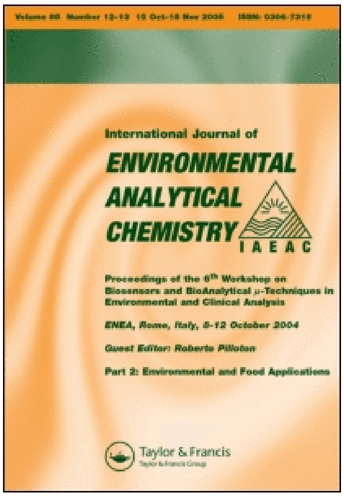

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Sorption of Pentachlorophenol on Lake Aquatic Humic Matter

Juhani Peuravuori[a]; Nina Paaso[a]; Kalevi Pihlaja[a]
[a] Department of Chemistry, Laboratory of Physical Chemistry, University of Turku, Turku

To cite this Article Peuravuori, Juhani , Paaso, Nina and Pihlaja, Kalevi(2001) 'Sorption of Pentachlorophenol on Lake Aquatic Humic Matter', International Journal of Environmental Analytical Chemistry, 79: 1, 37 — 51

To link to this Article: DOI: 10.1080/03067310108034152

URL: http://dx.doi.org/10.1080/03067310108034152

Intern. J. Environ. Anal. Chem., Vol. 79(1), pp. 37-51
Reprints available directly from the publisher
Photocopying permitted by license only

SORPTION OF PENTACHLOROPHENOL ON LAKE AQUATIC HUMIC MATTER

JUHANI PEURAVUORI*, NINA PAASO and KALEVI PIHLAJA

Department of Chemistry, Laboratory of Physical Chemistry, University of Turku, FIN-20014 Turku

(Received 7 March 2000; In final form 10 August 2000)

The sorption of pentachlorophenol (PCP) onto the aquatic humic matter (HM) for very wide concentration range (60 ng PCP/L – 1 mg PCP/L) was investigated. The binding affinity increased significantly with the acidity of the solution. The dissolved organic carbon (DOC) normalized sorption coefficients (log K_{OC}) of PCP were 3.39 at pH 3, 3.19 at pH 5.5 and 3.01 at pH 7. The binding of PCP took place via a two step binding mechanism: the rapid first step was followed by a second much slower one indicating that the surface of the HM is very heterogeneous containing binding sites with different binding affinities. It was possible to obtain a "fully saturated" HM-PCP adduct (also all possible micro-voids of the HM were occupied) in a very high PCP concentration. The log K_{OC} value for the whole concentration range was slightly smaller than that obtained under very low PCP concentration level. The Langmuir isotherm was the most suitable for the whole concentration range of PCP, whereas the Freundlich model was the most suitable for the low concentration range of PCP. The dissimilarities between different sorption models were as a whole marginal and thus it is possible without significant loss of information to describe the PCP sorption with a linear model. The results verify that the conventional humic (HA) and fulvic (FA) acid type humic solutes of fresh waters account for the main part of the PCP sorption.

Keywords: Sorption; pentachlorophenol; binding mechanism; structural features; humic substances

INTRODUCTION

PCP has been commercially produced for more than 60 years, and during this time it has been used in a wide variety of biological applications. At present, PCP is used predominantly as a wood preservative. Numerous studies have been conducted on this mildly lipophilic chemical spread all over the environment. PCP is a hydrophobic ionizable organic compound with an acid constant (pK_a) of 4.74.[1] In the protonated form, PCP can behave similarly to totally hydrophobic non-ionizable organic compounds. The octanol-water partition coefficient (log

---

* Corresponding author. Fax: +358-2-3336700, E-mail: juhpeur@utu.fi

K_{OW}, originally developed for the pharmaceutical industry) for the neutral form of PCP is ca. 5.01. PCP is slightly water-soluble (ca. 14 mg/L at 20°C and pH 5) and in the acidity of natural watercourses, the dissolved part occurs mainly in the dissociated form. Although the production and utilization of PCP have decreased during recent years, it still causes an environmental problem at many locations, e.g. in the soils and ground-waters of old sawmills and in the sediments of certain lakes and rivers. PCP has been found to bioaccumulate on living organisms, and adsorb onto sediments and organic matter in the water column. It is worth noting that the PCP adsorbed on organic matter in natural conditions is preserved for a very long time because the degradation process is slowed down.[2] PCP in the sediment will bind up to 90% on the macromolecular humic matter and forms a very permanent "chlorohumus" adduct.[3]

A classification has been proposed[4] for the interaction of organic chemicals with stationary phases: 1) sorption denotes uptake of chemicals by, e.g. soil without reference to a specific mechanism; 2) adsorption refers to a condensation of chemicals on surfaces or interior pores of a solid by physical or chemical forces; and 3) partitioning has been used to denote an uptake in which chemicals permeate into the network of a solid by forces common to the solution. It has recently been stated[5], in connection with the structural characterization of the HM, that PCP can be trapped and closely intercalated in the void of HM either without or with intermolecular hydrogen bonding between the hydrogen of the protonated carboxylic group (COOH) of HM and the phenolic oxygen of PCP. In the literature[e.g. 6], several partition coefficients have been determined for PCP with different natural solids and organic solutes from QSARs (quantitative structure-activity relationships). Various mechanisms or combinations of mechanisms have been shown to operate simultaneously in the sorption process, depending on the chemical, structural and functional properties of the interacting species. Nevertheless, the sorption mechanisms suggested for PCP even under similar experimental laboratory conditions are somewhat contradictory.

