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Sorption of hydrophobic organic pollutants on soils and sediments

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Abstract. Sorption interactions between selected hydrophobic organic pollutants as sorbates and various natural sorbents in two-phase systems sorbent – water were experimentally tested by means of both batch (static) and column elution (dynamic) methods. Relatively persistent priority pollutants such as polycyclic aromatic hydrocarbons (naphthalene, anthracene and fluoranthene), organochlorinated pesticides (methoxychlor, hexachlorobenzene and lindane) and triazine herbicides (simazine and atrazine) were used as model hydrophobic sorbates. The collection of the examined natural sorbents included lake sediments, soils, reference samples of subsoil sedimentary rocks and some technical products as synthetic reference materials.
By using batch methods, the distribution/sorption coefficients K_D and/or parameters K_F and 1/n of the Freundlich isotherm equation for the respective sorption systems were determined. In the case of natural sorbents with significant contents of organic matter, the corresponding normalised distribution/sorption coefficients K_{OC} or $K_{OC(F)}$ were calculated and compared with known reference values of these parameters. On the basis of some observed differences between experimental and expected data, the role of organic matter and some other factors affecting the sorption processes, limitations of the simple model of hydrophobic sorption and reliability of sorption data are discussed.
Elution sequences and phase distribution balances of the pollutants, determined by elutions of the sorbates with water from sorbent columns, also reflected differences in their sorption parameters in detail. In comparison with batch methods, however, the column methods are less effective and for numerous reasons unsuitable for the measurement of sorption parameters.

Key words: soil, sediment, chemical analyses, organic matter, hydrophobic organic pollutants, alkanes, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorinated pesticides, data quality, correlations, environmental interpretations

Introduction

The retention and migration of organic pollutants as potential sorbates in systems water – geosorbent (= soil, rock, sediment) are substantially influenced by the composition and nature of the solid phase of the investigated sorption systems (Smith et al. 1988, Schwarzenbach et al. 1993). Equilibrium distribution of the sorbed substance (sorbate) between solid (s) and water (w) sorption system phase is characterised by a distribution (sorption) coefficient K_D, defined by the equation

$$K_D = c_s / c_w, \quad (1)$$

where c_s and c_w stand for overall mass or molar sorbate concentrations in the corresponding phase of a system in equilibrium (e.g., in mg . kg^{-1} or mol . kg^{-1} for sorbent and in mg . L^{-1} or mol . L^{-1} for the conjugated water phase). K_D (in L . kg^{-1}) is a quantitative characteristic of the measure of interactions between the sorbate and the natural sorbent. Knowledge of K_D facilitates the estimate of the sorbate equilibrium concentration in one phase of a given system if the sorbate concentration in the other phase is known. K_D is usually experimentally determined using batch (static) or column (dynamic) methods.

Static methods are based on an experimental arrangement in which a defined amount (batch) of sorbent is added to a known volume of water phase, containing a known concentration of sorbate. Such model sorption system is then mechanically agitated in a closed container at constant temperature until an equilibrium is reached. Suspended solid phase residues are removed from the liquid phase (e.g., by filtration, decantation or centrifugation). The liquid phase is then subjected to analytical determination of equilibrium sorbate concentration. The corresponding equilibrium sorbate concentration in the solid phase is ordinarily calculated as a difference of the initial and the equilibrium concentration in the water phase. If necessary, the equilibrium sorbate concentration can also be determined directly in the tested sorbent.

A more general method of static determination of distribution coefficients (K_D or K_F) encompasses gauging and numerical or graphical analysis of a sorption isotherm, which describes the equilibrium sorbate distribution between the phases of the tested system, solid sorbent (s) – water (w), at constant temperature and in conveniently chosen intervals of overall solute concentrations in the system. The course of experimentally obtained real isotherms can often be fitted by the equation of a model Freundlich isotherm

$$c_s = K_F \,.\, c_w^{1/n}, \quad (2)$$

where c_s and c_w stand for equilibrium sorbate concentrations in both phases of the system in question, K_F is an empirical coefficient of the Freundlich equation, and the exponent 1/n is a measure of non-linearity of the investigated dependence for a given sorbent and a given sorbate. The values of $K_F \approx K_D$ and 1/n are gained from the equation (2) in a logarithmic shape

$$\log c_s = \log K_F + (1/n) \log c_w \qquad (3)$$

as a slope 1/n and an intercept log K_F of such linear dependence log c_s = f (log c_w).

The nature of the obtained isotherm, characterised by its shape, testifies to the prevailing sorption mechanism of a given substance in the system. Standard convex shape of $c_s = f(c_w)$ dependencies with exponent values $1/n < 1$ indicates the predominance of adsorption processes, which result in a decrease of the relative proportion of organic sorbate adsorbed to the solid phase with its increasing concentration in the water phase (a consequence of gradual saturation, unequal sorption affinities or impaired accessibility of remaining active centres on the sorbent).

In the opposite marginal case, where a concave course corresponds to exponent values $1/n > 1$, the surface of the solid phase is gradually modified by the retained sorbent. The relative sorbate proportion sorbed onto the sorbent increases with a growing sorbate concentration in the system. A characteristic example of such mechanism is a sorption of alkylbenzenesulphonate-like surfactants onto polar active surfaces of mineral sorbents, which become more and more hydrophobic as the oriented sorption of dipole molecules proceeds.

A linear course of an experimental isotherm, corresponding to exponent values $1/n \cong 1$, gives evidence for constant sorbate distribution between the solid and water phase within a wider range of concentrations c_w. The isotherm linearity usually indicates a partition mechanism of sorption equilibria, in which the molecules of organic solute are preferentially sorbed in the organic matter of a natural or artificial origin present in the examined solid material. Nevertheless, even generally non-liner sorption isotherms with exponent values $1/n \neq 1$ usually demonstrate a linear course in the range of the lowest concentrations c_w.

Dynamic methods used for the determination of distribution coefficients are usually based on experimental arrangement of column liquid chromatography. In standard elution experiment, a small amount of the chosen sorbate is, in a suitable way, applied to the top of the tested sorbate column (in a narrow starting zone). The column is then eluted by water mobile phase until the concentration maximum of sorbate elution zone appears in the effluent. The distribution coefficient is then calculated from the eluate retention volumes for the elution maxima of the sorbate and the reference compound (which is not retained in the column), from the sorbent mass and from the free interstitial space in the column. In addition to column methods used for the determination of K_D, which take advantage of elution chromatography principles, there are a number of methods, the experimental arrangement of which is derived from the chromatographic frontal analysis. Dynamic methods of K_D determination are, compared to batch methods, generally regarded as less universal and less reliable (see, e.g., Štamberg 1996).

Sorption studies (Karickhoff et al. 1979, Hasset et al. 1980, Kenaga and Goring 1980, Briggs 1981, Karickhoff 1981, Schwarzenbach and Westall 1981, Lyman 1982, Chiou et al. 1983, McCall et al. 1983) of numerous organic priority pollutants (neutral hydrophobic compounds such as polycyclic aromatic hydrocarbons, chlorinated hydrocarbons, pesticides, etc.) from water onto natural sorbents (sediments, soils, rocks) proved that K_D distribution coefficient values generally grow with the increasing hydrophobicity of sorbate molecules and also with the content of organic matter or organic carbon in the sorbent, respectively.

