderm (below-ground) with hydrophobic organic contaminants (HOCs). The distinct roles of the extractable lipids (waxes), the depolymerizable lipids (cutin/suberin), the nonsaponifiable lipids (cutan/suberan) and polysaccharide are discussed. The cutin/suberin rather than waxes dominates the sorption properties of bulk cuticle/periderm, but the sorption coefficient (K_d) is linearly correlated with the total lipid contents. Polysaccharide plays a negative role in HOC sorption due to its obviously poor affinity with HOCs and restriction effect on the other powerful sorptive regions in cuticle/periderm. The significantly lower sorption of periderm than cuticle is attributed to the former having higher polysaccharide and lower depolymerizable lipids. The linear correlation of K_d of bulk cuticle/periderm with polysaccharide content is observed for a potential prediction of plant uptake.

KEYWORDS: Potato periderm; fruit cuticle; phenanthrene; sorption; compositional effect

INTRODUCTION

The rate of compounds transferring through the outer surfaces of plant is believed to be the dominant limiting factor in the uptake of organic contaminants (*1*−*3*), which affects transport of organic pollutants and food safety. All primary aerial surfaces of vascular plants (e.g., fruit and leaf) are covered by cuticle, a noncellular and hydrophobic superficial film, to control the water loss and gas exchange. However, when damaged or destroyed by wounding or secondary growth of the stem, the cuticle is never regenerated but replaced by a completely new structure (named periderm (*4*)), which is prevailing below-ground plant tissue (e.g., tuber and root). The main compositions of plant cuticles and periderms are quite similar, including the extractable lipids (waxes), deploymerizable insoluble lipids (cutin vs suberin for cuticle vs periderm), nonsaponifiable biopolymers (cutan vs suberan for cuticle vs periderm), as well as polysaccharides. Cutin/suberin, which are made of branched polyester macromolecules mainly composed of long-chain hydroxylated fatty acid moieties, can be depolymerized by alkaline methanolysis but cannot be extracted by organic solvents (*5*). The chemical compositions play a critical role in affinity of plant cuticle/periderm with hydrophobic organic contaminants (HOCs), which are worth further investigating.

As the initial interaction of agrochemicals and contaminants with plant in transport processes, sorption behavior of cuticle/periderm receives increasing attention in various research fields (*1*−*3*, *6*−*13*). Plant cuticles have been reported to be high-efficiency natural sorbents for HOCs (*6*−*13*) and seemed to be a good reservoir for organic contaminant storage (*14*, *15*). Wang et al. (*15*) demonstrated that the total concentrations of 16 PAHs in the leaf cuticles were much higher than those in the inner leaf tissues. HOC uptake by plant was predicted presumably based on the extractable lipids for environmental transport models (*16*−*18*), but serious underprediction by the extractable lipid content and HOC's K_{ow} values were widely observed (ref *13* and therein). Recently, Chen et al. (*13*) suggested that the depolymerizable lipid fraction (i.e., cutin) was required to accurately predict plant accumulation of organic contaminants for the first time. The markedly high sorption capacities of cutin and cutan for HOCs were due to their hydrophobic nature and the presence of polar sites in their condensed glass-like structures (*12*). Since cutin and cutan were much more powerful than waxes as sorptive mediums, it is hard to accurately predict plant accumulation of organic contaminants only by the soluble lipid (i.e., wax) content (*13*).

Therefore, more work is needed to precisely understand the distinct roles of waxes, cutin, cutan and sugar in HOCs' affinity with plant surface. The previous reports were all focused on the sorption properties of plant cuticles (above-ground parts), especially on the cutin and cutan biopolymers, but little is known about the sorption characteristics of periderms (below-ground parts). The main objective of the current study is to elucidate the relationship between the sorption properties and compositional characteristics of plant skins varying from different species. To this end, four plant surfaces of grape, tomato and

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apple fruits, as well as potato tuber, were selected due to their large consumption in our daily life and distinctive compositional characteristics. Phenanthrene was chosen as the sorbate because it is a common organic contaminant storage by plant cuticles (*15*), and has been widely used in sorption experiments for its significant effect on the environment (*6, 7, 10, 12*).

MATERIALS AND METHODS

Isolation of Potato Periderm and Fruit Cuticle Fractions. The plant skins of different species, including potato tuber (below-ground parts) and three fruits (above-ground parts), were isolated using a modified version of an earlier method (*13*). Briefly, the skins of fresh potato (*Solanum tuberosum*) tubers and grape fruits (*Vitis heyneana Roem. et Schult*) were peeled after boiling in water, then incubated in a solution of oxalic acid (4 g/L) and ammonium oxalate (16 g/L) at 90 °C for 24 h and finally washed with deionized distilled water to remove any residual pulps materials and the used chemicals. This procedure yielded the bulk potato tuber periderm (PP1) and grape cuticle (GC1), respectively. Waxes of potato periderm (PW) and grape cuticle (GW) were extracted from PP1 and GC1 fractions, respectively, by Soxhlet extraction with chloroform/methanol (1:1) at 70 °C for 24 h, and then evaporated to dryness, while the extractive-free powder was named dewaxed-fraction (PP2 and GC2). To remove the suberin and cutin monomer, PP2 and GC2 fractions were saponified with 1% potassium hydroxide in methanol for 3 h at 70 °C under refluxing and stirrer-spinning conditions, producing the nonsaponifiable fraction (PP3 and GC3). Carbohydrates were removed from the GC3, PP3, PP2 and PP1 fractions by acid hydrolysis in 6 mol/L HCl solution with refluxing for 6 h at 100 °C, resulting in the cutan fraction (GC4), suberan fraction (PP4), dewaxed-hydrolyzed fraction (PP5), and desugared fraction (PP6), respectively. The resulting fractions of PP3, GC3, GC4, PP4, PP5 and PP6 were separated from the basic or acidic solution by filtration, and then the residues were washed with a mixed solution of methanol and deionized distilled water (V/V, 1:1) to adjust these fractions to neutral conditions and to remove dissolved organic matter (e.g., suberin/cutin monomer and carbohydrates) sorbed by these residues. All samples were oven-dried at 60 °C, ground, and sieved (<0.18 mm) before analysis and sorption experiments. The yield percentages of each periderm and cuticular fraction (PP1−PP6, PW; GC1−GC4, GW) were calculated.