This work was undertaken to further study the sorption capacity and binding mechanism of PCP with an aquatic HM isolated from a brown-water lake. The long-term sorption capacity of the high concentration PCP solution (600 µg/L, a concentration level obtained[7] from the ground-water of the Kärkölä municipality) on the aquatic HM was investigated at a constant humic concentration and at three different acidities. The sorption isotherm of PCP within a wide concentration range (0.06–1500 µg/L) on aquatic HM and the sorption coefficients (K_{OC}, L/kg of organic carbon) were determined.

EXPERIMENTAL

Reagents

PCP was purchased from Ega-Chemie/Aldrich (purity > 99%). Hexane was HPLC grade. The anhydrous sodium sulfate and potassium carbonate (Merck) were pro analyse grade. Acetic anhydride (Riedel-de Haën, p.a.) used as acetylation agent was distilled before use. High purity deionized water (Elgastat, UHQ-PS) was used for all solutions. The humic fresh water sample was collected from Lake Savojärvi (SS, colour as cobalt-platinum units ca. 150 mg Pt/L; DOC 19 mg C/L; pH 5.8), situated in a marsh region in the south-western part of Finland, in September 1994. The aquatic HM (SS.[DEAE]) was isolated[8] from the water sample by DEAE cellulose (diethylaminoethylcellulose). It has been stated[9–12] that the DEAE cellulose extracts practically all the organic macromolecular acids (equal to so-called humic substances) at the natural acidity of the fresh water sample. The SS.[DEAE] isolate of the present work accounted for ca. 78% of the DOC containing in addition to the larger molecular size aggregates also a significant amount of smaller size HM-like constituents It has also previously been shown[8,13–17] that the SS.[DEAE] isolate represents more real HM-solute fraction, especially from the structural chemistry's point of view, of fresh water than do other chromatographic isolates which usually have been defined as separate humic (HA) and fulvic (FA) acid fractions whose mixture accounts for ca. 50–55% of the DOC.

Binding capacity and kinetic measurements

The glassware used was washed with acetone, distilled water and ethanol (99%) to avoid contamination. The concentration of the SS.[DEAE] was kept constant in every set of measurements. The SS.[DEAE] (the amount 23.5 mg/L on a moisture- and ash-free basis being equivalent to 12.67 mg/L of dissolved organic carbon, SS.[DEAE]-OC, corresponded the concentration of this HM in the original water sample) was dissolved in distilled water and the acidity was adjusted with sodium hydroxide or hydrochloric acid. PCP was added in every experimental set from a stock solution (100 mg/L in ethanol), and the influence of the slight amount of ethanol on the concentration of HM solution was ignored. The mixtures were shaken in the dark (20°C) on a reciprocating shaker. The samples (50 mL) taken at different intervals for the determination of the unbound PCP were extracted four times with 20 mL portions of hexane. The hexane layers were combined, dried with anhydrous sodium sulfate, concentrated first with a vacuum evaporator and then with a mild nitrogen flow to 3 mL. The fourth hexane extraction did not contain any detectable PCP. Furthermore, the stability of PCP bound to the SS.[DEAE] (SS.[DEAE]-PCP) was verified by adding 20 mL of hexane into the residual aquatic layer and by shaking the mixture for two weeks. No more free PCP was found from this hexane layer confirming the stability of the formed SS.[DEAE]-PCP complex. The elution of SS.[DEAE]-PCP during the hexane extraction was verified by UV/vis-spectrophotometer indicating that no detectable amount of HM was coeluted. The accuracy of the hexane extraction was ensured by adding a known amount of PCP to the purified water (practically 100% recovery).

Analysis of the unbound PCP

The higher concentration experiments (50–1500 µg/L) of PCP were analysed by a UV-method (Perkin Elmer UV/vis Spectrometer Lambda 12) utilizing the second derivative of the UV spectra according to Secchieri *et al.*[18] The peakthrough values between 304–297 nm of the second derivative UV spectra correlated linearly ($r = 0.998$) to the PCP concentration of 1–60 µg/mL in hexane.

The lower concentration experiments (0.06–1 µg/L) of PCP were analysed by a gas chromatograph (GC, Perkin Elmer AutoSystem) connected to an electron capture detector (ECD). PCP in hexane extracts was acetylated according to methods reported[19] elsewhere. The acetylated sample (1 µL) was injected into the GC. The column was 30 m long HP-5 with 0.25 mm i.d. The temperature programme was 5°C/min from 70 to 120°C. The other conditions were: carrier gas helium (2 mL/min.), splitless mode, injector and detector temperature's 270 and 300°C using nitrogen as make-up gas (30 mL/min).

RESULTS AND DISCUSSION

Binding capacity

The binding capacities of PCP on the SS.[DEAE]-OC (C_s, g/g) were determined keeping the concentrations of PCP and SS.[DEAE]-OC constant (600 µg/L and 12.67 mg/L, respectively). The acidities of the solutions (pH 7, 5.5 and 3) were adjusted with sodium hydroxide and hydrochloric acid. The ionic strengths of the solutions were no more adjusted. The amounts of the PCP (initial concentration 600 µg/L) bound to the SS.[DEAE]-OC vs. the times at three different acidities have been plotted in Figure 1. The sorption equilibrium was reached in one week (ca. 168 h, 20°C) reaching the maximum binding capacities of 1414, 911 and 609 μg/g at the acidities of pH 3, 5.5 and 7, respectively.

