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Role of Chemical Components of cork on Sorption of Aqueous Polycyclic Aromatic Hydrocarbons

Olivella, M. À.[1*], Fernández, I.[2], Cano, L.[2], Jové, P.[2] and Oliveras, A.[2]

[1] University of Girona, Department of Chemistry, Campus Montilivi s/n, 17071 Girona,Spain

[2] Catalan Cork Institute, C/Miquel Vincke Meyer 13, 17200 Palafrugel, Girona, Spain

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ABSTRACT: In order to know the environmental behaviour of toxic pollutants it is fundamental to understand the role of chemical components of a material on sorption of such pollutants.In this study, the sorption of a mix of polycyclic aromatic hydrocarbons (PAHs) by cork fractions (i.e. raw cork (CF), free extractive cork (FEF) and nonsaponifiable (DESF)) has been investigated to better understand the role of biopolymers and extractable fraction of cork on their sorption behaviour. All samples were analyzed through elemental analysis and were examined using Fourier transform infrared spectroscopy. After removing the extractable fraction and the suberin from the cork, the sorption capacities (K_{oc}) of FEF and DESF exhibited mean reductions of 70% and 30% respectively. In addition, the sorption results of three pairs of cork samples with different chemical content confirm that the extractable fraction serves as the major sorption medium for PAHs. Considering only low molecular weight PAHs positive correlations between K_{oc} with K_{ow} (R^2=0.70) and F number (R^2=0.65) were found, showing that these parameters are involved in this adsorption process.

Key words: Cork, Biopolymers,Extractable fraction,Organic pollutants, PAHs

INTRODUCTION

The widespread occurrence of polycyclic aromatic hydrocarbons (PAHs) has become a serious environmental concern. Although they have a natural origin (i.e. volcanic eruptions and forest fires), nowadays anthropogenic combustion processes (i.e. traffic, industry, energy production, heating houses) can be considered as the main source of PAHs in the environment (Baek *et al.*, 1991; Mastral *et al.*, 2000). PAHs are listed in the European Union list of priority pollutants (WFD, 2000) because of their hazardous nature and high ongoing emission loadings.The environmental fate of toxic organic pollutants such as PAHs is strongly influenced by the sorption process: the sorption of pollutants can reduce the exposure to them and the environmental risks to organisms. Biopolymers including cellulose, hemicellulose, lignin and suberin are ubiquitous in the environment and are the main precursors of the plants (Gosselink *et al.*, 2004; Kolattukudy, 1980; Kurita, 2001). Because of this, understanding the role of the chemical components on the sorption of these pollutants is essential to the accurate assessment of their environmental behavior. Moreover, in order to develop sustainable technologies for soil and water remediation, the investigation of new adsorbents materials able to retain or immobilize pollutants is fundamental.

Cork is the bark of the cork oak tree (*Quercus suber* L) and it is a natural, renewable and biodegradable raw material. As trees are not cut down, cork oak harvesting is an environmentally friendly process: the bark is stripped every 9 to 12 years and the trees live on average between 100 and 300 years.Cork is mainly composed of suberin and lignin (hydrophobic biopolymers) and polysaccharides (cellulose and hemicellulose) with a hydrophilic character (Pereira, 2007). The extractives of cork include n-alkanes, n-alkanols, waxes, triterpenes, fatty acids, glycerides, sterols, phenols and polyphenols. They are classified in two groups: aliphatics or commonly named cork waxes that are solubilised with low-polarity solvents (e.g. hexane, dichlorometane. chloroform) and phenolics extracted by polar solvents (e.g. ethanol and water) (Pereira, 2007). This heterogeneous chemical composition of cork provides numerous bonding possibilities for a wide range of pollutants. This confers cork unique characteristics and makes it a very interesting natural material to investigate. To date, sorbent qualities of raw cork have not been

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*Corresponding author E-mail:angels.olivella@udg.edu extensively investigated (Domingues *et al.*, 2005; Domingues *et al.*, 2007; Olivella *et al.*, 2011).

The literature contains several references to the effectiveness of biomaterials as sorbents of PAHs: Boving and Zhang (2004) and Huang *et al.* (2006) used aspen wood fibers; Wang *et al.* (2007) used commercial biopolymers; Wang and Xing (2007) used biopolymer-derived chars; Zeledón-Toruño *et al.* (2007) used a low rank coal. Although these past studies indicate a good adsorption capacity for the most hydrophobic organic pollutants and lignin is thought to be the main compound responsible for the highest adsorption capability, little is known about the distinct roles of biopolymers and extractable fraction on sorption of PAHs. A recent report indicates that suberin could play a significant role on the sorption of phenanthrene by root tissues (Chen and Schnoor, 2009) but more studies are needed to verify this suggestion. Li and Chen (Li and Chen 2009) focused their study on determining the roles of extractable lipids, suberin, suberan in sorption of phenanthrene by plant skins.