The measure of sorbate hydrophobicity (lipophilicity) in a hydrophobic sorption model (which generalises the relations between the aforementioned quantities) is a distribution coefficient K_{OW}, defined as a ratio of the overall sorbate concentrations in the organic (o) and water (w) phase of an equilibrated extraction system n-octanol – water

$$K_{OW} = c_o / c_w. \qquad (4)$$

The content of organic carbon in the sorbent is usually expressed in the form of mass fraction f_{OC}. The relationships between the quantities are given by general equations

$$K_D = f_{OC} \,.\, K_{OC} = f_{OC} \,.\, b \,.\, K_{OW}{}^{a}, \qquad (5)$$

where K_{OC} stands for sorbate distribution coefficient recalculated on a notional 100 % organic carbon content in the solid phase (for a hypothetical sorbent of $f_{OC} = 1$); a and b are empirically determined constants, characteristic for individual categories (groups) of structurally related sorbates and, to a certain extent, also for various types of natural sorbents. Distribution coefficients deduced from the course of a Freundlich isotherm therefore fit the relationship

$$K_D \approx K_F = f_{OC} \,.\, K_{OC(F)}. \qquad (5a)$$

A model of hydrophobic sorption, based on the above mentioned relationships, is frequently cited in monographs (Smith et al. 1988, Schwarzenbach et al. 1993, Yaron et al. 1996, Domenico et Schwartz 1998) and used in practice. However, some of the more recent publications point out its limitations (see, e.g., Luthy et al. 1997).

The relationships (5) and (5a) cease to be valid for sorbents with very low organic matter contents, where, in addition to sorption onto organic matter, a competitive sorbate sorption onto mineral surfaces of natural sorbents comes into play. The share of hydrophobic sorbate sorption onto mineral surfaces in case of sorbents with higher organic matter contents ($f_{OC} > 0.001$) can usually be neglected (when compared to their sorption by organic matter) (Schwarzenbach et al. 1981, 1993). A growing hydrophilicity of neutral sorbate molecules results in a decrease of affinity with sorbent organic matter (a typical marginal example is methanol with log $K_{OW} = -0.66$) and in a failure of the hydrophobic sorption model (Domenico and Schwartz 1998). According to Karickhoff (1981), the hydrophobic sorption model is applicable only to organic sorbates of water solubility under 10^{-3} mol . L^{-1}.

The practical use of the hydrophobic sorption model for an estimation of behaviour of organic pollutants as sorbates both in model and natural sorption systems is limited by a smaller reliability of dispersedly published data on properties of individual prior pollutants. Equilibrium data on sorptions (K_D, K_{OC}, K_{OM}), solubilities in water (S_W), and pollutant distribution in model system n-octanol – water (K_{OW}) published by different authors are often conflicting (mostly because of different methodology) and in some cases differ even by orders of magnitude (Mackay et al. 1999).

Such an unsatisfactory situation is gradually improving thanks to critical revisions connected with statistic evaluation of compiled experimental data on environmentally significant parameters of organic pollutants (e.g., US EPA 1996). The average distribution coefficient values K_{OC}, statistically purged of the influence of outlying results, are in good agreement with their approved reference values. An empirical relationship between such revised K_{OC} values and independently determined K_{OW} values, derived from the equation (5),

$$\log K_{OC} = 0.7919 \log K_{OW} + 0.0784 \qquad (6)$$

is then valid in a wide range of values of both parameters ($\log K_{OC} = 0.78$ to 4.9 and $\log K_{OW} = 0.90$ to 5.9) and for a wide scale of pollutants/sorbates, including, e.g., benzene and its alkyl- and halogen-derivatives, halogenated derivatives of methane, ethane, ethylene and even organochlorinated pesticides such as endrine, diendrine, etc. (US EPA 1996).

Concurrently with the revision of the reliability of the published data on sorption interactions of organic pollutants with natural sorbents, the methods used for their determination are being improved and standardised. Determinations of distribution/sorption coefficients of chemical compounds using batch methods are adjusted by recently published amendments of systematic guidelines and norms (OECD Guideline 106 1998; US EPA Guideline OPPTS 835.1220 1998; ASTM Standard E 1195 – 2001). The amendments resulted from scholarly discussions held on the ground of OECD (OECD Workshop Belgirate 1995) and within the scope of harmonisation processes of US EPA technical directions and update of ASTM norms.

Attempts on systematic standardisation of retention measurements of chemical compounds by natural sorbents have been made in various dynamic arrangements. The proposal of OECD Guideline ***/D (1998) describes a simple column test for the evaluation of extractability of organic pollutants from a column of tested soils or sediments by water. The acquired result is a value of so-called RMF parameter (= relative mobility factor), defined by the ratio of migration paths, covered by elution zones of the tested and reference chemicals in a sorbent column within the same period of time. Relative pollutant retentions (expressed by an R_F factor) are also measured using chromatography on a thin layer (TLC) of the tested natural sorbent according to US EPA Guideline OPPTS 835.1210 (1998). This guideline takes advantage of ascending development of artificially prepared layers of tested samples and sediments by water (mobile phase) in the usual arrangement of analytical TLC.

Materials and methods

Chemicals, reagents, special materials and standards (if not stated otherwise) were, as far as their qualitative parameters were concerned, in compliance with the regulations of the aforementioned standardised and certified analytical methods. Ultra-pure water used as a mobile phase in the investigated sorption systems was prepared in a MilliQ RG filtration unit (Millipore, USA). Instrument systems used for the determination of individual organic pollutants by means of capillary gas chromatography (HRGC) and high-performance liquid chromatography (HPLC) were identical to the instrumentation employed in the organic matter characterisation in a wider selection of natural sorbents described in the preceding publication (Boháček et al. 2003).

The experimental arrangements and procedures of sorption interaction studies by means of column elution experiment and batch method are, on account of a better lucidity, discussed separately.

Experimental arrangements and procedures employed in column experiments

Natural sorbents investigated by means of column elutions

Five different natural materials were chosen to be subjected to column experiments. They were labelled as Žd, Le 4, HBS 2, HBS 6 and HBV 4 and their organic and mineral compositions are characterised in more detail in a separate publication (Koubová et al. 2003). In the process of their selection for column experiments, particle-size analyses and contents of both organic (C_{org}) and mineral/carbonate (C_{min}) carbon were taken into consideration. The basic data on the investigated natural sorbents and operating parameters of elution columns, filled with these materials, are summarised in Tab. 1. Pretreatments of the field samples for column experiments were limited to basic operations, suggested by a norm for soil sample preparation for physical and chemical analyses (ISO/DIS 11 464 – 1992); they encompassed drying of a wet sample at room temperature, delicate crushing of lumps and sieving of the sample material through a 2 mm sieve.

Elution columns

Elution experiments were carried out in simple glass columns, used in a Geochemical laboratory of pollutant migration associated with Masaryk University for parallel investigation of sorption interactions of the same materials with various inorganic pollutants (Müllerová et al. 2003).