Figure 1 demonstrates that the initial sorption of PCP on the SS.[DEAE] at all acidities was fast during the first two days being the greatest at the acidity of pH 3. The binding capacities during the first 48 hours were ca. 985, 668 and 386 g/g at pH 3, 5.5 and 7, corresponding to 70, 73 and 63% of the whole binding capacities, respectively. After the fast initial period, the sorption rate tends to become slower. Despite the overall shapes of the sorption curves at pH 3, 5.5 and 7 were quite similar, it is clearly seen that, after the fast initial stage, the slope of the sorption rate at pH 7 becomes decrease more strongly compared to those obtained in stronger acidities. This small, but significant, difference implies that the sorption at pH 7 appears to take place via somewhat a different mechanism.

DiVincenzo and Sparks[20] have also described a sorption mechanism of the same kind as shown in Figure 1: an extremely fast initial stage results in 68% of PCP being sorbed on soil HM at pH 4.1. It has been stated[21] that the sorption of hydrophobic ionizable organic compounds often occurs in two steps: a fast sorption followed by a second slow step. According to Figure 1, the acidity has a strong influence on the magnitude of PCP sorbed as stated[1,22–24] also in the literature. At pH 3 C_s, (the equilibrium concentration of PCP in SS.[DEAE]-OC) was ca. 2.3-fold that at pH 7.

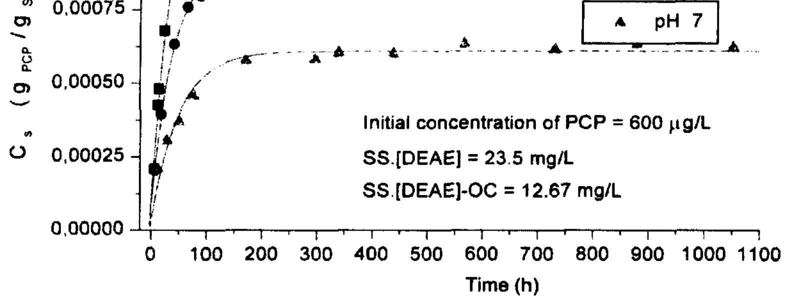

FIGURE 1 Sorption of PCP on SS.[DEAE]-OC at 20°C and different acidities as a function of time. C_s = equilibrium concentration of PCP in substrate

The sorption coefficients ($K_{OC} = C_s/C_b$, where C_s is the amount of PCP sorbed per unit weight of substrate and C_b is the equilibrium concentrate of PCP in solution) derived from the maximum binding capacities of Figure 1 were 2430, 1550 and 1030 L/kg at pH 3, 5.5 and 7, corresponding to the log K_{OC} values of 3.39, 3.19 and 3.01, respectively. According to the EPA (Environmental Protection Agency, Washington, D.C.), the soil sorption coefficient (log K_{OC}) of PCP is ca. 3.48–3.60 and sorption on soil and sediments appear to be strongly pH-dependent. For example, the log K_{OC} in soil for the total dissociated PCP is 3.10–3.26, while for the undissociated species of PCP the log K_{OC} may be as great as 4.40.

The chemical characteristics of the SS.[DEAE] has been given in Table I and more closely presented[8,13,14] previously. Up to nine distinct COOH-groups with different pK_a values were obtained[8] by titration with NaOH for the aquatic SS.[DEAE] sample studied, as shown in Table II. Average dissociation degrees for PCP and different COOH-groups of SS.[DEAE] were estimated in the water as their equilibrium concentrations from the Henderson-Hasselbach equation[25]. In reality the situation is more complicated, e.g. as the protonated form of PCP sorbs, the bulk of solution distribution will change and more of the ionized form will protonate. The influence of the degree of protonation of chlorinated phenols on the sorption has been thoroughly discussed by Schellenberg *et al.*[26]. However, in the semi-quantitative study of the present work the sorption at different acidities has been considered as steady state sorption, and during the sorption occurring increased concentration of the protonated form of PCP compared to the original equilibrium state has been omitted. The estimated mass balances at different acidities in Table II are based on this steady state approximation. The same kind of validity for the protonation degree of PCP has been also approximated in the literature[27] by the sorption studies of PCP. The average pK_a value of SS.[DEAE] is ca. 4.76 being practically the same as that of PCP but it is notable that the simply application of it would cause a serious error in the calculation of the degree of HM dissociation.

TABLE I The elemental composition, acidic functional groups and the relative abundance of different types of carbons of the SS.[DEAE]-humic matter (on moisture- and ash-free basis)

C (%)	*H (%)*	*N (%)*	*S (%)*	*O (%)*	*COOHtot (meq/g)*	*Ar-OH (meq/g)*	*weight-averaged molecular weight*
53.9	4.16	1.03	0.71	40.2	6.3	0.7	730
C_A (%)	C_B (%)	C_C (%)	C_D (%)	C_E (%)	C_F (%)	C_G (%)	C_H (%)
26.5	3.4	20.1	7.3	17.7	6.8	14.5	3.8

C_A = aliphatic carbons, C_B = mainly methoxyl carbons, C_C = e.g. carbohydrate-type carbons, C_D = anomeric carbons of polysaccharides, C_E = unsubstituted and alkyl-substituted aromatic carbons, C_F = phenols, aromatic ethers or amines, C_G = carboxyl carbons, C_H= carbonyl carbons of aldehydes and ketones.