This is the first study focused on elucidating the role of chemical components of cork (i.e. suberin, lignin, polysaccharides and extractable fraction) on the sorption organic pollutants (i.e. PAHs). The purpose of this study is to examine the sorption by raw cork and isolated cork fractions of a mix of thirteen PAHs. In addition, all fractions were analyzed by elemental analysis to calculate the polarity index (i.e. (O+N)/C) and were examined using Fourier transform infrared spectroscopy (FTIR). This, in conjunction with the sorption studies of six types of cork with different suberin, lignin, holocellulose and extractable fraction content (measured experimentally) will help us better understand the affinity of chemical components of cork on the sorption of PAHs. Correlations with sorption capacities (K_{oc}) and the properties of chemical contaminants (e.g. K_{ow} and F number) were also examined.

MATERIALS & METHODS

The remains supplied by a cork factory of cork strips, left over after stoppers had been punched out of them, have been used. The cork strips were cut into three sections with a hand saw: the back (the outermost bark), 6-10 mm thick; the cork (the middle part used for cork stoppers), 26-32 mm thick; and the belly, 3-5 mm thick. Each section was separately cut into small pieces (< 10 mm) and was milled in a ultra centrifugal mill ZM-200 (Retsch) and the granulometric fraction of 40-60 mesh (0.25-0.42 mm grain size) was used for the subsequent analyses. PAHs Mix (500 µg/mL in methylene chloride), containing acenaphthylene, anthracene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, chrysene, dibenz[a,h]anthracene, fluorene, indeno[1,2,3-cd]pyrene, phenanthrene, pyrene. 525 Fortification Solution (acenaphthene-d_{10}), [$^2H_{12}$] chrysene (chrysene-d_{12}) and [$^2H_{10}$] phenanthrene (phenanthrene-d_{10}) at 200 µg/mL were all purchased from (Bellefonte, PA, USA).

For standard solutions and batch experiments deionized water was used. Methanol was Super Purity grade from Romil (Cambridge). Solid phase microextraction (SPME) fibers of 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB) were supplied by Supelco (Bellefonte, PA, USA). The collection of aqueous samples of 18 mL was carried out using a glass lure tip syringe of 20 mL coupled to a stainless steel syringe needle (length 6 in., size 22 gauge) all supplied by Sigma Aldrich (St Louis, USA). Thirteen EPA PAHs were analyzed in this research. The low molecular weight compounds (LMW) were: ACE (acenaphthylene), FLU (fluorene), PHE (phenanthrene), ANT (anthracene) and PYR (pyrene); and high molecular weight compounds (HMW): BaA (benz(a)anthracene), CHR (chrysene), BbF (benzo(b)fluoranthene), BkF (benzo(k)fluoranthene), BAP (benzo(a)pyrene), IND (indeno(1,2,3-cd)pyrene), DBA (dibenz(a,h)anthracene) and BGP (benzo(ghi)perylene). Dry raw cork ground and sieved (0.25-0.42 mm) yielded the cork fraction (CF). Extractives were removed by successive Soxhlet extractions with dichloromethane (6 h), ethanol (8 h) and water (20 h). This procedure yielded the free extractive fraction residue (FEF) which was air-dried and kept for subsequent analysis.

To remove the suberin, the FEF was saponified using methanolysis for depolimerization (Pereira, 1988). A 1.5 g sample was refluxed with 250 mL of 3% $NaOCH_3$ in CH_3OH for 3 h, filtered and the residue refluxed again with 100 mL CH_3OH for 15 min. After filtration, the combined filtrates were acidified to Ph6 with 2M H_2SO_4 and evaporated to dryness in a rotating evaporator. This residue was suspended in 100 mL H_2O and extracted with 200 mL $CHC1_3$ three times. The combined extracts were dried over Na_2SO_4, filtrated, evaporated and weighed gravimetrically as suberin (SUB). The nonsaponifiable fraction is the desuberinized fraction (DESF). The amount of Klason lignin in the desuberinised material was determined gravimetrically after a standard acid hydrolysis (Tappi, 2002). The filtrate was used for determination of acid soluble lignin by UV measurement at 205 nm. Klason lignin and acid-soluble lignin were combined to give the total lignin content. Holocellulose was isolated from the desuberinized fraction by delignification for 2 h using the acid chlorite method (Wise *et al.*, 1946). The holocellulose content was determined after measuring the lignin content in holocellulose. All measurements were reported as a percentage of the original sample. Detailed chemical characterization of the three cork layers from different production areas has been investigated elsewhere (Jové *et al.*, 2011).

The C, H, N and S contents of cork fractions were determined using a Perkin Elmer EA2400 series II elemental Analyzer. Oxygen content was calculated by measuring the difference. The H/C, O/C, C/N, (O + N)/C atomic ratios were calculated. Limits of detection for N and S were 1.20% and 0.44%, respectively. FTIR spectra were obtained using KBr pellets and were recorded on a Galaxy 5000 FTIR spectrometer (Mattson Instrument Co., Madison, WI). All FTIR spectra were measured in the 3500-400/cm range by co-addition of 32 scans with a resolution of 4/cm.