Tab. 1. Parameters of sorbents and columns used in the elution experiments

Sorbent			Žd	Le 4	HBS 2	HBS 6	HBV 4
Particle size fractions:	silt + clay	(wt%)	33	63.5 + 15	2 + 1	40.0 + 8.5	80.5 + 18.5
	sand	(wt%)	67	13	74.5	51	1
	gravel	(wt%)	0	8.5	22.5	0.5	0
Mineral carbon C_{min}		(wt%)	1.3	0.6	< 0.05	< 0.05	< 0.05
Organic carbon C_{org}		(wt%)	1.2	1.68	0.22	1.58	3.54
Particle density ρ_p		(g/cm^3)	2.555	2.287	2.62	2.152	2.012
Weight of sorbent		(g)	125	125	125	125	100
Weight of dry sorbate admixture		(g)	8.8	8.03	8.27	8.37	5.74
Column internal diameter		(cm)	2.62	2.62	2.65	2.6	2.67
Height of sorbent column		(cm)	15	19.2	14.8	20	21.4
Height of water column		(cm)	10.2	7.5	11	5.7	1.8
Total volume of sorbent column		(cm^3)	80.9	103.5	81.6	106.2	119.8
Volume of solid phase in column		(cm^3)	48.9	54.7	47.7	58.1	49.7
Volume of water phase in column		(cm^3)	35.2	52.5	37.6	51.6	73.8
Water flow rate		(mL/h)	13.5	0.624	69.6	2	0.259
Total volume of eluate		(mL)	4 671	300	22 130	957	125
Total elution time		(h)	366	478	366	478	478

Glass tubes 30 cm in length and 2.6 cm in inner diameter were conically narrowed at the bottom and terminated by an outlet tubule (2–3 mm inner diameter). A short lateral tube, serving as an overflow for maintenance of the level of the elution medium (water) in the column, was linked to the main tube at a distance of 4–6 cm from its upper end. After the insertion of a glass wool wad into the constriction at the bottom, the columns were filled with batches of dry sorbents (usage of a vibrator) in such a way that the upper end of the sorbent column ended a few centimetres below the overflow level. Before the actual elution experiment, the column fillings deaerated by water were stabilised by washing with ultra-pure water in a recirculation mode.

Dimensions and other operating parameters of columns, prepared and used for the investigation of sorption interactions between the tested sorbents and model organic pollutants in dynamic elution arrangement, are summarised in Tab. 1.

Model sorbates for column experiments

Sorption properties of the analysed natural sorbents were tested by a seven-component mixture of model organic sorbates with neutral hydrophobic molecules. Polycyclic aromatic hydrocarbons as frequent constituents of contaminations produced by burning processes were represented by naphthalene, anthracene and fluoranthene. The other mixture constituents were hexachlorobenzene and methoxychlor as active substances of organochlorinated pesticide preparations and simazine and atrazine representing triazine herbicides frequently used in agriculture.

Physicochemical properties of all model sorbates, which may significantly affect the behaviour of these compounds in the analysed sorption systems, are characterised by data presented in Tab. 2. Owing to a considerable variability of these data in publications of different authors, Tab. 2 contains only revised values, suggested for environmental applications (Mackay et al. 1999).

Standard solutions of individual sorbates in dichloromethane (conc. 1 mg/ml) were prepared from chromatographically pure preparations of the basic substances (Supelco, USA). In order to eliminate a potential disruptive effect of dichloromethane as auxiliary solvent on interactions between the tested natural sorbents and model sorbates, the mixture of model sorbates was applied to the top of the stabilised sorbent column as a separately prepared dry mixed sample. The mixed sample was obtained by volatilisation of defined standard solution volumes with small amounts of the tested sorbent and contained 0.10 mg of each sorbate in 8 g of sorbent. When applied to the top of the column, the added dry sample formed an approximately 1 cm high layer.

A course of the column experiment

After the application of the mixed sample, the column with the tested sorbent was eluted by ultra-pure water for 2–3 weeks. The speed of gravitational elution in the used arrangement was controlled by the permeability of the column fill. Eluate fractions, continuously sampled at regular time intervals, were analysed for the contents of all model sorbates.

After the termination of the elution, the outer surface of a column tube was notched at appropriate places by a diamond cutter, and the column, containing wet sorbent, was cooled down in a freezer to –18 °C. The column, solidified by the frost, was then carefully rid of the glass coat and divided into several 3.0 cm long cylindrical segments (i.e., to 5–7 fractions, depending on the length of the original column), in which contents of all monitored sorbates were also determined.

Tab. 2. Physicochemical properties of pollutants used as model hydrophobic sorbates

Sorbate	CAS No.	Summary formula	Molecular weight	Melting point	Boiling point	Solubility in water (25° C)	Vapour pressure (25° C)	Henry's law constant	Partition coefficients		Sorption coefficient soil vs. water	Bioconcn. factor
									air vs.water	n-octanol vs. water		
						$C_{w,sat}$	P^0	K_H	K_{AW}	log K_{OW}	log K_{OC}	log BCF
			g/mol	°C	°C	mg/L	Pa	Pa . m^3 /mol				
naphtalene	91-20-3	$C_{10}H_8$	128.18	80.5	218	3.10E+01	1.04E+01	4.30E+01	1.73E-02	3.37	2.98	2.07
anthracene	120-12-7	$C_{14}H_{10}$	178.24	216.2	340	7.30E-02	1.00E-03	6.00E+00	nd	4.54	4.39	2.96
fluoranthene	206-44-0	$C_{16}H_{10}$	202.26	111	375	2.60E-01	1.23E-03	9.57E-01	3.86E-04	5.22	4.83	3.92
methoxychlor	72-43-5	$C_{16}H_{15}Cl_3O_2$	345.65	86-88	nd	1.00E-01	1.91E-04	9.99E-01	nd	5.08	4.9	3.92
hexachlorobenzene	118-74-1	C_6Cl_6	284.79	230	322	5.00E-03	2.30E-03	1.31E+02	5.29E-02	5.5	5.11	4.2
simazine	122-34-9	$C_7H_{12}ClN_5$	201.67	226	nd	5.00E+00	1.00E-06	4.21E-05	1.70E-07	2.18	1.79	0.879
atrazine	1912-24-9	$C_8H_{14}ClN_5$	215.68	174	nd	3.00E+01	4.00E-05	2.88E-04	1.16E-07	2.75	2.36	1.45
lindane	58-89-9	$C_6H_6Cl_6$	290.85	112.5	323	7.00E+00	7.40E-03	3.75E-01	1.51E-04	3.7	3.31	2.4

Note: nd – data not available

Determination of model sorbates in eluates

For the purpose of the analysis, the fractions of water eluates were divided into two parts. The first part was subjected to extraction of chlorinated pesticides and polycyclic aromatic hydrocarbons by hexane, the second one served for isolation of triazines by means of extraction into the solid phase (SPE).

Hexachlorobenzene and methoxychlor were analysed employing an HP 6890 gas chromatograph equipped with an electron capture detector (HRGC/ECD). The hexane extracts were injected directly on a HP-5 column with detection limits (LOD) of 2 ng/L for hexachlorobenzene and 8 ng/L for methoxychlor.

Polycyclic aromatic hydrocarbons were analysed using a certified method according to SOP V-3 (CGS Brno 1999b), based on the ČSN 75 7554 (1998) norm. The evaporation residues of hexane extracts were dissolved in acetonitrile and then analysed by means of high-performance liquid chromatography with fluorimetric detection (HPLC/FLD). The used experimental arrangement provided the following limits of detection: 5 ng/L for naphthalene and fluoranthene and 0.5 ng/L for anthracene. Relative standard deviations reached around 8 % for naphthalene and ranged from 5 to 6 % in the case of anthracene and fluoranthene.

Simazine and atrazine concentrations were determined employing a certified method according to SOP V-5 (CGS Brno 2001a), based on the ČSN ISO 11 369 (1998) norm. Triazines were isolated from eluates using solid phase extraction (SPE) on AccuBOND II ODS-C18 1000 mg columns (Agilent Technologies), and after the extraction by acetonitrile analysed by means of HPLC with UV diode-array detection (DAD). This method facilitated the analysis of both triazines with LOD of 25 ng/L and a relative standard deviation of around 6 %.

Sorbate determinations in layers of sorbent columns

The sample material from the individual layers, acquired by carving of a sorbent column after the termination of the elution, was air-dried, homogenised and extracted by a mixture of dichloromethane and methanol (95 : 5, vol %). Aliquot volumes of extracts from every single layer of the column were subjected to analyses of all model sorbates.