TABLE II Concentrations of carboxylic groups of SS.[DEAE] in protonated form, PCP in protonated form and on SS.[DEAE] bound PCP

Amounts of different COOH-groups, their acid constants and concentrations in SS.[DEAE] solution of 23.5 mg/L				*Concentrations of different COOH-groups in protonated forms at different acidities*		
	meq/g	*pK_a*	*μmol/L*	*pH 3 (μmol/L)*	*pH 5.5 (μmol/L)*	*pH 7 (μmol/L)*
1	0.53	2.91	12.455	5.585	0.032	0.001
2	0.62	3.06	14.570	7.787	0.053	0.002
3	0.55	3.28	12.925	8.476	0.077	0.002
4	0.53	3.58	12.455	9.861	0.148	0.005
5	0.65	3.95	15.275	13.734	0.419	0.014
6	0.53	4.39	12.455	11.967	0.897	0.030
7	0.78	4.83	18.330	18.063	3.229	0.123
8	0.69	5.53	16.215	16.167	8.387	0.531
9	1.41	7.31	33.135	33.133	32.630	22.242
	total	pK_a (wg.)	total	total	total	total
	6.29	4.76	147.815	124.775	45.872	22.950
				Steady state concentrations of PCP in protonated form in different water solutions		
				pH 3 (μmol/L)	*pH 5.5 (μmol/L)*	*pH 7 (μmol/L)*
				2.208	0.315	0.011
				PCP bound on SS.[DEAE] in different water solutions		
				pH 3 (nmol/L)	*pH 5.5 (nmol/L)*	*pH 7 (nmol/L)*
				67.3	43.4	29.0

wg. = weighted value. The total concentration of PCP in water solution was 2.253 μmol/L (600 μg/L). The concentrations of the protonated forms for COOH-groups and PCP ($pK_a = 4.74$) at different acidities were estimated using the Henderson-Hasselbach equation derived for the dissociation degree: $1/(1+10^{pH-pK_a})$.

According to the mass balances of Table II, at least 98% of PCP is in the protonated form at pH 3 and even 45% of the most acidic ($pK_a \approx 2.91$) COOH-groups of SS.[DEAE] are protonated. Consequently, it is statistically very likely that practically all PCP can act at pH 3 via intermolecular hydrogen bonding between the hydrogen of the protonated COOH-group of HM and the phenolic oxygen of PCP provided that there occurs no steric hindrance for the interaction – otherwise the sorption may take place through hydrophobic bond formation similarly to totally hydrophobic non-ionizable organic compounds. Table II demonstrates that theoretically all protonated PCP can form at pH 3 hydrogen bond between even the most acidic COOH-group of HM. However, at this acidity on the SS.[DEAE] bound PCP is only ca. 3% of the protonated form of PCP indicating the importance of the steric influence on the sorption. At the acidity of pH 5.5 the situation is from the binding site's point of view identical with that of pH 3. The correlation occurring at pH 5.5 between the decreased amount on the SS.[DEAE] bound PCP and especially the powerfully decreased concentrations of the most acidic COOH-groups ($pK_a < 5$) suggests the essential role of these acidic COOH-groups for the sorption.

The mass balances of Table II are at the acidity of pH 7 totally different from those dominating at pH 3 and 5.5. Only ca. 0.5% of PCP is now in its protonated form at the beginning of the sorption and nevertheless ca. 2.6 times as much of PCP is bound on the SS.[DEAE]. This imbalance indicates that at best ca. 62% of PCP must be bound on the SS.[DEAE] via other binding mechanisms than hydrogen or possible hydrophobic bonds, e.g by anionic phenolate sorption, even if the freshly protonated PCP formed during the equilibrium process of the bulk solution may slightly decrease this proportion. The overall view from the binding mechanism of the phenolate anions of PCP and partly of its neutral form on HM is very complicated process being due to the multicomponent chemical equilibria. In the literature[28,29], two different mechanisms have been proposed for the association of PCP with organic solutes in an aqueous phase: solvation of ion pairs or free ions in the bulk of organic solutes and sorption of organic ions on lipophilic surfaces with counter-ions in electronic double layers, the former being strongly dependent on the ionic strength of the solution. In the present work, the ionic strength ($I \approx 1 \cdot 10^{-4}$) of the solution and also the ash content (ca. 2 %) of the HM were very low and, hence, the possibility of ion pairs being formed is almost minor. It has been also stated[30] that the neutral PCP can form PCP-conjugates with carbohydrates (e.g. glucuronic acid). Independent of the binding types of PCP with the SS.[DEAE] (hydrogen or/and hydrophobic bonds or simple "mechanical" penetration into the voids of the HM network), the association between SS.[DEAE]-PCP was weak enough to break up during the cation exchange process of the mixture producing no detectable amount of PCP from the effluent.

In the literature[24,26], it is stated that at the acidities dominating in natural waters (ca. 4–6 pH-units) the overall sorption of chlorinated phenols on natural organic solutes is in general dominated by non-dissociated species (i.e. protonated form). Furthermore, if the pH of water is no more than one unit above the pK_a of the chlorinated phenol, the contribution of phenolate sorption is practically negligible. The mass balances estimated in Table II at pH 5.5 unambiguously support the above statement thus being an important assistance by considering the sorption of chlorinated phenols in natural fresh waters.