Tomato (*Solanum lycopersicum*) and apple (*Malus domestica*) cuticular fractions [i.e., TC1, TC2, TC3, TC5 and TC6 for tomato; AC1, AC2, AC3, AC4, AC5, AC6 and waxes (AW) for apple] were produced in our previous work (*13*). The number in the name of each cuticular fraction is identified as follows: "1" for bulk cuticle, "2" for dewaxed, "3" for nonsaponifiable, "4" for cutan, "5" for dewaxed-hydrolyzed, "6" for desugared.

Characterization of the Potato Periderm and Grape Cuticular Fractions. Elemental (C, H, N) analyses were conducted using an EA 112 CHN elemental analyzer (Thermo Finnigan), while the oxygen content was calculated by the mass difference because the ash content was neglected. The H/C and (O + N)/C atomic ratios were calculated to evaluate the aliphatic nature and polarity of the isolated potato periderm and grape cuticular fractions. For comparison, the CHNO compositions of tomato and apple cuticular fractions were cited from our previous reports (*13*).

Batch Sorption Experiment. Phenanthrene was chosen as a representative polycyclic aromatic hydrocarbon (PAH), and the selected physicochemical properties are as follows: molecular weight of 178.2 g/mol; aqueous solubility of 1.1 mg/L (room temperature); octanol−water partition coefficient (K_{ow}) of 28840. Batch phenanthrene sorption by all isolated fractions (PP1−PP6, GC1−GC4, AC1−AC6, TC1−TC6, PW, GW and AW) was performed as described elsewhere (*13*). In brief, initial concentrations of phenanthrene ranged from 0.005 to 0.95 mg/L, and each isotherm consisted of ten concentration points; each point, including the control and calibration, was run in duplicate. The background solution included 0.01 mol/L $CaCl_2$ and 200 mg/L NaN_3, at pH = 7. The specific solid-to-solution ratios were adjusted to achieve 30−80% removal rate of sorbate at apparent equilibrium in comparison with initial concentration. The solid−solution ratio for a given sorbent is constant over the range of an isotherm. The 8 mL vials were filled with sorbate solution to minimize the headspace volumes of vials, sealed with aluminum foil-lined Teflon screw caps to avoid sorbate's evaporation, and then agitated in the dark for 3 days at 25 ± 0.5 °C (prior tests indicated the apparent sorption equilibrium was reached before two days). The solution was separated by centrifugation at 4000 rpm for 20 min, and 0.5 mL aliquots were mixed with 0.5 mL of methanol for HPLC analysis. Phenanthrene concentrations were measured with an Agilent 1200 high performance liquid chromatograph (HPLC) fitted with G1314B variable wavelength detector and Agilent Eclipse XDB-C 18 column (4.6 mm × 250 mm × 5 μm). Injection volumes of 50 μL, a mobile phase of 90% methanol/10% water with a flow rate of 1 mL/min, and an absorbance wavelength of 250 nm were used. Because of minimal sorption by the vials, and negligible losses from evaporation, biodegradation and photodegradation, the sorbed amount was then determined by difference in aqueous concentration between nominal aqueous concentration without sorbent and with sorbent.

Data Analysis. The Freundlich parameters (K_f and N) were calculated using the logarithmic form of the equation $Q = K_f C_e^N$ by OriginPro7.5, where Q is the amount sorbed per unit weight of sorbent, mg/kg; C_e is the equilibrium concentration in the aqueous solution, mg/L; K_f [(mg/kg)/(mg/L)^N] is the Freundlich capacity coefficient, and N (dimensionless) describes the isotherm curvature. Sorption coefficients (K_d) were calculated from the slope of the linear isotherms. K_{oc} values were calculated by normalizing K_d to the carbon level (f_{oc}) of each fraction. The relative contribution (RC) of each component was estimated by the radio of the $f_i K_{d,i}$ (where i represents wax, cutin or suberin, cutan or suberan, and sugar) to K_d of bulk cuticle or periderm.

RESULTS AND DISCUSSION

Characterization of the Potato Periderm and Fruit Cuticle Fractions. The yields and elemental composition of isolated potato periderm and grape cuticle fractions (PP1−PP6, GC1−GC4, GW and PW) are presented in **Table 1**. The yields were all calculated to the percentage contents of bulk plant skins (PP1 and GC1). Based on the mass balance, the elemental compositions of depolymerizable lipids (i.e., cutin vs suberin for above-ground vs below-ground part) and sugar were also calculated in **Table 1**. The characterization of tomato and apple cuticle fractions has been reported in our previous report (*13*), and is also presented in **Table 1**. The chemical compositions and elemental characteristics of plant skins vary from different species, and distinctive differences of structural characteristics between plant cuticle (above-ground) and potato periderm (below-ground) were also observed.

According to **Table 1**, the percentage content of the extractable lipids (i.e., waxes) by organic solvents in bulk sample ranges widely and follows the order of 6.5% (tomato cuticle) < 13.4% (potato periderm) < 25.1% (grape cuticle) < 44.7% (apple cuticle). The depolymerizable lipids or the soluble polymeric lipids (i.e., cutin and suberin) were determined by saponification in methanolic KOMe (KOH solution in methanol), which also significantly varied from plant species: potato periderm (21.5%) < grape cuticle (27.4%) < apple cuticle (34.6%) < tomato cuticle (69.5%). Suberin in dewaxed potato periderm (24.8%) was almost same with the literature result (24.6%) determined by saponification in methanolic $NaOCH_3$ (*19*). The resemblance between cutin and suberin in chemical composition has been emphasized in many reports (*19−23*). Suberin and cutin are both aliphatic polyesters, and the substance classes detected after depolymerization consisted of linear long-chain aliphatic compounds and of aromatic compounds (*5, 19, 21, 23*). In addition, the aromatic domain of suberin in potato periderm was present only in traces and never amounted to more than 5% of the total (*20*). The relative magnitudes of the extractable lipids (waxes) and the depolymerizable lipids (cutin or suberin) in plant skins support the