For the purpose of determination of organochlorinated pesticides, the initial extract was concentrated, diluted by n-hexane and analysed employing HRGC/ECD and the same method as for eluate analysis. LOD values reached 2 μg/kg for hexachlorobenzene and 4 μg/kg for methoxychlor.

Polycyclic aromatic hydrocarbons were analysed using a certified method SOP Z-3 (CGS Brno 1999a). The extract evaporation residue was dissolved in acetonitrile and analysed by means of HPLC/FLD with LOD of 2 μg/kg for naphthalene and fluoranthene and 0.2 μg/kg for anthracene.

Triazines were determined by a certified method according to SOP Z-6 (CGS Brno 2001b). The evaporation residue of the extract was dissolved in acetonitrile and purified by a sorption of ballast substances on silica gel and SPE column AccuBOND II ODS-C18 500 mg (Agilent Technologies). The purified solution of the sample in acetonitrile was analysed for the contents of both triazines using HPLC/UV-DAD (by the method used for the analysis of water eluates) with LOD equal to 20 μg/kg and relative standard deviation around 3 % for both simazine and atrazine.

Experimental arrangements and procedures of batch method

Investigated sorbents

The list of all sorbents, the sorption parameters of which were gauged by using batch methods, is presented in Tab. 3. Set A of the examined samples comprised some reference samples of subsoil sedimentary rocks (Žd A, H1 A, St 2 A) and a lake sediment (HBS A) (all containing organic matter), completed with technical preparations of a chemically purified marine sand (MP A) and synthetic wide-porous silica gel (SKG 100 A) with merely mineral matrices of different internal porosities. Samples of series A were prepared in a standard manner (according to ISO/DIS 11 464 – 1992), i.e., by sieving air-dried and gently crushed field samples through a 2 mm sieve.

Markedly finer-grained preparations of the reference subsoil rock samples used in the measurements of the Freundlich sorption isotherms originated both from the above-mentioned localities (H 1, St 2) and localities in their close vicinity (R 4, TvP 5). In this case, the sample pretreatment included a more efficient two-stage particle-size reduction by crushing and sieving of the materials gradually through 2 mm and 0.25 mm sieves as well.

Some basic characteristics of all examined sorbent samples are given in Tab. 3, a more detailed information concerning the origin and properties of the samples has been described elsewhere (Müller et al. 1997, Koubová et al. 2003, Boháček et al. 2003).

Testing sorbates

The chosen hydrophobic organic sorbates used for measurements of sorption interactions with tested sorbents are presented in Tab. 2. Water phases of the investigated sorption systems with conveniently chosen initial sorbate concentrations were usually prepared by injection of defined volumes of compound standard solutions in acetonitrile (with concentrations ranging from 0.1 to 1 mg/mL) into the initial volume of ultra-pure water. The added standard solution volume was always smaller than 0.1 % of the overall water phase volume.

Experimental arrangement of batch method (basic parameters)

The experimental arrangement of the batch method for the determination of K_D respected general regulations of the aforementioned methodical standards (ASTM Standard E 1195-01 2001; OECD Guideline 106/D 1998; US EPA Guideline OPPTS 835.1220 1998).

Agitated reactors for phase equilibration of the investigated sorption systems consisted of reaction vessels made of brown glass (100 or 1000 mL volumes) and hermetic screw caps with PTFE gaskets. The bigger vessels were used for systems with smaller values of the phase ratio $R = m / V_o$ (where m stands for the mass of the batch and V_o for the volume of water phase). The weights of sorbent batches (in an air-dried form) and water phases were determined gravimetrically.

Composition and the mutual phase ratio

The initial sorbate concentrations in water phases of the investigated sorption systems $c_{w,o}$ were chosen to be smaller than a half of the value of a sorbate solubility in water, i.e., $c_{w,o} < 0.5\ S_W$, and, at the same time, by 2–3 orders of magnitude higher than the limit of detection (LOD) of a given sorbate. The volume of acetonitrile (auxiliary solvent) present in the additions of standard sorbate solutions was always smaller than 0.1 % of the overall water phase volume and its ratio to the water phase volume was kept constant throughout the whole series of measurements.

Tab. 3. Natural sorbents tested on sorption properties using the batch method

Sorbent code	Sample type	Locality, origin	Grain size fraction	Dry weight	Mass fractions of carbon				pH of water suspension
					C_{tot}	C_{min}	C_{org}	f_{OC}	
			(mm)	(wt%)	(wt%)	(wt%)	(wt%)		1 : 5 (m/v)
MP A	sea sand chemically purified	Merck	0.1–0.3	99.91	< LOD	< LOD	< LOD	< LOD	5.59
SKG 100 A	silica gel 100 for preparative LCC	Merck	0.063-0.200	98.44	< LOD	< LOD	< LOD	< LOD	7.04
Žd A	fine-grained sandstone	Bučovice	< 2.0	99.53	2.50	1.30	1.20	0.0120	8.65
HBS A	lake sediment depth 0–28 cm	Horní Bečva central part	< 2.0	97.18	2.90	0.05	2.85	0.0285	6.90
H 1 A	dusty fine-grained sandstone	Hevlín	< 2.0	99.41	1.97	0.86	1.11	0.0111	8.12
ST 2 A	siltstone	Stavěšice	< 2.0	99.16	1.51	0.57	0.94	0.0094	8.29
H1	see H1 A	see H1 A	< 0.250	99.07	1.77	0.96	0.81	0.0081	7.96
St 2	see St 2 A	see St 2 A	< 0.250	99.23	1.22	0.44	0.78	0.0078	7.88
R 4	siltstone	Rohlenka	< 0.250	95.75	1.65	1.26	0.39	0.0039	7.86
TvP 5	fine-grained sandstone	Tvaroženský potok	< 0.250	97.19	2.88	2.6	0.28	0.0028	7.90

In all examined sorption systems, the recommended optimal phase ratios $R = m / V_o$ were kept, at which the proportion of sorbates adsorbed by solid phase ranged from 20 to 80 % of the total sorbate amount in the system (see ASTM E 1195 – 2001). In the case of natural sorbents with known contents of organic carbon, the suitable phase ratios were estimated using the relationship

$$R = m / V_o = 1 / ((m_o / m_s - 1) . K_D) = 1 / ((m_o / m_s - 1) . K_{OC} . f_{OC}). \quad (7)$$

In this relationship, m and V_o stand for a weight of the sorbent batch (g) and a system water phase volume (mL), resp.; m_o is the overall weight of the sorbent in a given system and m_s stands for a sorbate mass sorbed by the solid phase of such system. The other quantities are defined by equations (1) and (5). Rough calculations of optimal R values for all tested sorbates were carried out using reference values of the distribution coefficients K_{OC} according to Tab. 2. In the case of sorbents free of organic matter, the convenient phase ratios were determined tentatively by preliminary tests.

Equilibration of sorption systems

The investigated sorption systems were equilibrated by an efficient mechanical agitation of phase batches in hermetically closed reaction vessels – either on a shaker with horizontal table movement (100 mL vessels) or on a rotational overturn shaker (1000 mL vessels). All operations related to preparation and equilibration of sorption systems were carried out in an air-conditioned laboratory at 25 °C.