Sorption studies

For obtaining more accurate insight into the sorption of PCP on the natural fresh water HM the experiments were carried out at the acidity of pH 5.5 (most typical for natural conditions) with a very wide concentration range of PCP. The sorption isotherms of PCP with different initial concentrations on SS.[DEAE]-OC (the concentration of the HM was kept constant in every experiment) after two weeks equilibration time at pH 5.5 are shown in Figures 2.a and 2.b. The data set of the PCP sorption has been divided into two categories according to their initial concentrations: high concentration range (1, 50, 150, 300, 600, 900, 1200 and 1500 μg/L) and low concentration range (0.06, 0.08, 0.16, 0.32, 0.64 and 1 μg/L).

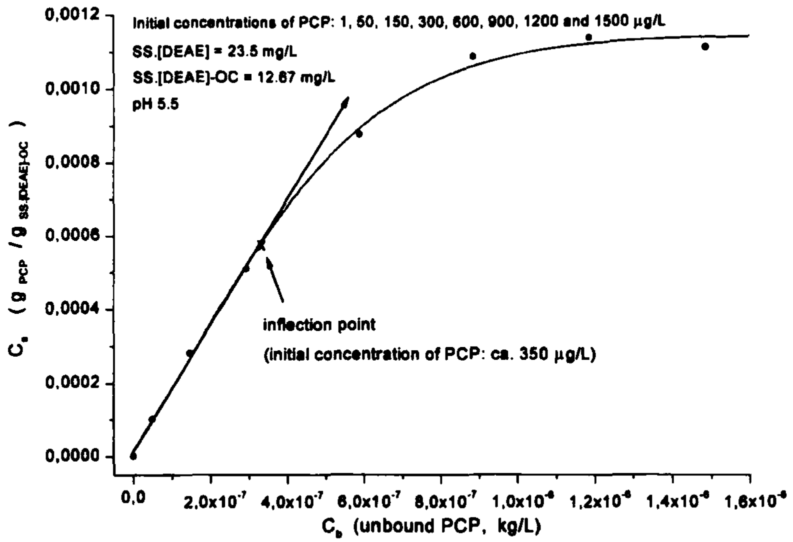

FIGURE 2A Sorption isotherm of PCP with different initial high concentrations on SS.[DEAE]-OC after two weeks (336 h) equilibrium time at 20°C and pH 5.5. C_s= equilibrium concentration of PCP in substrate. C_b = equilibrium concentration of PCP in solution

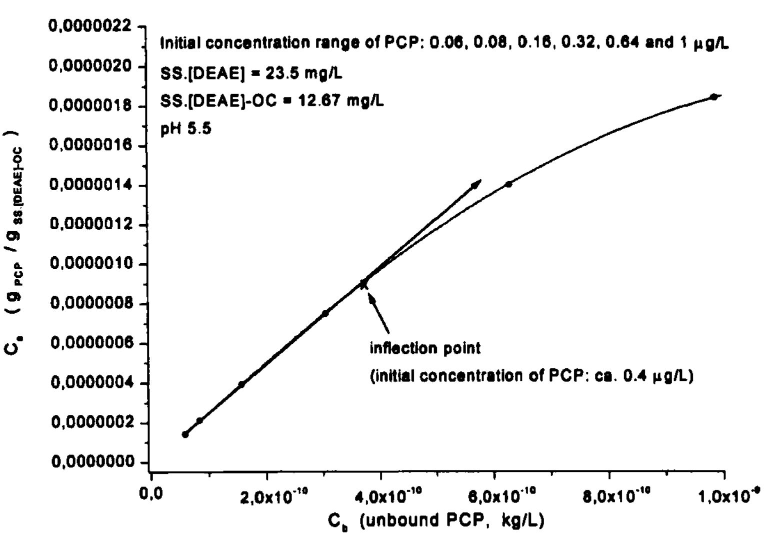

FIGURE 2B Sorption isotherm of PCP with different initial low concentrations on SS.[DEAE]-OC after two weeks (336 h) equilibrium time at 20°C and pH 5.5. C_s= equilibrium concentration of PCP in substrate. C_b = equilibrium concentration of PCP in solution

The results of Figures 2.a and 2.b indicate that the equilibrium of the sorption is strongly dependent on the initial PCP concentration. The maximum binding capacity ($C_s$max.) of ca. 1100 μg/g was reached at the initial PCP concentration between 900–1000 μg/L. For the high concentration range calculated non-linear sorption curve (Boltzmann equation, Chi-square test: 6.35305E-10) of Figure 2.a was reasonably linear (an inflection point occurred at the initial concentration of PCP of ca. 350 μg/L) up to the initial concentration of ca. 600 μg/L but after this the sorption began more strongly to curve and became lastly saturated. This phenomenon may potentially indicate that a certain "over-concentration" of PCP is required for obtaining "fully saturated" SS.[DEAE]-PCP adduct (all micro-voids of the HM network has been occupied, e.g. by "mechanical" penetration). The occurrence of such micro-voids in the HM structures and their participation in the sorption of organic pollutants has also been discussed[e.g. 5,31] in the literature. Within the low initial concentration range of PCP the calculated non-linear sorption curve (Boltzmann equation, Chi-square test: 5.9848E-18) of Figure 2.b was practically linear for the extremely low initial concentrations of PCP. An inflection point was found at the initial PCP concentration of ca. 0.4 μg/L and after this point the sorption of PCP began slightly to resemble a non-linear model. Apparently, the surface of the HM studied contains binding sites with different binding energies, i.e. as these strong energy sites become filled, sorption takes place at sites with lower binding energies, which is reflected as a decrease in the slope.