Sorption experiments were conducted by the batch equilibrium technique. 0.3 g of cork was weighted into each 250 mL capacity Pyrex glass bottle and placed with 100 mL of aqueous solution of a PAH mix of varied concentration (1, 5, 10, 20, and 50 μg/l). The solutions were closed, wrapped with aluminium foil to prevent photo degradation and mixed with a "Vibromatic" oscillating shaker at 700 oscillations/min. After 1 h of equilibrium time, determined in a previous work (Olivella *et al.*, 2011), aqueous samples of 18 mL were collected and analyzed as described below (section 2.4). The amount of PAH sorbed was considered to be the difference between the initial PAH concentrations and the equilibrium concentrations. All sorption data were fitted to the Freundlich model according to the equation:

$$q = K_F C_{eq}^{\frac{1}{n}} \tag{1}$$

where q is the adsorbed amount (μg/g); C_{eq} is the equilibrium concentration of adsorbate in solution after adsorption (μg/l); K_F is an indication of the adsorbent capacity [(μg/g)/μg/l)]$^{1/n}$; and $1/n$ is a measure of the nature and strength of adsorption process or an indicator of the surface heterogeneity. To determine the constants n and the linear form of eq (1) was used. The plot of vs. give us the values of and from the slope and intercept, respectively. The distribution coefficient (K_d) is the ratio between the content of the substance in the sorbent and the mass concentration of the substance in the aqueous solution, under the test conditions, when adsorption equilibrium is reached. K_d values were calculated from the slope of the isotherms. The organic carbon normalized adsorption coefficient (K_{oc}**)** relates the K_d to the content of organic carbon of the soil sample (f_{oc}) according to the equation $K_{oc} = K_d/f_{oc}$. Duplicate experiments were performed.

With the aim to control the loss of PAHs onto the glass walls, three blanks were performed following the same procedure as the samples: (1) 100 mL of deionized water plus 1 μg/l PAHs; (2) 0.3 g of cork plus 100 mL of deionized water; and (3) 100 mL of deionized water. The results indicate that, at an initial concentration of 1 μg/L, the concentrations of PAHs in solution were less than 1%.

The extraction of PAHs and the GC-MS conditions were performed following the procedure described by Fernández *et al.* 2007. For the SPME extraction, 18 mL of de-ionised water in 20 mL vials, capped with PTFE-coated septa, were used. The fibers were immersed into the aqueous phase with agitation at 60$^{æ\%}$C for 60 min. After extraction, the fiber was thermally desorbed for 10 min into the liner of the GC injector port at 300$^{æ\%}$C. The splitless time was set at 4 min and desorption time at 10 min. GC was performed with a 6890N Agilent chromatograph equipped with a MPS2 Gerstel auto-sampler and coupled to a MS 5973N. The separation was achieved using an HP-5MS column (30m, 0.25mm, 0.25μm film thickness) (J&W Scientific, Folsom, CA, USA) and the GC oven program was: 50^{o}C (3 min), increased by 6^{o}C/min to 325^{o}C (held for 20 min). The carrier gas was Helium (99.999%) with a constant flow rate of 1 mL/min. The transfer line temperature was set at 300^{o}C and the ion source temperature at 250^{o}C. The mass spectrometer was operated in selected ion monitoring mode (SIM), detecting the following ion masses: 152, 166, 178, 202, 228, 252, 278, 276. The quantification of PAHs was based on comparisons of the areas for the monitored molecular ions to that of the internal standard, with calibration response curves generated from five different concentrations (0.05, 0.1, 0.5, 1, and 5 μg/L) of each target PAH. The calibration curves for the compounds were linear (r > 0.99) over the established range.

RESULTS & DISCUSSION

The yields and elemental compositions of the cork fractions are presented in Table 1. The study of the chemical composition of the selected raw cork samples reveals that suberin (41.3%) is the main structural component of the cell wall, followed by extractives (19.7%), lignin (13.4%), and holocellulose (7.4%). Lignin biopolymer, mainly composed of phenylpropane units, exhibits a more aromatic nature than suberin with a polyester structure composed of long chain fatty acids, hydroxyl fatty, and phenolic acids linked by ester groups (Pereira, 2007).

Table1. Relative yields of the cork fractions, their elemental analysis and atomic ratios

		Component distribution % mass				Elemental composition % mass			Atomic ratios		
Sample[a]	Yield[b] (%wt)	Extractives	Suberin	Total Lignin	Holocellulose	C	H	N	H/C	O[c]/C	(O + N)/C
CF	100	19.7	41.3	13.4	7.4	58.5	7.37	1.25	1.51	0.45	0.44
FEF	80.3	0	41.3	13.4	7.4	60.4	7.86	3.23	1.57	0.35	0.40
DESF	39.0	0	0	13.4	7.4	42.9	5.58	1.39	1.57	0.88	0.90
SUB	41.3	0	100	0	0	64.5	9.67	5.61	1.8	0.23	0.31

[a] CF: raw cork; removal of extractives from CF yielded free extractive cork (FEF); saponification of FEF produced nonsaponifiable fraction(DESF); the saponified fraction is the suberine (SUB).

[b] The yields were obtained in duplicate for each fraction and presented as average.

[c] Oxygen content was calculated by the mass difference.

The organic carbon content of SUB was the highest (64.5%), while C% of nonsaponifiable fraction (DESF) was the lowest (42.9%). The H/C ratios for CF, FEF and DESF were in the same order (~ 1.55), while SUB was higher (1.8). In this study the polarity ((O+N)/C) of the cork fractions was in the following order: DESF(0.9)< CF(0.44)< FEF(0.40)< SUB(0.31) (Table 1). These elemental composition data indicate that cork fractions were mainly aliphatic components with a wide range of polarities, which is in agreement with subsequent spectroscopic studies.