Table 1. Relative Mass Fractions of the Potato Periderm and Fruit Cuticles and Their Elemental Analysis and Atomic Ratios

plant	sample[a]	yield, % wt[b]	C, % wt	H, % wt	N, % wt	O, % wt[c]	H/C	(N + O)/C
potato	PP1	100	47.44	6.46	2.92	43.18	1.62	0.74
	PP2	86.6	48.46	6.23	2.98	42.33	1.53	0.71
	PP3	65.1	39.45	5.16	2.78	52.62	1.56	1.06
	PP4 (suberan)	21.2	49.42	5.44	2.23	42.92	1.31	0.69
	PP5	37.4	59.14	6.84	1.59	32.43	1.38	0.43
	PP6	45.1	61.65	7.54	1.36	29.45	1.46	0.38
	PW (wax)	13.4	67.54	9.78	1.29	21.39	1.72	0.25
	suberin[d]	21.5	75.76	9.47	3.61	11.17	1.49	0.15
	sugar[d]	43.9	36.91	5.45	3.76	53.87	1.76	1.18
grape	GC1	100	60.07	8.57	2.28	29.07	1.70	0.40
	GC2	74.9	55.86	7.92	2.75	33.47	1.69	0.49
	GC3	47.5	42.15	5.42	2.78	49.64	1.53	0.94
	GC4 (cutan)	16.0	56.50	6.03	1.36	36.10	1.27	0.50
	GW (wax)	25.1	77.61	11.24	0.43	10.72	1.73	0.11
	cutin[d]	27.4	79.63	12.24	2.69	5.43	1.83	0.08
	sugar[d]	31.5	34.88	5.11	3.50	56.51	1.75	1.30
tomato[e]	TC1	100	63.45	8.78	1.45	26.31	1.65	0.33
	TC2	93.5	63.33	8.66	1.29	26.71	1.63	0.33
	TC3	28.8	44.34	6.21	2.60	46.86	1.67	0.84
	TC5	70.4	69.41	9.45	0.45	20.69	1.62	0.23
	TC6	75.3	70.16	9.59	0.43	19.82	1.63	0.22
	wax[d]	6.5	65.12	10.55	3.75	20.58	1.93	0.29
	cutin[d]	69.5	71.81	9.75	0.71	17.73	1.62	0.19
	sugar[d]	24.0	43.91	6.27	4.23	45.59	1.70	0.86
apple[e]	AC1	100	69.57	10.04	0.84	19.55	1.72	0.22
	AC2	55.3	61.16	8.76	1.29	28.79	1.71	0.37
	AC3	20.7	42.61	5.85	2.79	48.75	1.64	0.92
	AC4 (cutan)	7.5	57.80	5.44	1.43	35.33	1.12	0.48
	AC5	41.7	67.06	9.12	0.39	23.43	1.62	0.27
	AC6	84.0	72.26	10.28	0.30	17.16	1.70	0.18
	AW (wax)	44.7	77.83	11.30	0.20	10.67	1.73	0.11
	cutin[d]	34.6	72.28	10.50	0.39	16.85	1.73	0.18
	sugar[d]	13.2	33.98	6.08	3.56	56.38	2.13	1.34

[a] PP: potato tuber periderm. GC: grape cuticle. TC: tomato cuticle. AC: apple cuticle. The number in the name of each peridermal or cuticular fraction is identified as follows: "1" for bulk periderm or cuticle, "2" for dewaxed, "3" for nonsaponifiable, "4" for suberan or cutan, "5" for dewaxed-hydrolyzed, "6" for desugared. [b] The yields of each fraction were calculated to the percentage contents of correspondingly bulk sample (PP1, GC1, TC1 or AC1). [c] Oxygen content was calculated by the mass difference. [d] Calculated results based on mass balance. [e] The CHNO data for tomato and apple cuticular fractions were cited from our previous report (*13*).

conclusion that the depolymerizable lipids should be included to gain more accurate readings of plant lipid content besides waxes (*13*). Interestingly, the polysaccharide and the insoluble polymeric lipids (suberan) contents of potato periderim (below-ground) are higher than those of fruit cuticles (above-ground), following the order of potato periderm (43.9%) > grape cuticle (31.5%) > tomato cuticle (24.0%) > apple cuticle (13.2%) for polysaccharide content, and potato periderm (21.2%) > grape cuticle (16.0%) > apple cuticle (7.5%) > tomato cuticle (0%) for cutan or suberan.

The distinct chemical composition results in different elemental characteristics of bulk fruit cuticles and potato periderm (see **Table 1**). The percentage content of carbon in bulk potato periderm (PP1, 47.44%) is less than that of GC1 (60.07%), TC1 (63.45%) and AC1 (69.57%), while PP1 exhibits the highest oxygen content (43.18%) following the order of GC1 (29.07%) > TC1 (26.31%) > AC1 (19.55%). Therefore, for the tested plant skins, the polarity indices [(N + O)/C] decrease with the sequence of PP1 (0.74) > GC1 (0.40) > TC1 (0.33) > AC1 (0.22), which is positively related to the sugar content ($y = 0.0172x - 0.0641$, $R^2 = 0.929$, see **Figure 1**), confirming that sugar component is the main polar contributor in plant cuticles and periderm. For example, the potato periderm exhibits the highest polarity among the tested bulk plant skins because the

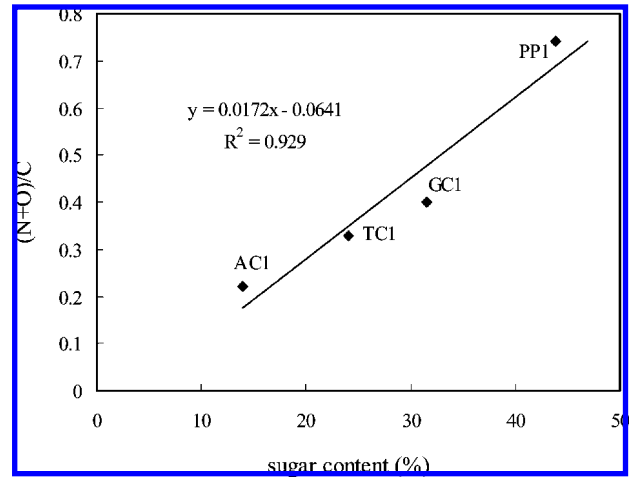

Figure 1. Relationship between polarity index [(N + O)/C] and polysaccharide content in bulk fruit cuticles and periderm. AC1: apple bulk cuticle. TC1: tomato bulk cuticle. GC1: grape bulk cuticle. PP1: potato bulk periderm.