The equilibrium of the sorption and the maximum binding capacity was reached at the initial concentration between 900–1000 μg PCP/L, as shown in Figure 2.a, and after this point the unbound PCP concentration in the solution will continues to increase producing too low values for the linear distribution coefficient K_{OC}. For that reason the highest two points (1200 and 1500 μg/L) within the high initial concentration range of PCP were rejected in determination of K_{OC}. The sorption coefficients K_{OC} based on the best-line slope of C_s vs. C_b were for the high and low concentration ranges of PCP 1233 ($\log K_{OC} = 3.09$, $r = 0.969$, $n = 6$) and 2245 L/kg ($\log K_{OC} = 3.35$, $r = 0.988$, $n = 6$), respectively. The K_{OC} value estimated for the combined data set of high and low concentration ranges (0.06–900 μg PCP/L) was 1313 L/kg ($\log K_{OC} = 3.12$, $n = 11$) but the correlation coefficient (r,) for the best-line slope was only 0.925 being worse than those obtained for the isolated cases of high and low concentration ranges speaking for that the sorption is not linear but takes place via different steps within a very wide PCP concentration range (i.e. 60 ng/L-1 mg/L).

The log K_{OC} values obtained in this work were somewhat smaller than that of 3.73 estimated[32] for a PCP-soil system by means of a linear relationship based on octanol-water partition coefficients ($\log K_{OC}$ vs. $\log K_{OW}$). It is notable that the utilization of $\log K_{OW}$, as the only structural descriptor, is at best an approximation because it merely represents a partition between two well-defined non-miscible phases. Therefore, it is essential to take into account the real matrix effect between the sorbate and dissolved/solid HM, as also emphasized by Lassen *et al.*[33]. Whereas, the log K_{OC} value obtained within the low concentration range of PCP was practically equal to the average value of 3.40 given[27] at pH 5 for a synthetic mixture of HA and FA type solutes isolated from a fresh water system. This close similarity reflects that HA and FA type aquatic solutes account for the main part of the PCP sorption because the previous structural-statistical proofs[8,13–17] verified that the SS.[DEAE] sample was predominantly composed of HA and FA type constituents. The K_{OC} values (considered as the total of both neutral and ionized PCP forms) obtained were good enough in keeping with the above presented EPA values of soil sorption coefficients. On the other hand, the K_{OC} values of the present work are significantly greater than $K_{OC} = 500$ L/kg ($\log K_{OC} = 2.70$) calculated in the literature[34] as an average practical value for the total PCP in both fresh water and marine environments. The order of magnitude of this average literature K_{OC} value is almost equal to the values obtained by, e.g. Lee *et al.*[24] and Seip *et al.*[29] for different clay and soil samples with very low organic carbon contents. This dissimilarity emphasizes the important role of the sorbent matrix (primarily the content and chemical characteristics of organic carbon) for the sorption, among other things, of PCP, and that it is practically impossible to find some generally applicable K_{OC} value for, e.g. PCP.

As a speciality, it is noteworthy to note that the variation of K_{OC}values given in the literature for the PCP sorption is very large (the maximum even greater than $\log K_{OC} = 4.5$) depending on analytical methods, algorithms applied, the nature of HM, the acidity and ionic strength of the solution, etc. It is also essential to take into consideration that the isolation and fractionation procedures of, e.g. aquatic humic solutes will apparently strengthen their binding affinities on organic contaminants compared with the original situation predominating in the water system, as demonstrated[35] in another context for a neutral hydrophobic organic pollutant. The maximum concentration of the total PCP in natural fresh water environments is as a rule clearly below 1 µg/L being mostly at the concentration level of ng/L.[19,34] Thus, it is important to take notice of the multiform differences predominating between the laboratory and real natural conditions by adapting the obtained results to use.

In addition to the above linear sorption ($C_s/C_b= K_{OC}$), the non-linear Freundlich equation ($C_s= K_F C_b{}^{1/a}$) and the Langmuir equation ($C_s = (n_m K_L C_b)/(1+K_L C_b)$) were checked for conformity of sorption isotherms at the acidity of pH 5.5 and 20°C. The constants K_F and K_L are the measure of the magnitude of sorption or the sorption capacity of the substrate, the constant 1/a indicating the degree of nonlinearity between solution concentration and amount sorbed, and n_m representing the Langmuir sorption maximum (monolayer capacity).[36–41] Despite the Langmuir isotherm has originally been derived to describe the chemisorption of a gas monolayer on a solid surface an analogous form has been also adopted[42] for aqueous systems. At low concentrations, the term $K_L C_b$ becomes small compared to 1 and the Langmuir isotherm reduces to the linear form ($C_s/C_b = n_m K_L= K_{OC}$). Accordingly, when the exponent constant (a) in the Freundlich equation is near unity, the constant K_F can be referred to as a linear distribution coefficient K_{OC}.

The fitness of the empirical Freundlich equation ($\log C_s$ vs. $\log C_b$) for the sorption was rather moderate ($r = 0.847$) for the whole concentration range of 0.06–900 µg PCP/L and significantly better ($r = 0.917$) for the low concentration range alone. The exact physical meaning of the exponent of concentration in the Freundlich equation is generally speaking an enigma. The value of the exponent has generally in soil science been found to be < 1 and related to the characteristics of the adsorbent. It has been stated[38], on the basis of a large experimental material, that in the majority of cases the value of the exponent constant around unity indicates that the L-type sorption isotherm is involved while 1/a above unity is indicative for cooperative sorption. The constants 1/a obtained in the present work for the high and low concentration ranges were 0.74 and 0.91, respectively.