Fig. 1A shows a Fourier transformed spectrum of raw cork (CF). The peak at 3428/ cm indicates the presence of OH groups. The spectrum is dominated by the absorbance bands of suberin: two peaks at approximately 2925 and 2855/cm corresponding to asymmetric and symmetric vibration, respectively, of C-H in the olefinic chains and an intense band at 1738/ cm corresponding to the carbonyl C=O in aliphatic acids esters. The band at 1161/cm can also be attributed to the C-O-C of the ester groups in suberin. Through the epoxide group suberin also contributes to the 1262/ cm peak corresponding to C-O stretch, The bands at 1511/cm (vibration of C=C aromatic rings) and 814 (aromatic C-H out of plane deformations) are typical of guaiacyl lignin (Faix *et al.*, 1992).
The bands at 1101/cm and 1041/cm are characteristic of polysaccharides (CH and CO deformation). They have a relative smaller intensity.

During the saponification treatment, broken ester bonds corresponded to the removal of hydroxyl fatty acids. The FTIR spectrum of the desuberinized sample (DESF) is shown in Fig. 1B. It was dominated by polysaccharides (e.g. 1035/ cm) and ionized carboxyl groups –COO- (e.g. 1635/cm). This is also consistent with the increase of the O/C ratio in DESF sample (Table 1). Bands at 1161/cm and 1738/cm are characteristic of suberin; and their absence confirms its absence. The presence of aromatic structures in the nonsaponifiable fraction, usually used to monitor the presence of lignin (Hergert, 1971), is shown by the peaks at 1595/cm and 1505/cm. The pronounced band at 1368/cm is indicative of C-H deformation in guaiacyl lignin.

The FTIR spectrum of suberin is shown in Fig.1C. The strong bands at 2915/cm (νass C-H) and 2849/cm (νass C-H) together with those at 1463/cm and 1435/ cm (δ C-H) clearly indicate the dominant aliphatic nature of suberin. Ester moieties, produced by methanolysis of suberin chains at the corresponding ester functions, were characterized by the strong bands at 1708 (ν C=O) and 1252 (ν C-O-C). The band at 1635/cm may be attributed to C=C double bonds. These data are consistent with previous studies (Cordeiro *et al.*, 1998; Rocha *et al.*, 2001).

The sorption of PAHs by cork fractions (CF, FEF and DESF) were measured by batch sorption experiments. It was observed that variability between the duplicate sorption experiments was higher for the HMW PAHs (<18%) than for LMW PAHs (<10%). The isotherms fit the Freundlich equation ($0.83 < r < 1.00$) and the regression parameters are listed in Table 2. A precise comparison between K_F values is not possible because their units are different as a result of the nonlinearity. Therefore, the sorption coefficients (K_d and K_{oc}) were also calculated (Table 2). All the isotherms can be considered nonlinear because the n values were outside the $0.95<n<1.05$ range established by Pignatello *et al.* (2006); n values range from 1.1 to 2.4 for CF; from 1.2 to 2.1 for FEF and from 1.0 to 2.1 for DESF.(Fig.2).

Nonlinear isotherms have also been found for the sorption of several PAHs using aspen wood (Boving and Zhang, 2004); Spanish leonardite (Zeledón-Toruño *et al.*, 2007); black, carbon-free biopolymers (Huang *et al.*, 2007; Pignatello *et al.*, 2006; Wang and Xing, 2007); wooden chars of aspen wood (Huang *et al.*, 2006); wood chars (Wang *et al.*, 2006); as well as in soil humic acids (Kang and Xing, 2005; Xing, 2001); and in aliphatic-rich humin (Chefetz *et al.*, 2000). Previous studies also reported the nonlinearity of the nonsaponifiable fraction (n= 1.068) isolated from root tissue (Chen and Schnoor, 2009). The nonlinearity was

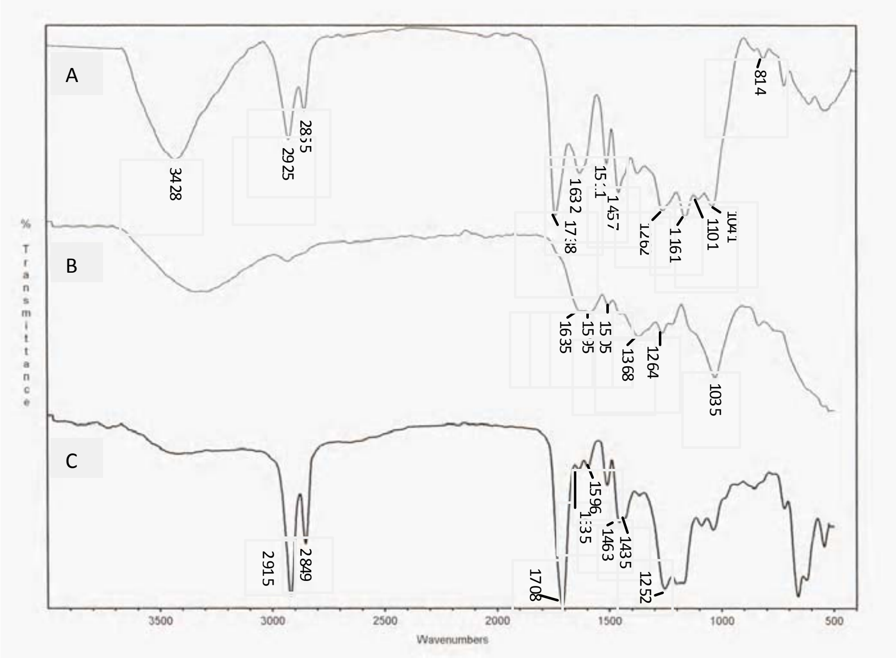


Fig. 1. Infrared spectra of (A) raw cork (B) nonsaponifiable fraction and (C) suberin