polysaccharide is the main chemical component in potato periderm (43.9%). After being dewaxed and depolymerized, the nonsaponifiable fractions (PP3 and GC3) presented the highest polarity [(O + N)/C = 1.06 and 0.94] among the potato peridermal fractions and the grape cuticular fractions, respectively. The nonsaponifiable−nonhydrolyzable fraction (PP4 or GC4) showed the highest aromaticity (H/C = 1.31 vs 1.27) in comparison with other corresponding fractions (H/C = ∼1.6−1.7). These observations were consistent with the apple and tomato cuticular fractions (*13*). The H/C ratio of isolated waxes of potato periderm (PW) was similar to waxes in grape cuticle (GW), i.e., 1.72 vs 1.73, consistent with the value of wax in apple (AW, 1.73), which suggested that the amounts of aliphatic fractions in these fractions were significantly higher than aromatic fractions (*20*). The polarity indices [(O + N)/C] of sugar and wax component in grape cuticle were 1.30 and 0.11, approaching those in apple cuticle (1.33 and 0.11). Cutin of grape cuticle exhibited the lowest polarity [(O + N)/C, 0.08] in comparison with that in potato periderm (0.15), apple cuticle (0.18), and tomato cuticle (0.19). The polarities of all sugar-free fractions including GC4, PP4, PP5, and PP6 were much lower than their origin fractions, i.e., GC3, PP3, PP2, and PP1, respectively. The distinct chemical compositions and elemental characteristics regulate sorption properties of plant skins including above-ground and below-ground parts, and then favor to elucidate the role of chemical components (waxes, cutin/suberin, cutan/suberan, and polysaccharide) in sorption behavior of plant cuticle and periderm.

Sorption Results. Sorption of phenanthrene to three bulk fruit cuticles (GC1, AC1 and TC1) and potato periderm (PP1), along with their isolated fractions (GC2−GC4, AC2−AC6, TC2−TC6, PP2−PP6, GW, AW and PW), were conducted. Isotherms fit well to the Freundlich equation, and the regression parameters are listed in **Table 2**. Sorption coefficients (K_d and K_{oc}) and K_{oc}/K_{owc} ratios were also calculated in **Table 2**, where the K_{owc} is the carbon-normalized K_{ow} ($K_{owc} = K_{ow}/f_{oc}$, where f_{oc} is the percentage of carbon content of octanol, i.e., 73.8%).

Phenanthrene Sorption to Bulk Fruit Cuticles and Potato Periderm. Sorption isotherms of bulk fruit cuticles (AC1, TC1, and GC1) and potato periderm (PP1) are presented in **Figure 2**. Isotherms for GC1, AC1 and TC1 were linear, while PP1 showed a relatively nonlinear isotherm (Freundlich *N* value of 0.90) due to its higher polarity. The cuticle (periderm)/water partition coefficient (K_{cw} or K_{pw}) is defined as the ratio of the

Table 2. Sorption Regression Parameters of Phenanthrene by Peridermal and Cuticular Fractions, and Their Sorption Coefficients (K_d and K_{oc})

		Freundlich regression parameters[b]							
plant	sorbent [a]	log K_f	N	R^2	K_d (mL/g) [c]	linear R^2	K_{oc} (mL/g)	K_{oc}/K_{owc} [d]	n [e]
potato	PP1	4.117 ± 0.020	0.904 ± 0.010	0.998	16222 ± 183	0.998	34195	0.90	19
	PP2	4.260 ± 0.020	0.953 ± 0.011	0.998	19732 ± 361	0.994	40718	1.07	20
	PP3	3.221 ± 0.037	0.878 ± 0.022	0.990	1934 ± 21	0.998	4902	0.13	20
	PP4	3.993 ± 0.036	0.860 ± 0.018	0.993	12628 ± 376	0.986	25552	0.67	18
	PP5	4.375 ± 0.053	1.016 ± 0.030	0.986	21713 ± 278	0.997	36715	0.97	20
	PP6	4.403 ± 0.042	1.029 ± 0.023	0.993	22626 ± 539	0.990	36701	0.97	19
	PW	4.105 ± 0.013	1.013 ± 0.008	0.999	12575 ± 185	0.996	18619	0.49	20
grape	GC1	4.607 ± 0.042	1.066 ± 0.021	0.994	34319 ± 692	0.993	57132	1.51	19
	GC2	4.666 ± 0.037	1.076 ± 0.023	0.993	38645 ± 521	0.997	69182	1.83	20
	GC3	3.551 ± 0.015	0.986 ± 0.012	0.998	3463 ± 61	0.995	8216	0.22	20
	GC4	4.198 ± 0.013	0.859 ± 0.008	0.998	18572 ± 329	0.994	32871	0.87	20
	GW	4.422 ± 0.037	0.878 ± 0.021	0.991	34988 ± 906	0.989	45082	1.19	20
tomato	TC1	4.739 ± 0.096	1.093 ± 0.045	0.980	40747 ± 966	0.992	64219	1.69	17
	TC2	4.802 ± 0.071	1.053 ± 0.032	0.987	54836 ± 725	0.997	86588	2.28	18
	TC3	3.563 ± 0.022	0.999 ± 0.013	0.997	3811 ± 104	0.985	8595	0.23	20
	TC5	4.935 ± 0.072	1.017 ± 0.030	0.988	87898 ± 990	0.998	126636	3.34	18
	TC6	4.881 ± 0.066	0.967 ± 0.027	0.988	89518 ± 1829	0.993	127591	3.37	19
apple	AC1	4.709 ± 0.059	0.996 ± 0.026	0.988	54017 ± 576	0.998	77644	2.05	19
	AC2	4.847 ± 0.083	1.075 ± 0.037	0.988	57022 ± 924	0.996	93234	2.46	18
	AC3	3.242 ± 0.026	0.949 ± 0.016	0.995	1835 ± 29	0.995	4307	0.11	20
	AC4	4.271 ± 0.027	0.842 ± 0.014	0.995	20404 ± 418	0.992	35301	0.93	20
	AC5	5.016 ± 0.046	1.041 ± 0.023	0.993	87647 ± 1161	0.997	130699	3.45	19
	AC6	4.767 ± 0.031	0.962 ± 0.016	0.996	65758 ± 1176	0.995	91002	2.40	20
	AW	4.744 ± 0.034	0.923 ± 0.016	0.996	63806 ± 1293	0.994	81981	2.16	18

[a] The meaning for the sorbent name was presented in **Table 1**. [b] The Freundlich parameters (K_f and N) were calculated using the logarithmic form of the equation $Q = K_f C_e^N$, where Q is the amount sorbed per unit weight of sorbent, mg/kg; C_e is the equilibrium concentration, mg/L; K_f [(mg/kg)/(mg/L)^N] is the Freundlich capacity coefficient; and N (dimensionless) describes the isotherm curvature. R^2 is regression coefficient. [c] K_d is the sorption coefficient ($K_d = Q/C_e$), calculated from the slope of linear equation. [d] K_{oc} is the carbon-normalized sorption coefficient ($K_{oc} = K_d/f_{oc}$), and K_{owc} is the carbon-normalized octanol−water partition coefficient of phenanthrene (K_{owc} = 37900). [e] n is the number of sorption data.