The Langmuir isotherm (C_b/C_s vs. C_b) for the whole data set was almost linear up to the concentration of PCP ca. 900 μg/L after which the sorption began strongly to curve verifying that the maximum binding capacity was reached between the PCP concentration of 900–1000 μg/L under the concentration of organic carbon of HM 12.67 mg/L. The correlation of Langmuir isotherm between the PCP concentration range of 0.06–900 μg/L was 0.942 but for the low concentration range alone clearly worse ($r = 0.895$). The fitting of the Langmuir equation to the whole data set at pH 5.5 indicated that the ratio of $C_s$max./n_m was ca. 49% of the binding sites of SS.[DEAE]-OC solutes that theoretically can be filled with PCP, and for the corresponding K_{OC}a value of 2290 L/kg (log K_{OC} = 3.37) was generated.

The different isotherm constants for Freundlich and Langmuir isotherms have been collected in Table III. The physical significance of Freundlich or Langmuir isotherms are actually only approximative because: there is no credible evidence that the PCP sorption occurs mainly by adsorption, and according to the impossibility that the all implicit assumptions of these theories would be valid, e.g. the surface of the adsorbent is not homogenous, that is, the affinity of each binding site for the adsorbate is the same. The number of data points generated has strong influence on correlation analyses and distinguishing between linear, Freundlich or Langmuir models is difficult. Despite of certain inaccuracies it is possible to draw some conclusions about the sorption of PCP on the aquatic HM studied. It is very likely that the Langmuir type sorption fits best in with the whole concentration range of the PCP (from the level of ng/L up to mg/L). Whereas, the Freundlich model is the most suitable for the low concentration range of PCP (at the level of ng/L).

TABLE III Constants obtained for Freundlic and Langmuir isotherms at pH 5.5 and 20°C

concentration range of PCP	*Freundlich isoterm*			*Langmuir isotherm*		
	1/a	*K_F (g/g)*	*correlation*	*n_m (g/g)*	*K_L (L/kg)*	*correlation*
whole	0.85	99.02	0.847	2.283E-3	1.02E6	0.942
high	0.74	17.46	0.754	2.565E-3	0.85E6	0.998
low	0.91	380.21	0.917	7.319E-6	3.58E8	0.895

The results obtained in the present work are somewhat contradictory, especially in the case of the adaptation of the Langmuir model, to those presented in the literature[43]. Fytianos *et al.*[43] have namely stated that the linear isotherm fits best the sorption of 2,4-dichlorophenol on marine sediments even though there occurred overlapping between the linear and Freundlich model. Whereas, the goodness of fit was very poor for the Langmuir model in the above literature study. The most important explanation for this dissimilarity is apparently, in addition to the few data points generated in the above literature study, the individual origin of the HM, i.e. specific aquatic HM sample vs. the whole unprepared sediment sample containing as well all organic as inorganic constituents. If any specific binding mechanism or sorption isotherm is not the subject of the interest the sorption of PCP can be as well described with a linear model without significant loss of the accuracy. Accordingly, the results indicated that the L2-type sorption[38,39] is potential for the high and, correspondingly, the L1-type for the low concentration range of PCP.

Acknowledgements

The authors thank the Finnish Cultural Foundation for financial support.

References

[1] World health organization geneva. *Environmental Health Criteria 71 Pentachlorophenol* (World Health Organization, ISBN 92–4–154271-3, Vammala, Finland, 1987), 236 pp.

[2] M. Salkinoja-Salonen, M. Saxelin, M. and J. Pere, In: *Advanced in the Identification & Analysis of Organic Pollutants in Water, vol. 2* (L.H. Keith, ed., Ann Arbor Science, Michigan, 1981), pp. 1131–1164.

[3] J. Paasivirta, H. Hakala, J. Knuutinen, T. Otollinen, J. Särkkä, L. Welling, R. Paukku and R. Lammi, *Chemosphere*, **21**, 1355–70 (1990).

[4] C.T. Chiou, In: *Reactions and Movement of Organic Chemicals in Soils* (SSHA Special Publication No. 22, B.L. Swahney and K. Brown, eds., Madison WI, 1989) pp. 1–29.

[5] H.-R. Schulten, *Int. J. Environ. Anal. Chem.*, **64**, 147–162 (1996).

[6] W. Karcher and J. Devillers (eds.), *Practical Applications of Quantitative Structure-Activity Relationships (QSAR) in Environmental Chemistry and Toxicology* (Kluwer Academic Publishers, Dordrecht, 1990), 475 pp.

[7] P. Lampi, T. Vartiainen and J. Tuomisto, *Chemosphere*, **6**, 625–634 (1990).

[8] J. Peuravuori, K. Pihlaja and N. Välimäki, *Environ. Int.*, **23**, 453–464 (1997).

[9] C.J. Miles, J.R. Tuschall and P.L. Brezonik, *Anal. Chem.*, **55**, 410–411 (1983).

[10] C. Pettersson, J. Ephraim and B. Allard, *Org. Geochem.*, **21**, 443–451 (1994).

[11] M.B. David and G.F. Vance, *Biogeochemistry*, **12**, 17–41 (1991).