Except for the verification measurement of equilibration kinetics, all investigated systems were mixed by shaking for 24 hours. This period is generally considered as sufficient for equilibrium distribution of hydrophobic organic sorbates in soil sorption systems (Hance 1967, all mentioned standards). Verification measurements of kinetics of fluoranthene sorption by the tested sorbents with the agitation of bigger reaction vessels on the overturn shaker proved that the chosen constant period of agitation was sufficient for an achievement of equilibrium sorption in all tested systems. During the sorption kinetics measurements by serial method, the agitation was interrupted in convenient time intervals (for a period as short as possible), during which the water phase samples of approximately 1.5 mL were collected and analysed. Results of the continuous measurements of fluoranthene in the water phase, acquired using serial method for two concurrently processed samples of each sorbate, are shown in Fig. 1. The results of sorption kinetics measurements in the same systems employing parallel method were less reproducible and also less reliable.

Separation of solid particles by centrifugation

Before the determination of equilibrium sorbate concentrations, the analysed water phases were rid of suspended solid sorbent particles by centrifugation using a T 23 centrifuge (MLW, GDR) in closed vessels at 5000 rpm for at least 40 minutes. According to the aforementioned standard methods, the experimental arrangement of the centrifugation should guarantee a separation of solid particles bigger than 0.1 µm in diameter.

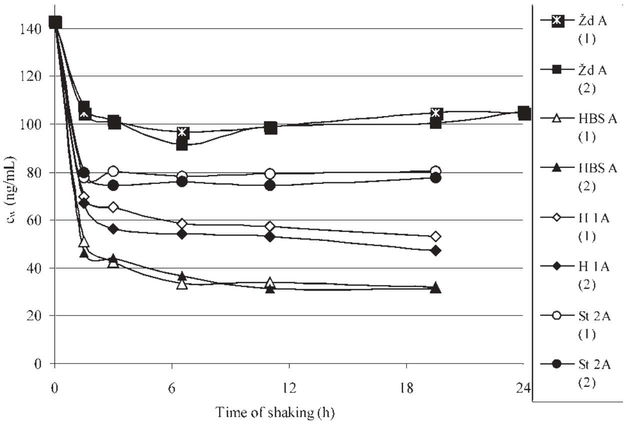

Fig. 1. Kinetics of fluoranthene sorption on natural sorbents Žd A, HBS A, H1 A, St2 A – measured in duplicate (1) and (2) using the serial method; sorbate concentrations in the aqueous phase c_w are plotted vs. time of shaking.

The experimental conditions (time and speed) ensuring the required centrifugation efficiency were calculated by using a general relationship (derived from the Stokes Law for spherical particles) in the form presented in the ASTM E 1195 – 01 (2001) standard

$$t = 9/2 . [n / [\omega^2 . r_p^2 . (\rho_p - \rho)]] . \ln R_b / \ln R_t, \quad (8)$$

where t stands for the total time of centrifugation (in seconds), n for water viscosity at 25 °C (= 8.95 × 10^{-3} g/s . cm), ω is an angular velocity (= $4\pi^2$ (turns per minute)^2 / 3600), r_p is a particle diameter (cm), ρ_p stands for particle density (g/cm^3), ρ_p for water density (g/cm^3), R_b is a distance (cm) from the rotation axis to the bottom of the solution and R_t is a distance (cm) between the rotation axis and the top of the solution.

Periods of time required for separation of spherical particles of various diameters (0.1 to 0.7 µm) and densities ranging from 1.5 to 2.65 g/cm^3 were calculated by introduction of the centrifuge parameters (5000 turns per minute, R_b = 14 cm, Rt = 7 cm) to the equation (8). Double periods of calculated times for the mentioned solid phase particle parameters, guaranteeing a better phase separation by the given arrangement, are shown in Fig. 2. The graph implies that the 40-minute-long centrifugation in the used arrangement and under the above mentioned conditions resulted in a separation of all spherical particles with densities over 1.8 g/cm^3 and diameters over 0.1 µm.

Determination of sorbate phase distributions

The equilibrium sorbate concentrations in water phases c_w were analysed by multicomponent methods of HRGC and HPLC, used for eluate analyses in column experiments. The equilibrium sorbate concentrations in the sorbent solid phase c_s were calculated as a difference between the initial

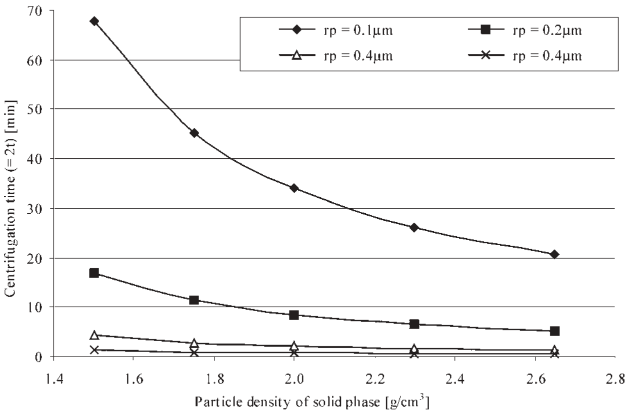

Fig. 2. Centrifugation times (double values) to remove spherical sorbent particles (with particle radii r_p = 0.1–0.4 μm and densities ρ_p = 1.5–2.65 g/cm^3) from aqueous phases at 25 °C; calculated from equation (8) for the conditions used with T-23 centrifuge: rotation speed 5000 rpm, distances R_b = 14 cm, R_t = 7 cm.

and the equilibrium sorbate concentration in the water phase according to the relationship

$$c_s = m_s / m = (c_{w,o} - c_w) \,.\, V_o / m, \qquad (9)$$

where m_s (g) stands for a mass of the sorbate fixed on the sorbent solid phase, m (g) is a mass of the tested sorbent batch, $c_{w,o}$ and c_w (g/mL) stand for initial and equilibrium sorbate concentrations in the water phase and V_o (mL) is the initial volume of this water phase.

Results and discussion

Sorption of model sorbates/pollutants on columns of natural sorbents (column elution experiment)

Retentions of seven model hydrophobic sorbates on columns of five different natural sorbents under conditions of gravitational elution by water were investigated in a column arrangement described in the experimental section. Physical and chemical properties of the sorbates are presented in Tab. 2, basic characteristics of the tested sorbents and column parameters are, together with experimental elution conditions for the individual columns, summarised in Tab. 1.

Sorbate distributions in column eluates (elution curves)

Changes in the concentrations of individual sorbates in continuously collected eluate fractions are shown in the form of elution diagrams (curves) in Fig. 3, a–e. The diagrams graphically indicate the penetration of pollutants, thus their interactions with individual sorbents during the elutions, carried out within 16–20 days (unceasingly), until the end of the experiment.

A diagram showing elutions of all tested pollutants from the column of weathered sandstone Ždánice (Žd) is shown in Fig. 3a. Both triazines and naphthalene, as the least hydrophobic constituents of the tested sorbate mixture, passed through the column at the very beginning of the elution. The sorbent column retained the other sorbates proportionally to their growing hydrophobicity (most of all hexachlorobenzene with the smallest solubility in water, see Tab. 2) and their elution from the column was not complete at the time of termination of the experiment.

Analogous elution diagram (Fig. 3b) for a column with Lelekovice soil (Le 4) indicates that all hydrophobic sorbates remained retained in the fill and only triazines passed through the column into the eluate at the end of the experiment (partially due to a very low flow rate of the mobile phase through a relatively impermeable column).

A coarse-grained lake bottom sediment of Horní Bečva (HBS 2) was found to be the most permeable of all tested natural sediments (rate of flow around 70 mL per hour). According to the elution diagram (Fig. 3c), only the least hydrophobic triazines and naphthalene passed through the column without any retention, other sorbates (excluding relatively more soluble methoxychlor) were present in the eluate in imperceptible concentrations only.