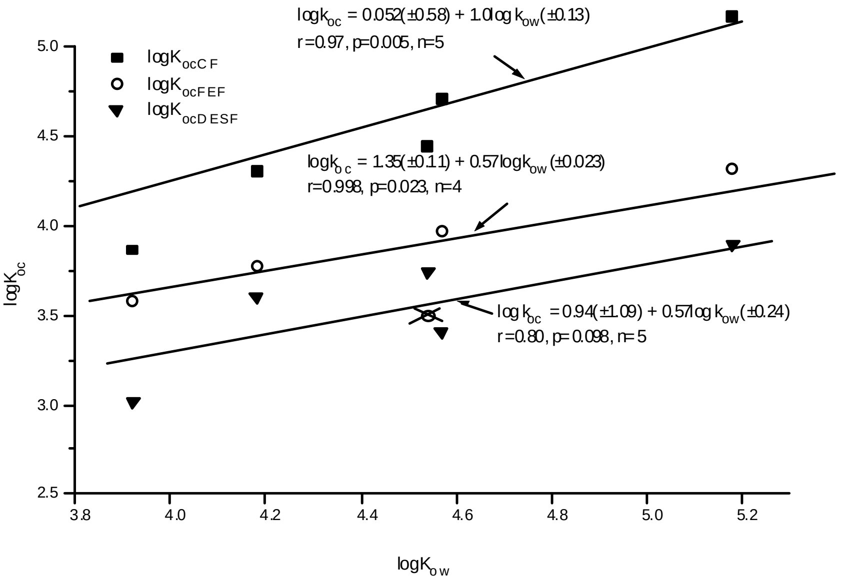
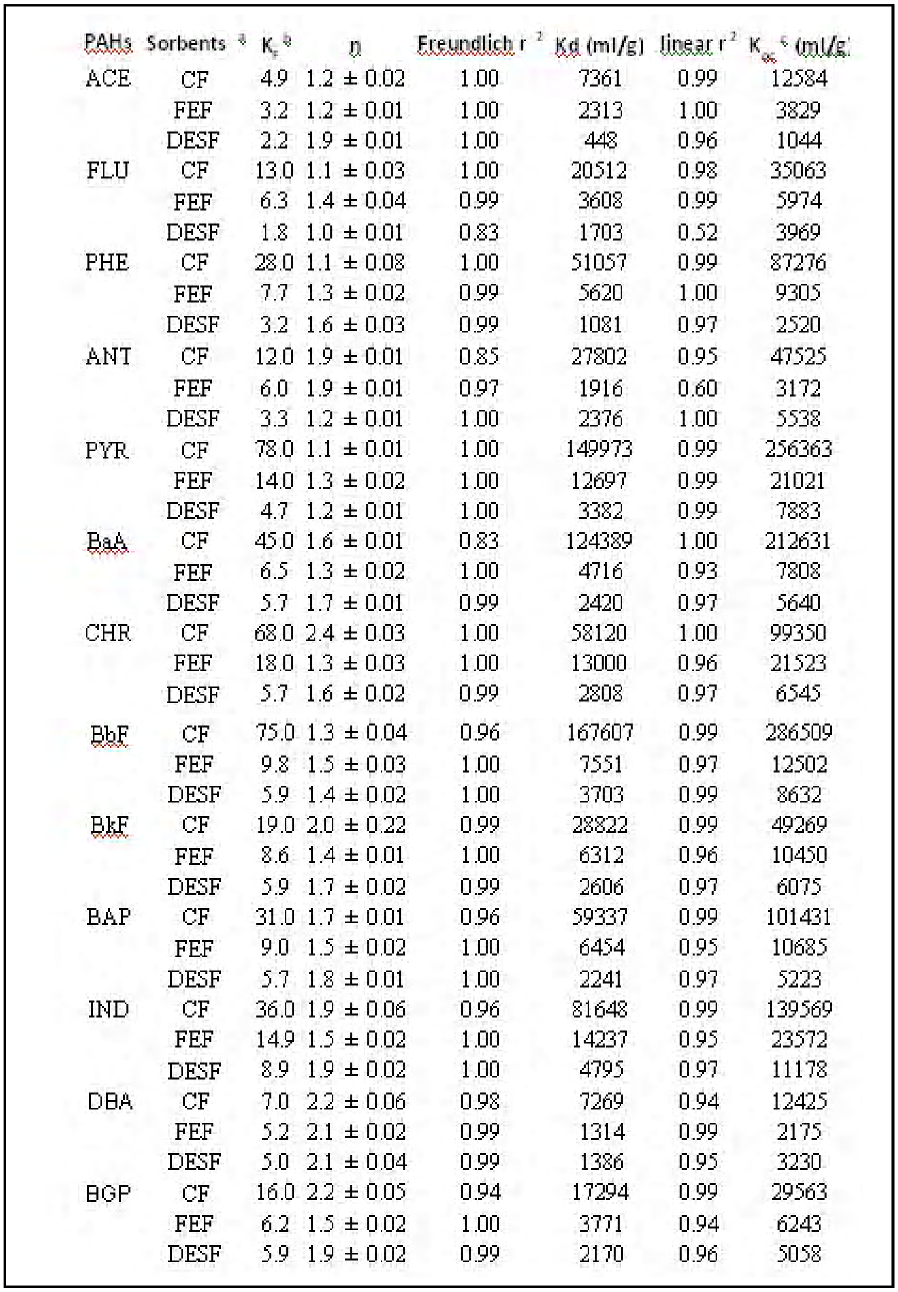