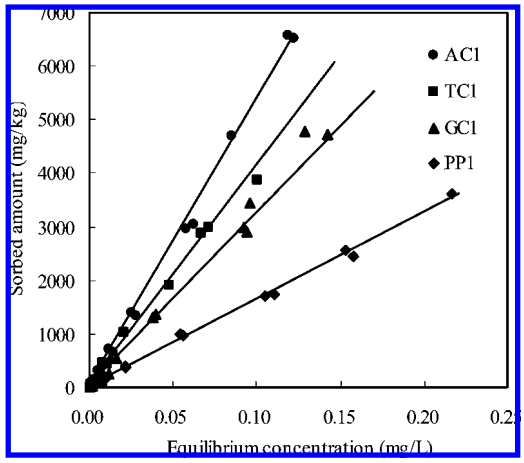

Figure 2. Sorption isotherms of phenanthrene by bulk fruit cuticles and potato periderm. AC1: apple bulk cuticle. TC1: tomato bulk cuticle. GC1: grape bulk cuticle. PP1: potato bulk periderm.

equilibrium concentration in the cuticle (periderm) to the equilibrium concentration in the aqueous phase, calculated from the slope of the linear sorption isotherms (i.e., K_d of GC1, AC1, TC1 and PP1, list in **Table 2**). Cuticle/water partition coefficients (K_{cw}) are useful to evaluate the efficiency of pesticides application and interpret foliar uptake and accumulation of many organic contaminants from aqueous solutions which appear, for instance, due to wet deposition by fog or rain (*1*−*3*). Periderm/water partition coefficient (K_{pw}) is a significant parameter for potato tuber, as the uptake of HOCs into potatoes is most likely via diffusion through the periderm (*24*). Based in **Figure 2** and **Table 2**, sorption magnitude of phenanthrene are in the order of potato periderm (PP1, 16222 mL/g) < grape cuticle (GC1, 34319 mL/g) < tomato cuticle (TC1, 40747 mL/g) < apple cuticle (AC1, 54017 mL/g), opposite to the polarity order of these biopolymers. The calculated ratios K_{oc}/K_{owc} for three cuticles were all larger than one unity (see **Table 2**), suggesting that these biopolymers were more powerful medium for HOCs than octanol. However, K_{oc}/K_{owc} for potato periderm was less than unity (0.90), much lower than that of fruit cuticles, by factors between 2.12 and 3.33. Periderm/water partition coefficient (K_{pw}) of potato periderm (1.62×10^4 mL/g) is close to the root concentration factor (RCF) for phenanthrene by maize plants (1.8×10^4 mL/g, (*16*)).

Sorption variations among different cuticles and periderm cannot be explained by the extractable lipids (waxes) which were widely used to predict plant uptake ((*17*) and therein), and are also unable to be accounted for the depolymerizable lipids (cutin or suberin) alone, see **Figure 3A**. Linear correlation K_d with the sum content of waxes and cutin/suberin is observed (linear $R^2 = 0.89$), and correlation K_d with the sum content of waxes + cutin/suberin + cutan/suberan exhibits high linear (linear $R^2 = 0.99$), presented in **Figure 3A**. As mentioned above, the sorption variation was due to polarity differences of the sorbents, which were governed by the sugar contents. Therefore, the K_d values are negatively and linearly correlated with the sugar content of bulk plant skins, demonstrated in **Figure 3B**. For example, the relative lowest sorption coefficient of potato periderm was attributed to its highest polarity [(N + O)/C = 0.74], contributing the highest sugar content (43.9%).

Phenanthrene Sorption to the Isolated Cuticular and Peridermal Fractions. Selected sorption isotherms of the fruit cuticular and potato peridermal fractions are presented in **Figure 4**. The isotherms of dewaxed-fractions were close to bulk cuticles/periderm, and the isotherms of dewaxed-hydrolyzed fractions were approximate to desugared-fractions, hence the isotherms of dewaxed-fractions and dewaxed-hydrolyzed fractions are not presented in **Figure 4** for clear demonstration. Sorption isotherms by bulk fruit cuticles of tomato, apple and