[12] N. Paxéus, *Studies on Aquatic Humic Substances* (Ph.D Thesis, ISBN 91–7032–185-X, University of Gothenburg, Sweden, 1985), 78 pp.

[13] J. Peuravuori and K. Pihlaja, *Anal. Chim. Acta*, **337**, 133–149 (1997).

[14] J. Peuravuori and K. Pihlaja, *Anal. Chim. Acta*, **363**, 235–247 (1998).

[15] K. Hautala, J. Peuravuori and K. Pihlaja, *Environ. Int.*, **24**, 527–536 (1998).

[16] J. Peuravuori, N. Paaso, and K. Pihlaja, *Thermochim. Acta*, **325**, 181–193 (1999).

[17] J. Peuravuori, N. Paaso and K. Pihlaja, *Anal. Chim Acta*, **391**, 331–334 (1999).

[18] M. Secchieri, C.A. Benassi, S. Pastore, A. Semenzato, A. Bettero, M. Levorato and A. Guerrato, *J. Assoc. Off. Anal. Chem.*, **74**, 674–678 (1991).

[19] J. Peuravuori, K. Pihlaja and K. Korhonen, *Analysis of chlorinated phenols in water sample. An intercalibration study 1-2b* (in Finnish, ISBN 951–29–0346–6, University of Turku, Finland, 1995), 156 pp.

[20] J.P. DiVincenzo, and D.L. Sparks, *Environ. Sci. Tech.*, **31**, 977–983 (1997).

[21] G.F.R. Gilchrist, D.S. Gamble, H. Kodama and S.U. Khan, *J. Agric. Food Chem.*, **41**, 1748–1755 (1993).

[22] D.G. Crosby, K.I. Beynon, P.A. Greve, F. Korte, G.G. Stil and J.W. Vonk, *Pure Appl. Chem.*, **53**, 1051-1080 (1981).

[23] P. Lampi, K. Tolonen, T. Vartiainen and J. Tuomisto, *Chemosphere*, **24**, 1805–1824 (1992).

[24] L.S. Lee, P.S.C Rao, P. Nkedi-Kizza and J.J. Delfino, *Environ. Sci. Technol.*, **24**, 654–661 (1990).

[25] D.C. Harris, *Quantitative Chemical Analysis* (W.H. Freeman & Co., USA, ISBN 0–7167–2170–8, 1991), p. 195.

[26] K. Schellenberg, C. Leuenberger and R.P. Schwarzenbach, *Environ. Sci. Technol.*, **84**, 18, 652–657 (1984).

[27] F. De Paolis and J. Kukkonen, *Chemosphere*, **34**, 1693–1704 (1997).

[28] J.C. Westall, C. Leuenberger and R.P. Schwarzenbach, *Environ. Sci. Technol.*, **19**, 193–198 (1985).

[29] H.M. Seip, J. Alstad, G.E. Carlberg, K. Martinsen and R. Skaane, *Sci. Total Environ.*, **50**, 87–101 (1986).

[30] K. Kobayashi, In: *Pentachlorophenol Chemistry, Pharmalogy and Environmental Toxicology* (K.R. Rao ed., Plenum Press, New York, 1977), pp. 89–105.

[31] L.T.C. Bonten, T.C. Grotenhuis and W.H. Rulkens, *Chemosphere*, **38**, 3627–3636 (1999).

[32] A. Sabljić, H. Güsten, H. Verhaar and J. Hermens, *Chemosphere*, **95**, 31, 4489–4514 (1995).

[33] P. Lassen and L. Carlsen, In: *The Role of Humic Substances in the Ecosystems and in Environmental Protection* (J. Drozd, S.S. Gonet, N. Senesi and J. Weber, eds., PTSH-Polish society of humic substances, ISBN 83–906403–2–5, Wroclaw, Poland, 1997), pp. 703–708.

[34] J. Muir and G. Eduljee, *Sci. Total Environ.*, **236**, 41–56 (1999).

[35] J. Peuravuori, *Anal. Chim. Acta*, in press, (2000).

[36] J.I. Drever, *The Geochemistry of Natural Waters Surface and Groundwater Environments* (Prentice Hall, Inc., New Jersey, 1997), pp 87–105.

[37] F.J. Stevenson, *Humus Chemistry – Genesis, Composition, Reactions* (Wiley, New York, 1982), pp. 376–394.

[38] G.G. Choudhry, *Humic Substances – Structural, Photophysical, Photochemical and Free Radical Aspects and Interactions with Environmental Chemicals* (Gordon and Breach Science publisher, Glasgow, 1984), pp. 95–139.

[39] C.H. Giles, T.H. MacEwan, S.N. Nakhwa and D. Smith, *J. Chem. Soc.*, 3973–3993 (1960).

[40] J. Kozak, In: *Humic Substances in Terrestrial Ecosystems* (A. Piccolo, ed., Elsevier, Amsterdam, 1996), pp. 625–664.

[41] M. Schnitzer and S.U. Khan, *Soil Organic Matter* (Elsevier, Amsterdam, 1978), pp. 137–171.

[42] W. Stumm, *Chemistry of the Solid-Water Interface – Processes at the Mineral-Water and Particle-Water Interface in Natural Systems* (Wiley, New York, 1992). 448 pp.

[43] K. Fytianos, E. Voudrias and E. Kokkalis, *Chemosphere*, **40**, 3–6 (2000).