Fig. 2. Relationships between logarithm of the sorption partition coefficients (logK_{oc}) and logarithm of the octanol-water partition coefficients (logK_{ow}) of the raw cork fraction (CF), free extractive cork (FEF) and nonsaponifiable fraction (DESF) for the low molecular weight PAHs. The point marked with a cross was not used in the correlation analysis

explained with the degree of condensed structures or glassy character (Chefetz *et al.*, 2000). As a glassy biopolymer, lignin is highly aromatic. In our study, the high presence of lignin in cork could be responsible for the nonlinear isotherms.

After removing the extractable fraction and suberin from cork, the K_{oc} of FEF and DESF exhibited a significant reduction (Table 2). The K_{oc} values of CF ranged from 12425 to 286509 mL/g, for FEF fraction ranged from 2175 to 23572 mL/g and for DESF fraction

Table 2. Sorption coefficients and Freundlich model parameters of PAHs with cork fractions



PAHs	Sorbents [a]	K_F [b]	n	Freundlich r^2	Kd (ml/g)	linear r^2	K_{oc} [c] (ml/g)
ACE	CF	4.9	1.2 ± 0.02	1.00	7361	0.99	12584
	FEF	3.2	1.2 ± 0.01	1.00	2313	1.00	3829
	DESF	2.2	1.9 ± 0.01	1.00	448	0.96	1044
FLU	CF	13.0	1.1 ± 0.03	1.00	20512	0.98	35063
	FEF	6.3	1.4 ± 0.04	0.99	3608	0.99	5974
	DESF	1.8	1.0 ± 0.01	0.83	1703	0.52	3969
PHE	CF	28.0	1.1 ± 0.08	1.00	51057	0.99	87276
	FEF	7.7	1.3 ± 0.02	0.99	5620	1.00	9305
	DESF	3.2	1.6 ± 0.03	0.99	1081	0.97	2520
ANT	CF	12.0	1.9 ± 0.01	0.85	27802	0.95	47525
	FEF	6.0	1.9 ± 0.01	0.97	1916	0.60	3172
	DESF	3.3	1.2 ± 0.01	1.00	2376	1.00	5538
PYR	CF	78.0	1.1 ± 0.01	1.00	149973	0.99	256363
	FEF	14.0	1.3 ± 0.02	1.00	12697	0.99	21021
	DESF	4.7	1.2 ± 0.01	1.00	3382	0.99	7883
BaA	CF	45.0	1.6 ± 0.01	0.83	124389	1.00	212631
	FEF	6.5	1.3 ± 0.02	1.00	4716	0.93	7808
	DESF	5.7	1.7 ± 0.01	0.99	2420	0.97	5640
CHR	CF	68.0	2.4 ± 0.03	1.00	58120	1.00	99350
	FEF	18.0	1.3 ± 0.03	1.00	13000	0.96	21523
	DESF	5.7	1.6 ± 0.02	0.99	2808	0.97	6545
BbF	CF	75.0	1.3 ± 0.04	0.96	167607	0.99	286509
	FEF	9.8	1.5 ± 0.03	1.00	7551	0.97	12502
	DESF	5.9	1.4 ± 0.02	1.00	3703	0.99	8632
BkF	CF	19.0	2.0 ± 0.22	0.99	28822	0.99	49269
	FEF	8.6	1.4 ± 0.01	1.00	6312	0.96	10450
	DESF	5.9	1.7 ± 0.02	0.99	2606	0.97	6075
BAP	CF	31.0	1.7 ± 0.01	0.96	59337	0.99	101431
	FEF	9.0	1.5 ± 0.02	1.00	6454	0.95	10685
	DESF	5.7	1.8 ± 0.01	1.00	2241	0.97	5223
IND	CF	36.0	1.9 ± 0.06	0.96	81648	0.99	139569
	FEF	14.9	1.5 ± 0.02	1.00	14237	0.95	23572
	DESF	8.9	1.9 ± 0.02	1.00	4795	0.97	11178
DBA	CF	7.0	2.2 ± 0.06	0.98	7269	0.94	12425
	FEF	5.2	2.1 ± 0.02	0.99	1314	0.99	2175
	DESF	5.0	2.1 ± 0.04	0.99	1386	0.95	3230
BGP	CF	16.0	2.2 ± 0.05	0.94	17294	0.99	29563
	FEF	6.2	1.5 ± 0.02	1.00	3771	0.94	6243
	DESF	5.9	1.9 ± 0.02	0.99	2170	0.96	5058

[a] CF: raw cork; removal of extractives from CF yielded free extractive cork (FEF); saponification of FEF produced nonsaponifiable fraction (DESF). Duplicate experiments were used.