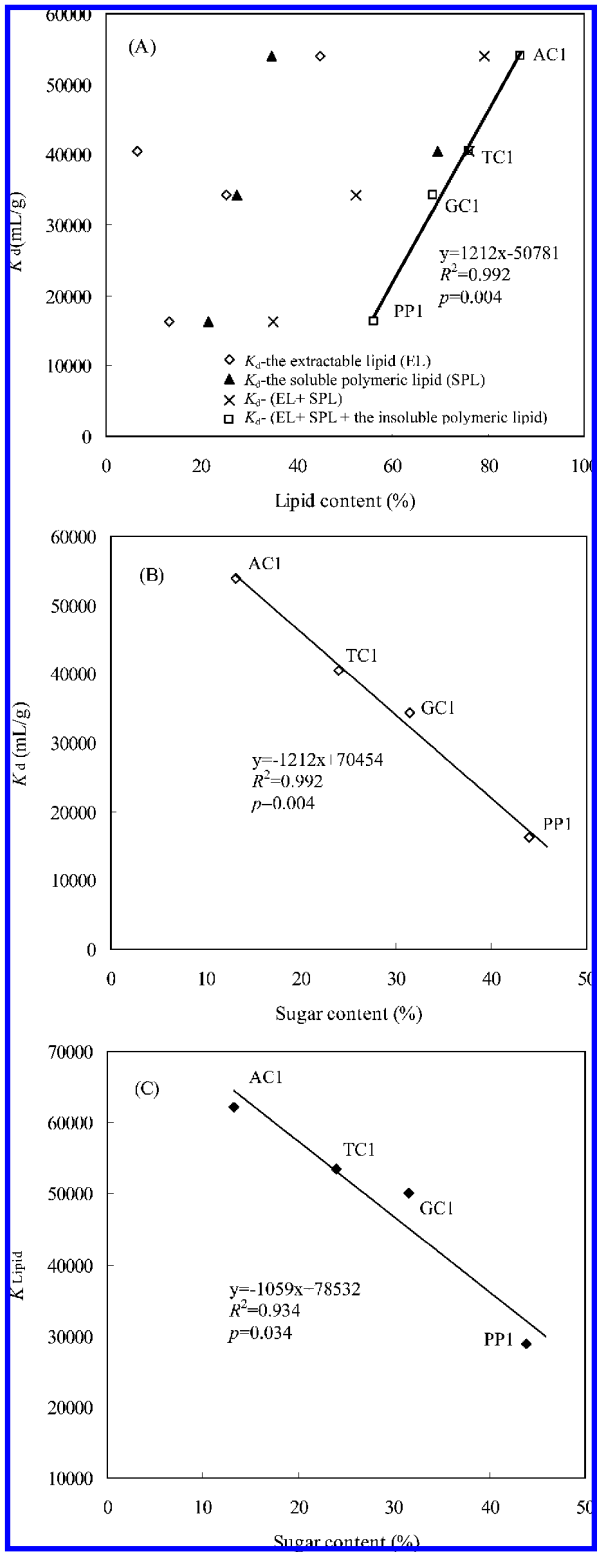

Figure 3. Correlations of K_d and K_{lipid} with chemical compositions of fruit cuticles and potato periderm. (**A**) K_d ~ lipid contents. (**B**) K_d ~ sugar contents. (**C**) K_{lipid} ~ sugar contents. $K_{lipid} = K_d/f_{lipid}$, where K_d is the sorption coefficient, f_{lipid} is the total lipid content including the extractable lipids, the soluble polymeric lipids (cutin or suberin), and the insoluble polymeric lipids (cutan or suberan). AC1: apple bulk cuticle. TC1: tomato bulk cuticle. GC1: grape bulk cuticle. PP1: potato bulk periderm.

grape were relative linear (Freundlich $N = 1.00$), suggesting the sorption was dominated by the partition process. To the sorption properties of phenanthrene by fruit cuticular fractions, several conclusions are drawn: (i) sorption coefficients (K_d) appreciably increased after wax removal (TC2/TC1 = 1.35; AC2/AC1 = 1.06; GC2/GC1 = 1.13); (ii) cutin (polymeric lipids) is the dominant sorption medium of the cuticle fractions, and K_d value reduced significantly after cutin was removed by saponification (TC3/TC2 = 0.07; AC3/AC2 = 0.03; GC3/GC2 = 0.09); (iii) K_d values increased after acid hydrolysis, and sorption capacity of nonsaponifiable fractions (TC3, AC3, and GC3) was the lowest; (iv) isotherms of cutan components (AC4 and GC4) exhibited high nonlinearity (Freundlich N values of 0.84 and 0.86, respectively) due to their higher aromaticity. These observations were consistent with the previous reports (*13*).

Similar to the nonsaponifiable biopolymers (i.e., cutan) in plant cuticles, suberan (PP4) presented the highest nonlinearity (Freundlich N value of 0.86). The nonlinearity of suberan and cutan may be attributed to the condensed domains in the periderm and cuticles (relative high content of aromatic moieties, H/C), which offered adsorption sites for phenanthrene (*7*). The affinity of the extractable lipids of periderm (K_d = 12575 mL/g) was a little lower than bulk potato periderm (16222 mL/g). The K_d value of the periderm increased slightly (PP2/PP1 = 1.22) after removal of waxes. The absence of suberin monomer sharply decreased the K_d value (PP3/PP2 = 0.10). These phenomena indicate that the deploymerizable lipids (i.e., suberin) rather than the extractable lipids (i.e., waxes) in periderm play a significant role in sorption of HOCs. The sorption capability of the nonsaponifiable fraction (PP3) with phenanthrene was the lowest (K_{oc}/K_{owc} = 0.13) due to its highest polysaccharide content. Sorption coefficient (K_d) of the nonsaponifiable faction (PP3) increased greatly after sugar removal (PP4/PP3 = 6.53), while K_d values of PP1 and PP2 just slightly increased (PP6/PP1 = 1.40; PP5/PP2 = 1.10) after acid hydrolysis. Consequently, sorption variations among the isolated fruit cuticular fractions (above-ground parts) were similar to those of the isolated potato peridermal fractions (below-ground parts).

The Role of Chemical Compositions in Sorption of Plant Skins. *(i) The Soluble Lipids.* Sorption isotherms to waxes of apple and grape cuticles as well as potato periderm are presented in **Figure 5**. From **Figure 5** and **Table 2**, the relative magnitudes of sorption capabilities (K_d) of the isolated waxes were in the order of potato periderm (PW, 12575 mL/g) < grape cuticle (GW, 34988 mL/g) < apple cuticle (AW, 63806 mL/g). Similarly, the differences in K_d values were also attributed to the different polarity and carbon content. Waxes, the soluble lipids extracted by organic solvents, have been widely used to predict for plant accumulation of organic contaminants due to their high affinities with organic contaminants in comparison with carbohydrates (*17*, *18*). Based on this presumption, sorption coefficients (K_d) for bulk fruit cuticles and potato periderm should be close to $f_{wax} \times K_{wax}$, i.e., 28521 L/mg (apple cuticle), 8782 L/mg (grape cuticle) and 1685 L/mg (potato periderm). However, these data were much lower than the real situation (**Table 3**, and the dashed lines in **Figure 4**), indicating that the soluble lipid is not the main sorption medium for organic contaminants, and there must be other powerful sorption mediums besides waxes. Therefore, the plant accumulation of organic contaminants would be seriously under-predicted if only by the soluble lipid content (*13*). Indeed wax/water partition behavior has been extensively investigated with regard to its action as a potential barrier to the penetration of pesticides and pollutants. Generally, wax/water partition coefficients (K_{ww}) were found to be significantly smaller than the cuticle/water partition coefficients (K_{cw}) and K_{ow} (ref *3* and therein). The relative lower sorption capacity of waxes was attributed to its