Well developed elution curves of both triazines obtained with the HBS 6 sorbent (Fig. 3d) substantiate a significant increase in retentions of hydrophobic sorbates on this sorbent with a higher organic matter content (C_{org} = 1.58 %). Other sorbates including naphthalene eluted to a negligible extent only during the experiment.

Another lake bottom sediment from the Horní Bečva Reservoir (HBV 4) collected in a proximity of the outlet, contained the highest proportion of organic matter (C_{org} = 3.54 %) but was also the most fine-grained of all tested sorbents and therefore demonstrated the smallest rate of gravitational water flow through the column. Its elution diagram (Fig. 3e) implies that even the least sorbed triazines did not reach their elution maxima at the end of the experiment. Other model sorbates eluted only to a very small extent.

Distribution of sorbates fixed on sorbent columns

After the termination of elution experiments, the columns of the investigated sorbents were cut into 3.0 cm long cylindrical segments, and each such layer was subjected to analyses on all model sorbates. Results of sorbate determinations in individual layers of the tested sorbents are shown in balance diagrams (Fig. 4, a–e). The balances using column graphs compare the amounts of individual sorbates found in various layers of a given sorbent column with the overall sorbate mass eluted by water during the experiment.

The tested sorbates were least retained by the column of Ždánice sandstone (Žd, Fig. 4a). At the end of the elution experiment (under conditions shown in Tab. 1), both triazines were virtually quantitatively eluted from the sorbent column. Concentrations of the other model sorbates in the uppermost layer of this sorbent were also negligible, compared to their overall concentrations in the system. As far

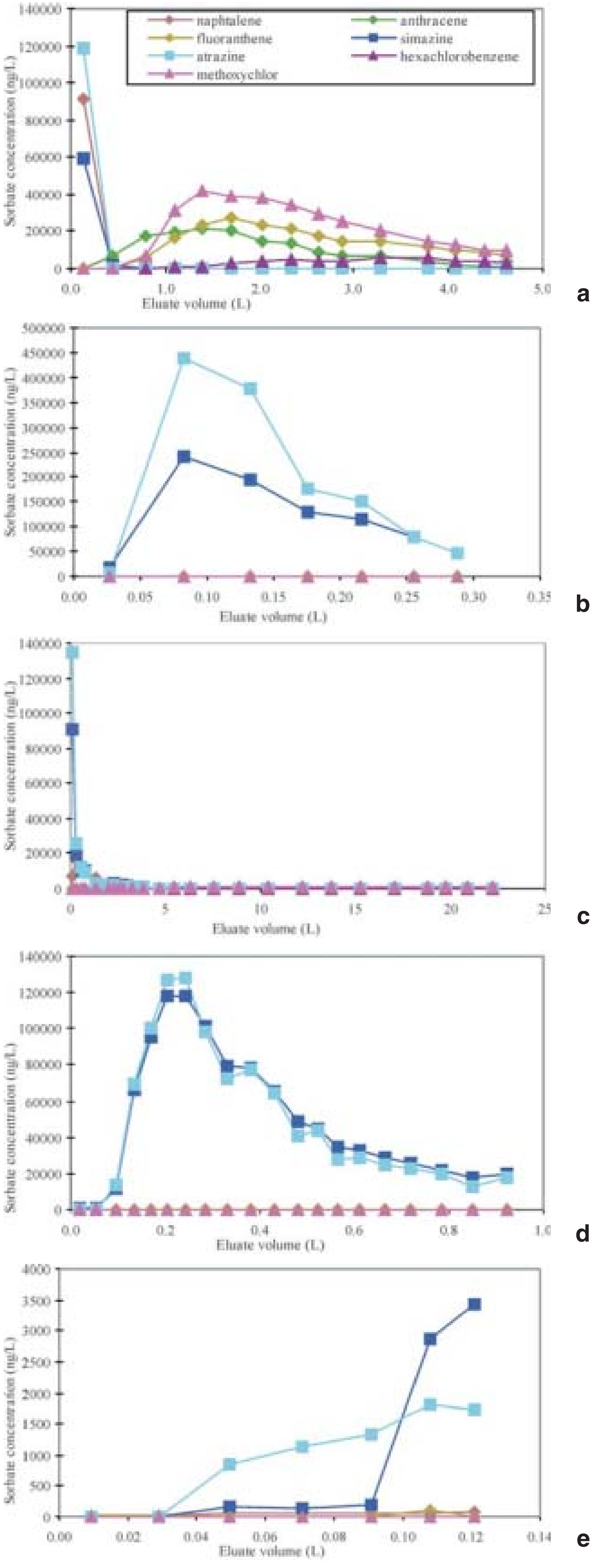

Fig. 3. Curves of elution of model sorbates with water from columns filled with a – Žd; b – Le 4; c – HBS 2; d – HBS 6; e – HBV 4.

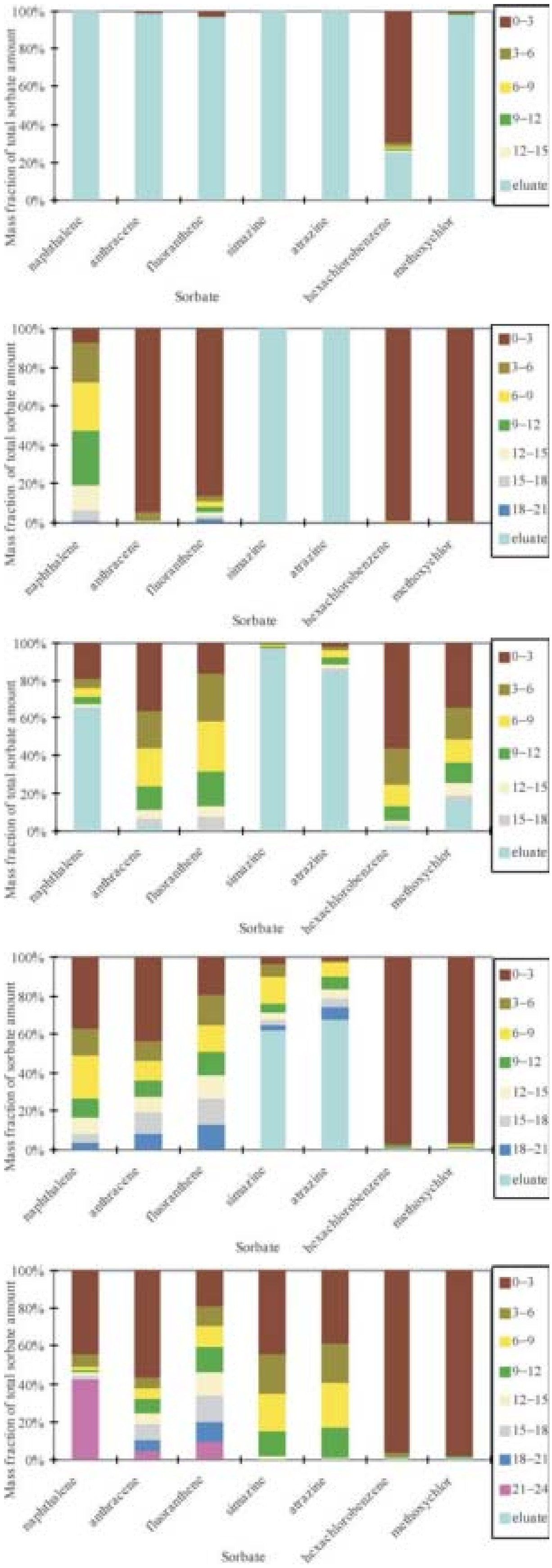

Fig. 4. Mass fractions (in %) of total sorbate amounts found in water eluates and in segments of sorbent columns filled with a – Žd; b – Le 4; c – HBS 2; d – HBS 6; e – HBV 4.

as hexachlorobenzene (HCB) is concerned, 75 % of its overall mass remained in the uppermost part of the column. Surprisingly, the bottom part of a column did not contain any HCB at all – the rest (ca. 25 %) appeared directly in the eluate. Owing to the fact that the sorption coefficient value for HCB is not much different from those of fluoranthene and methoxychlor (see Tab. 2), the asymmetric fixation of HCB on the top of the column was very likely caused by its limited solubility in water. The HCB breakthrough into the eluate without corresponding retention in the bottom part of a column in the given experimental arrangement might then be due to fast water flow-through in the column (see Tab. 1, applicable also for the column with HBS 2 sorbent).