[b] K_F is the Freundlich sorption coefficient $[(\mu g/g)/\mu g/l)]^{1/n}$.

[c] $K_{oc}=K_d/f_{oc}$ where f_{oc} is the organic carbon content of sorbent.

from 1044 to 11178 mL/g. These results suggest that the extractives could be a dominant sorption medium of hydrophobic chemicals on cork. Previous results also reported that plant lipids were considered to be the main storage for PAHs (Xing and Pignatello, 1997). In contrast, other studies indicate that the removal of waxes from plants did not significantly affect the sorption capacities of some PAHs (Chen and Schnoor, 2009; Zhang and Zhu, 2009).

It is interesting that the DESF sample contains 39% of lignin and holocellulose, but the K_{oc} values exhibited the minimum values (1044-11178 mL/g). Several studies have indicated that cellulose and hemicelluloses, which mainly consist of polar aliphatic moieties, exhibit little affinity for aromatic hydrocarbons, while lignin, containing primarily aromatic moieties, showed great affinity for these solutes (Wang *et al.*, 2007; Chen *et al.*, 2005). For DESF, lignin-rich moieties may be dispersed among polysaccharides rich in polyhydroxyl and carboxylic groups. These functional groups can produce strong hydrogen bonds within the primary wall cell and also with water, possibly preventing PAH molecules from accessing the aromatic cores as a result of the surrounding polar components (Wang *et al.*, 2007). In order to better understand the role of lignin, suberin and extractable fraction on the sorption of PAHs, PAH sorption studies with two different types of cork samples (i.e. outermost back and middle part) were investigated. These bark layers exhibit significant differences in experimentally determined chemical composition.

Three pairs of raw cork samples from different origin (CF, CF1 and CF2) and two bark layers of each were used for sorption studies: outermost back 'B' and middle part 'C'. Therefore, a total of six samples were selected (CFB, CFC, CF1B, CF1B, CF2B, CF2C). Chemical composition of the selected cork samples selected is shown in Table 3.

A study was also conducted to consider the correlation between the sorption coefficients (K_{oc}) considering all types of cork and the properties of the organic pollutants (e.g. K_{ow} and F number, used as a descriptor of the molecular size of PAHs). The log form of K_{ow} and K_{oc} was used to decrease the uncertainly of the results. Little correlation was found between $\log K_{oc}$ and $\log K_{ow}$ and between K_{oc} and F when all the PAHs were considered. However, considering only LMW PAHs, a higher correlation coefficient was obtained, indicating the great importance of this parameter in this adsorption process. The corresponding equation was: $\log K_{oc} = 0.4666 + 0.7875 \log K_{ow}$ ($R^2=0.70$; $p < 0.001$; n=30). This equation may offer a model to predict the adsorption of organic compounds (hydrocarbons and pesticides) with hydrophobicities within a range of $\log K_{ow} = 3.92$ to 5.18.

It was also observed that for LMW PAHs, K_{oc} and F were directly correlated according to the equation: $K_{oc} = -145193 + 22999F$ ($R^2=0.65$; $p < 0.00001$; n=30).

The relationship between soil/sediment organic carbon-water partitioning and $\log K_{ow}$ is assumed to be (Karichoff *et al.*, 1979):

$\mathrm{Log}K_{oc\text{-}soil} = 1.0 \log K_{ow} - 0.21$

The sorption of LMW PAHs by cork appears to be in the same order as the sorption by soil/sediment organic matter (Karickoff *et al.*, 1979). Sorption of HMW PAHs was between 2 to 100 times lower than sorption by soil/sediment, except for CHR.

And as compared with cellulose (Jonker, 2008),

$\mathrm{Log}K_{oc\text{-}cellulose} = 1.0 \log K_{ow} - 2.02$

Table 3. Chemical composition (% related to dry cork) of *Quercus Suber* samples

			Chemical composition (%)[a]			
Sample[b]	Part[c]	Sample code	Suberin	Total Lignin	Holocellulose	Extractives
CF	B	CFB	40.7	23.9	8.6	11.8
	C	CFC	41.3	13.4	7.4	19.7
CF1	B	CF1B	21.1	27.9	10.1	12
	C	CF1C	33.5	31.0	2.5	12.6
CF2	B	CF2B	33.8	25.1	12.6	13
	C	CF2C	48.7	22.7	10.3	11.7

[a] Chemical composition results were obtained in duplicate for each sample and presented as average.

[b] CF, CF1 and CF2: raw cork samples from different origin.

[c] Bark layers selected for each sample: back (B) and middle part or exactly named cork (C).

sorption is considerably lower: approximately 50 times for LMW PAHs and about 5 times for HMW PAHs.