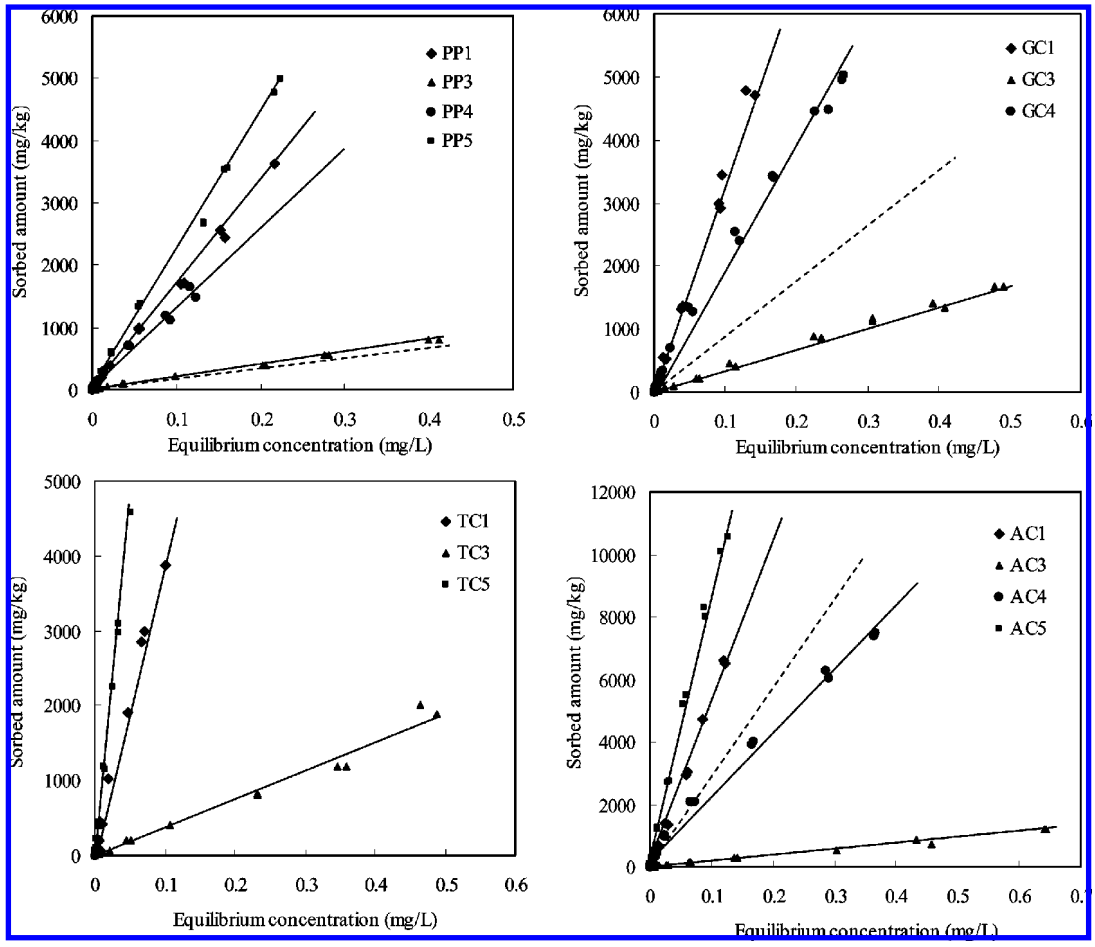

Figure 4. Selected sorption isotherms of phenanthrene by potato peridermal and fruit cuticular fractions. AC: apple cuticular fractions. TC: tomato cuticular fractions. GC: grape cuticular fraction. PP: potato peridermal fractions. The dashed line is the predicted sorption isotherm of bulk sample based on K_d of waxes and percentage content of waxes.

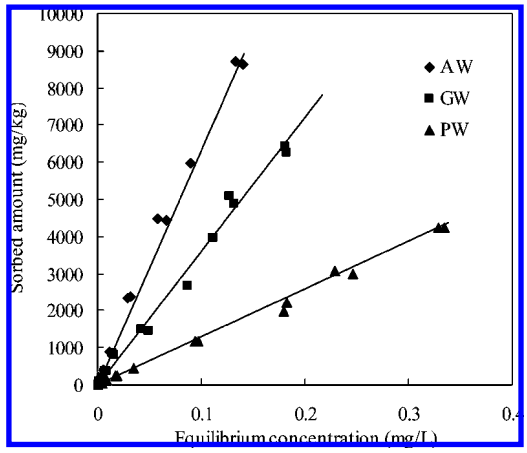

Figure 5. Sorption isotherms of phenanthrene by the isolated waxes of fruit cuticles and potato periderm. AW: apple cuticular waxes. GW: grape cuticular waxes. PW: potato peridermal waxes.

solid and partially crystalline nature at room temperature which reduced the accessibility of sorbents for organic contaminants (*3*, *13*).

(ii) The Depolymerizable Lipids. Cutin has been demonstrated to be most powerful sorption medium due to the amorphous nature, and suberin was assumed to have a similar dominant sorption capacity due to the similar chemical composition. It is hard to investigate the sorption behavior of the pure cutin in apple and grape cuticles as well as suberin in potato periderm directly because the cutan (suberan) component could not be removed without disturbing the depolymerizable lipids by enzymatic or chemical methods. To assess the sorption properties of the depolymerizable lipids (i.e., cutin and suberin), their sorption coefficients (K_d) were estimated through mass balance, i.e., $K_{d,2} \times f_2 = K_{d,3} \times f_3 f + K_{d,SPL} \times f_{SPL}$, where $K_{d,2}$, $K_{d,3}$, and $K_{d,SPL}$ are sorption coefficients of the dewaxed fraction, the nonsaponifiable fraction and the soluble polymeric lipids (SPL),

Table 3. Relative Contribution of Waxes, Cutin/Suberin, and Cutan/Suberan to the Sorption of Phenanthrene by Bulk Fruit Cuticles and Potato Periderm[a]

		RC, %[c]			
plant	K_d, mL/g[b]	waxes	cutin/suberin	cutan/suberan	∑ RC, %[d]
potato	16222 ± 183	10.39	97.58	16.50	124
grape	34319 ± 692	25.63	79.52	8.64	114
tomato	40747 ± 966	—[e]	124	—[e]	—[e]
apple	54017 ± 576	52.80	57.67	2.83	113