Data related to other tested sorbents have to be regarded likewise. At the end of the experiment with column of soil Le 4 (Fig. 4b), both triazines were eluted quantitatively, main proportions of other sorbates remained retained in the uppermost part of the column (excluding naphthalene, which was evenly distributed in the whole volume of column filling).

The lake bottom sediment HBS 2 (Fig. 4c) retained only small proportions of triazines (more of a less hydrophilic atrazine), around 30 % of naphthalene and 75 % of methoxychlor. The remaining pollutants were retained almost quantitatively. A small-extent breakthrough of more hydrophobic sorbates into the eluate might have been caused not only by a higher water flow but also by a relatively low content of organic matter ($f_{OC} = 0.0022$).

The column filled with sediment HBS 6 (Fig. 4d) retained about 1/3 of the overall amounts of both triazines, and the other sorbates were retained virtually quantitatively. The main shares of the least soluble hexachlorobenzene and methoxychlor remained fixed in a narrow zone on the top of the column.

During the experiment with sediment HBV 4 (Fig. 4e), containing the highest proportion of organic matter ($f_{OC} = 0.0354$), virtually no significant infiltration of any sorbate into the eluate took place. The concentration distribution of pollutants in the column reflected the known values of their sorption and solubility parameters, however, it should be mentioned that such distribution was largely a consequence of an elution by a very small volume of water in the least permeable column (see Tab. 1).

The Overall Appraisal of Column Experiments

The column experiments explored in detail the distribution balances of chosen hydrophobic sorbates/pollutants between the phases of investigated systems in a dynamic elution arrangement. The retentions of individual sorbates generally grew with their increasing hydrophobicity and also with the content of organic carbon in the sorbents. Based on the comparison of elution and balance diagrams (Figs 3 and 4), the model sorbates of the tested mixture can be lined up in a series according to their growing sorption affinities to the investigated sorbents: simazine and atrazine < naphthalene < methoxychlor < anthracene < fluoranthene < hexachlorobenzene. This sequence broadly agrees with the estimations of their sorption behaviour based on the known physicochemical data and remains the same for the majority of the tested sorbents.

A relatively long-term elution by water resulted in leaching of the least hydrophobic sorbates from the columns; main proportions of other sorbates remained retained in the column fills. Vertical distributions of sorbates in sorbent columns reflected at the same time the above elution sequences. Insignificant concentrations of more hydrophobic sorbates in eluates were more or less in agreement with the A criterion values for background concentrations of investigated sorbates in groundwaters (MP MŽP ČR 1996). Elution curves with well-developed real maxima were, in the given experimental setup, obtained only for elutions of the least hydrophobic sorbates from sufficiently permeable columns (Figs 3 a, b, d). Asymmetric concentration profiles of the curves with sharp fronts and tailing of elution zones corresponded to non-linear adsorption isotherms; however, the asymmetric convex shape of the curves might have been (in the given experimental arrangement) partially due to dynamic factors.

The described column experiment was already used in the research into similar environmental problems (Müller et al. 1997). It represents actually a methodical modification of a leaching test defined by the OECD guideline ***/D (1998) suggested for testing of retentions of pesticides by soils. Our inquiry into the sorption of hydrophobic organic pollutants by miscellaneous natural sorbents proved that the simple experimental setup with gravitational elution in columns of fixed dimensions at a low input hydrostatic pressure of water as a mobile phase is, to a certain extent, limited. These limitations also apply to the cited OECD methodical guideline.

- The procedure is applicable only to sorbents, the particle size distribution of which guarantees higher flow rates of water through the column.
- Retention measurements of unequally hydrophobic sorbates on sorbent columns with different hydraulic parameters and different organic matter contents are difficult to compare.
- Long duration times of elution experiments, induced by considerable dimensions of a sorption bed, small flow rates of the mobile phase, sorbate hydrophobicity and high proportions of organic matter in sorbents are associated with a risk of hardly controllable changes in sorbate and sorbent organic matters composition.

Some of these limitations could most likely be eliminated by technical innovations of column elutions, based on the usage of mid-pressure liquid chromatography (MPLC) instrumentation.

Sorption measurements of hydrophobic pollutants using batch method

The distribution/sorption coefficients K_D or K_{OC} obtained by using batch methods largely depend on the nature of phases and constituents of the sorption systems in question and also on the experimental arrangement and conditions of the measurements. With respect to the environmental and ecotoxicological risks associated with possible incorrect determinations of sorption data, the batch methods are being gradually standardised. In addition to valuable methodological recommendations (see, e.g., Beneš et al. 1994; Štamberg 1996), some general technical directions and norms were published recently (OECD Guideline 106 – 1998; US EPA OPPTS 835.1220 – 1998; ASTM Standard E 1195 – 2001). The methods used for the determination of distribution coefficients in our study respect all basic recommendation of the above directions, especially those of the ASTM standard.

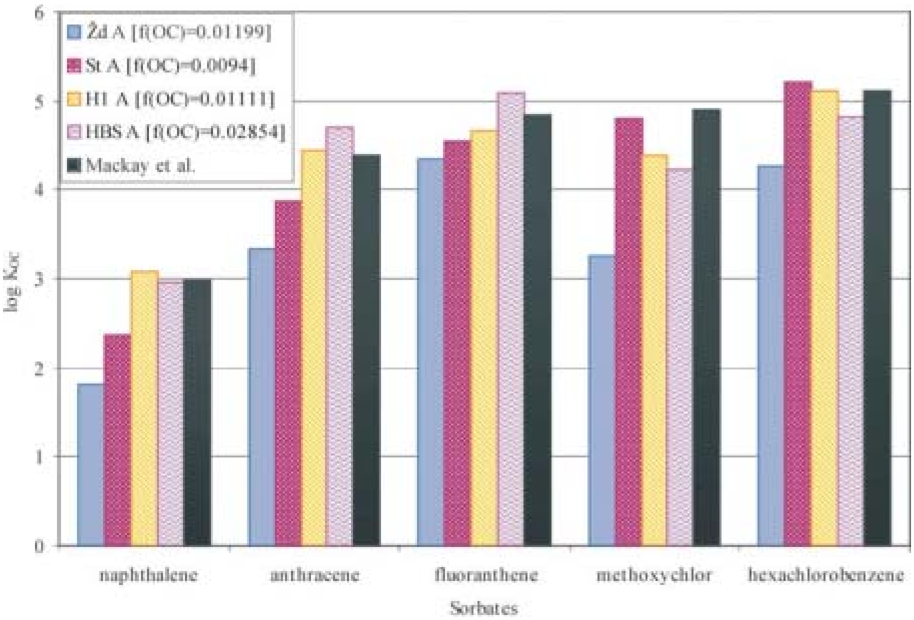

Fig. 5. Mean experimental values of K_{OC} characterizing sorption of selected model sorbates on natural sorbents Žd A, St 2 A, H1 A and HBS A – in comparison with the respective reference values of the parameter (Mackay et al. 1999).