The higher affinity of LMW PAHs than of HMW PAHs for cork, despite their higher hydrophobicity, could be explained by the molecular size would initially control PAH access to the cork matrix; the smaller size of the LMW PAH molecules would have facilitated their penetration into the cork matrix and prevented larger molecules (i.e. HMW PAHs) from penetrating and localizing bonding sites. The larger the molecules, the more difficult the penetration, despite their higher hydrophobicity. Previous studies reported that the main factors that may block the pyrene sorption are the molecular size and hydrophobicity of competitors (Wang *et al.*, 2006). The mean K_d values obtained for all PAHs against suberin, lignin, holocellulose and extractives content are illustrated in Fig. 3. It is shown that the highest affinity for PAHs sorption was observed for CFC sample showing the highest extractives content, a high suberin content and low lignin and holocellulose contents. In addition, a significant correlation was found between K_d and the percentage of extractives according to the following equation: $K_d = -73211 + 6774E$ ($R^2=0.88$; $p=0.004$; $n=6$) where E is the percentage of extractives. Recently, Li and Chen (2009) also found a direct relationship between K_d and the waxes. Little correlation was found ($R^2=0.09$; $n=6$) between K_d and percentages of suberin ($R^2=0.09$; $n=6$) and percentage of lignin ($R^2=0.43$; $n=6$). However, more studies are needed to establish a clear trend between the influence of biopolymers of cork on sorption capacity by PAHs.

The main mechanism involved in the adsorption of PAHs on cork could imply the formation of electron donor-acceptor complexes in which the hydroxyl and carboxyl groups would act as donors and the aromatic ring of the PAHs as acceptor (Oki and Iwamura, 1962). The carboxyl and hydroxyl groups located at the extractable fraction could be more accessible than the phenylpropane units from lignin, due to the higher steric hindrance of the alcohols and the methoxyl substitutions on the ring. This study is part of a project focused on the use of by-products of cork as an effective and economical (0.35 euros/Kg) biosorbents for the treatment of stormwater runoff. The effectiveness of cork and the estimated dosage as biosorbent of PAHs has been previously investigated (Olivella *et al.*, 2011[a]; Olivella *et al.*, 2011[b]).

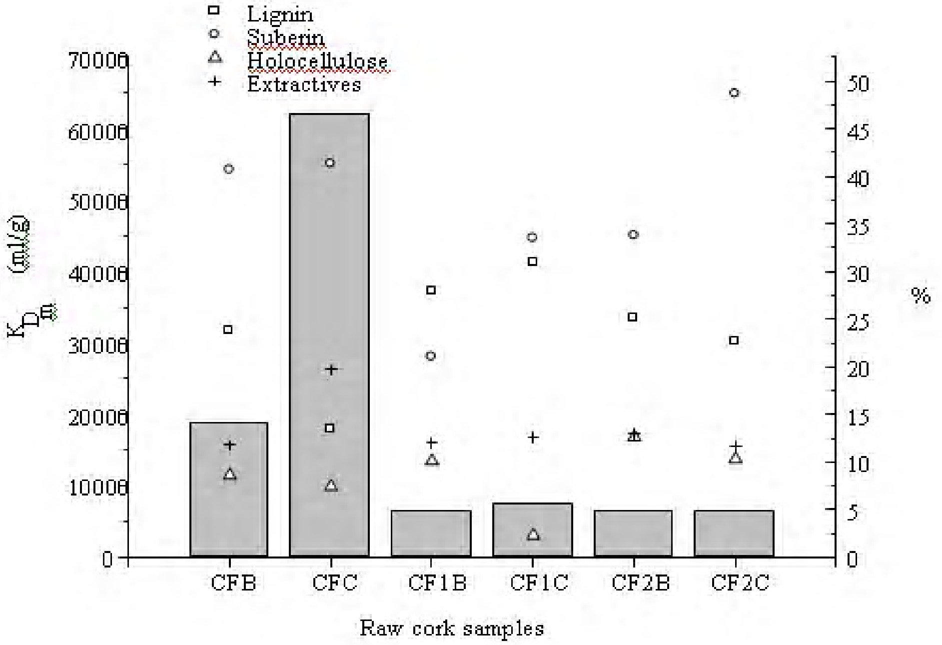


Fig. 3. Relationships between mean sorption partition coefficients (K_{ocm}) and percentages of biopolymers (i.e. lignin, suberin and holocellulose) of three raw cork samples from different origin (CF, CF1 and CF2) and two bark layers of each: back (B) and the middle part or exactly named cork (C)

CONCLUSION

The results presented in this paper show that the extractable fraction, in particular the aliphatic extractives, rather than suberin serves as a dominant medium for sorption of PAHs on cork samples examined. A direct correlation was even observed between the sorption capacity (K_d) and the percentage of extractives and an inverse relationship existed between the sorption capacity and percentage of lignin of six cork samples. This study indicates a higher sorption affinity of low molecular weight PAHs than the high molecular weight PAHs for cork, probably attributed to the lower molecular size of the former PAHs that facilitate access to the bonding sites. In addition, the equation obtained $\log K_{oc} = 0.4666(\pm 0.53) + 0.7875(\pm 0.12)\log K_{ow}$ ($R^2=0.70$; $p < 0.001$; $n=30$) indicates that K_{ow} is an important factor governing the adsorption process and may offer a model that could predict the adsorption of semivolatile organic compounds on cork.

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