[a] Waxes are the extractable lipids by organic solvents. Cutin/suberin are the solubly polymeric lipids by saponification. Cutan/suberan are the insoluble polymeric lipids. Cutin and cutan are for cuticular composition of above-ground fruits (grape, tomato, and apple), while suberin and suberan are for the periderm composition of below-ground tissue of plant (potato). [b] Sorption coefficients ($K_d = Q/C_e$) were calculated from experimental isotherms of bulk cuticles and periderm. [c] The relative contribution (RC) of each component was calculated by the ratio of the $f_i K_{d,i}$ to K_d of bulk cuticle or periderm. The symbol i represents wax, cutin/suberin and cutan/suberan; f_i is the percentage of i component in bulk sample (see **Table 1**); $K_{d,i}$ is the sorption coefficient of i component. [d] ∑ RC is the sum of RC of waxes, cutin/suberin, and cutan/suberan. [e] The data are not presented due to lack of experimental results.

respectively; The f_2, f_3, and f_{SPL} are their corresponding contents in the bulk cuticle or periderm, and $f_{SPL} = f_2 - f_3$ (*13*), presented in **Table 1**. The calculated results are as follows: 72193 mL/g for cutin in tomato cuticle, 73623 mL/g for suberin in potato periderm, 90039 mL/g for cutin in apple cuticle, and 99636 mL/g for cutin in grape cuticle. As expectation, these data were in a similar range and much higher than the K_{ow} value of phenanthrene (28840). Contributions of the depolymerizable lipids to sorption of bulk cuticles (periderm) were much higher than those of waxes (see **Table 3**). Note that the calculated K_d for the tomato cutin (TC5) was 72,421 mL/g, whereas the experiment value was 87,939 mL/g (see **Table 2**). This difference was attributed to the finding, reported by Chefetz (*6*), that some of the cuticle and periderm fractions are intermediate between physical and chemical mix. The higher sorption capability of tomato cutin (87,939 mL/g) was suppressed by the coexisting components (e.g., sugar) in the dewaxed tomato cuticular fractions (TC2), which results in the lower calculated K_d values (72,421 mL/g) than the direct experiment value.

(iii) The Nonsaponificable Lipids. Consistent with the homologous chemical compositions, K_{oc} values of the nonsaponifiable lipids (i.e., cutan and suberan) were similar: AC4 (35301 mL/g), GC4 (32871 mL/g) and PP4 (25552 mL/g). The sorption differences of these biopolymers were also attributed to their differences in polarity: AC4 [(N + O)/C = 0.48] < GC4 (0.50) < PP4 (0.69). A linear negative relationship exists between K_{oc} values and the polarities of these biopolymers (figure not shown). However, these data were lower than the purified cutan fraction in the leaves of *A. americana* (91200 mL/g, (*12*)). Contributions of nonsaponicable lipids to sorption of bulk cuticles/periderm) were very low (see **Table 3**), due to the small contents.

(iv) Polysaccharide. As mentioned above, all nonsaponifiable fractions (PP3, GC3, TC3, and AC3) presented the lowest sorption capacity, due to their highest sugar contents. In a plot of K_{oc} values of bulk cuticle/periderm versus their sugar contents, a negative linear relationship was observed, suggesting the negative role of polysaccharide in organic contaminants accumulation. The poor affinities of polysaccharides with HOCs have been widely reported in previous studies (*11*, *25*−*29*). The sorption coefficients of the cellulose with HOCs were much lower than other natural organic matter, suggesting that carbohydrates were not important in sorption of HOCs because of its high polarity (*17*, *18*, *25*). Chen et al. (*11*) reported a negative linear relationship between sorption coefficients (K_{oc}) and sugar contents in the isolated tomato cuticular fractions, and demonstrated the negative role of sugar in sorption of HOCs. Wang et al. (*29*) found the sorption capabilities of cellulose with HOCs was much lower than that of lignin. Jonker (*28*) investigated the sorption of a series of PAHs (log K_{ow} range of 4.6−7) to cellulose, and found that the affinity of PAHs for cellulose appeared to be about 400 times lower than that of octanol. In this study, a negative linear trend of K_{oc} with polarity (N + O/C) in bulk cuticle/periderm (PP1, GC1, TC1 and AC1) was also obained (linear $R^2 = 0.98$), further confirming the regulating role of polarity in sorption of organic contaminants.

The total sorption contributions of all lipids (∑ RC) in **Table 3** were all higher than 100%, indicating that the accessibility of each cuticle component with organic contaminants is restricted. There are two reasons: (1) the high crystalline phase of soluble lipids (i.e, waxes) reduces the effective accessibility of polymeric lipids (*13*); (2) the cuticle fractions are not only physical mixed but some of them also are intermediate between physical and chemical mix (*6*), which impacts the accessibility of these lipids to the organic contaminant. On the other hand, the over 100% ∑ RC of lipids is a good evidence that these lipid components are the main sorption contributors in cuticle and periderm. Sorption coefficients (K_d) of bulk cuticle/periderm normalized by lipids were calculated by $K_{lipids} = K_d/f_{lipid}$, where f_{lipid} represents the mass content of the total lipids including waxes, depolymerizable insoluble lipids and nonsaponifiable lipids. Interestingly, a linear negative relationship between K_{lipid} values and the sugar contents of the cuticle/periderm was observed [**Figure 3C**], indicating sugar would restrict the sorption efficacy of lipids. Sugar functions in a dual role in plant accumulation of organic contaminants: it functions as a weak sorption medium and then restricts the sorption capacity of other powerful sorptive zones (such as lipids). Based on the linear equation in **Figure 3B**, it is practical to predict sorption of plant cuticle/periderm of different species with their polysaccharide content, determined by acid hydrolysis.

In summary, the distinct sorption properties of fruit bulk cuticles (above-ground) and potato periderm (below-ground) are attributed to their different compositional characteristics. The roles of the extractable lipids (waxes), the soluble polymeric lipids (cutin/suberin), the insoluble polymeric lipids (cutan/suberan) and the polysaccharide in sorption of plant skins are clearly elucidated. The cutin/suberin rather than waxes serve as the main component to control affinity of bulk cuticle/periderm with HOCs, but the K_d values of skins are linearly correlated with the total lipid contents of plant cuticle/periderm. Polysaccharide plays a negative role as a sorption medium for its obviously poor affinity with HOCs and restriction effect which suppresses the high sorption ability of other powerful sorptive regions in cuticle/periderm (such as lipids). The significantly lower sorption of the bulk periderm (below-ground) than the cuticle (above-ground) is explained by the former having higher polysaccharide and lower soluble polymeric lipids.

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