Hydrophobic organic sorbates used for testing of sorption interactions by using batch method are presented in Tab. 2. In addition to the basic selection of five model sorbates, including naphthalene, anthracene, fluoranthene, methoxychlor and hexachlorobenzene, lindane (γ-hexachlorocyclohexane) was also used in some measurements.

The list of sorbents, the sorption parameters of which were measured by means of batch method, is presented in Tab. 3 together with some basic characteristics of the materials. The sample series A comprised natural sorbent samples from the localities of Ždánice (Žd A), Horní Bečva (HBS A), Hevlín (H 1 A) and Stavěšice (St 2 A). Symbol A denotes independently prepared and characterised sample lots from given localities, pretreated by the standard routine procedure of sieving through a 2 mm sieve. Commercially available technical preparations of marine sand (MP A) and chromatographic wide-porous silica gel (SKG 100 A) served as comparative reference samples with mineral matrixes differing in active surface areas.

In the measurements of Freundlich sorption isotherms, special finer-grained preparations (with particle size ≤ 0.25 mm) of reference samples of some subsoil sedimentary rocks from the above mentioned (H 1, St 2) and neighbouring (R 4, TvP 5) sampling sites were used.

Distribution/sorption coefficients acquired using batch method

The distribution coefficients K_D evaluating sorption of naphthalene, anthracene, fluoranthene, methoxychlor and hexachlorobenzene onto the sorbents of set A are presented in Tab. 4. The K_D values were determined by repeated gauging of equilibrium sorbate distributions between phases of the investigated systems under conditions mentioned in the methodical section and by the calculation according to the relationship (1). In the case of natural sorbents with known contents of organic carbon (f_{OC}), the K_D values were recalculated using equation (5) on the normalised distribution coefficients K_{OC}.

Average values of log K_{OC} shown in Tab. 4 are also shown in column graphs in Fig. 5 together with the recommended reference log K_{OC} values for given sorbates, suggested by Mackay et al. 1999 (see also Tabs 2 or 6). Comparison of the experimental and reference data demonstrates that in the case of polycyclic aromatic hydrocarbons and hexachlorobenzene, experimental log K_{OC} values acquired for HBS A and H 1 A sorbents are in a good agreement with reference values from the literature. On the other hand, values of log K_{OC} for St 2 A and especially for Žd A sample are substantially lower. Systematic decrease in the acquired distribution coefficient values K_{OC} for sorption interactions of all investigated sorbates with sample Žd A and partly also with sample St 2 A is most likely caused by different nature and/or limited accessibility of organic matter in these sorbents. These factors are not yet taken into consideration in the existing definition of K_{OC} parameter by the equation (5).

Sorption measurements of chosen model sorbates by reference sorbent samples with mineral surfaces (MP A, SKG 100 A) provided substantially lower K_D values than those acquired in parallel measurements of natural sorbents containing organic matter. At the same time, K_D values of specifically structured chromatographic silica gel (with declared active surface area of 420 m^2/g) were for most sorbates (excluding naphthalene) several times higher than those of the technical marine sand preparation. Results summarised in Tab. 4 are in good agreement with data from the literature (see, e.g., Schwarzenbach et al. 1993; Fetter and Fetter 1999), according to which the values of distribution coefficients K_D describing sorptions of similar organic sorbates on

Tab. 4. K_D and K_{OC} values of model sorbates determined using the batch method

Sorbate	Sorbent	f_{OC}	n	K_D				K_{OC}	log K_{OC}
				mean	min	max	RSTDEV	mean	mean
							%		
Naphthalene	MP A	< LOD	2	2.89	2.86	2.91	nd	nd	nd
	SKG 100 A	< LOD	4	1.56	1.16	1.85	nd	nd	nd
	Žd A	0.012	3	0.78	0.32	1.64	nd	64.9	1.81
	HBS A	0.0285	3	26.6	22.5	33.8	nd	933	2.97
	H 1 A	0.0111	3	13.1	9.25	19.7	nd	1 177	3.07
	St 2 A	0.0094	3	2.23	1.55	2.66	nd	237	2.37
Anthracene	MP A	< LOD	6	0.63	0.35	1.05	35	nd	nd
	SKG 100 A	< LOD	5	6.18	4.92	8.82	22	nd	nd
	Žd A	0.012	5	25.4	10.4	46.3	49	2 118	3.33
	HBS A	0.0285	5	1405	1017	2026	26	49 219	4.69
	H 1 A	0.0111	5	306	219	411	22	27 539	4.44
	St 2 A	0.0094	5	54.3	30.6	90.1	36	5 777	3.76
Fluoranthene	MP A	< LOD	6	2.61	1.42	4.87	46	nd	nd
	SKG 100 A	< LOD	6	18.4	10.1	29.3	40	nd	nd
	Žd A	0.012	5	266	117	538	54	22 159	4.35
	HBS A	0.0285	5	3579	2309	4721	27	125 415	5.1
	H 1 A	0.0111	4	514	367	675	21	46 241	4.67
	St 2 A	0.0094	5	321	183	508	41	34 148	4.53
Methoxychlor	MP A	< LOD	2	0.49	0.44	0.54	nd	nd	nd
	SKG 100 A	< LOD	1	1.84	nd	nd	nd	nd	nd
	Žd A	0.012	2	21.3	12.9	29.8	nd	1 779	3.25
	HBS A	0.0285	2	1 813	1 684	1 943	nd	63 541	4.8
	H 1 A	0.0111	2	265	135	395	nd	23 880	4.38
	St 2 A	0.0094	2	157	96	219	nd	16 724	4.22
Hexachlorobenzene	MP A	< LOD	2	3.53	3.25	3.82	nd	nd	nd
	SKG 100 A	< LOD	2	12.4	6.43	18.3	nd	nd	nd
	Žd A	0.012	1	223	nd	nd	nd	18 603	4.27
	HBS A	0.0285	2	4 548	4 539	4 557	nd	159 356	5.2
	H 1 A	0.0111	2	1 423	1 176	1 671	nd	128 115	5.11
	St 2 A	0.0094	2	612	558	667	nd	65 159	4.81

Notes: nd – value not determined; LOD – limit of detection; n – number of independent measurements; RSTDEV – relative standard deviation.

sorbents with mainly mineral surfaces range from tenths to tens of mL/g (L/kg), depending on the size and hydrophobicity of sorbate molecules and also on sorption parameters of the sorbent.

In agreement with the general recommendations of the guidelines and standards for distribution coefficient measurements employing the batch method (OECD Guideline 106/D, 1998; US EPA Guideline OPPTS 835.1220, 1998; ASTM Standard E 1195-01, 2001), all tested natural sorbents of series A were prepared for tests by standard procedures of soil sample modification before physicochemical analyses (ISO/DIS 11464, 1992). These procedures comprised a gentle disintegration of lumps and sieving of the analytical sample through a 2 mm sieve. Soil and sediment samples prepared in this way might also contain larger particles of Recent organic matter (in various stages of transformation), the presence of which negatively affects both phase and chemical homogeneity of the preparations. The gauging of Freundlich sorption isotherm parameters with fluoranthene and lindane as model sorbates was therefore realised with more efficiently pulverised and homogenised sorbent samples which were prepared by using a two-step particle-size reduction of dried materials with gradual crushing and sieving of the material through 2 mm and 0.25 mm sieves.

Results of sorption isotherm measurements with fluoranthene and lindane in systems with finer-grained preparations of the examined sorbents are shown in Figs 6 and 7. Experimental sorption isotherms of the investigated systems (according to equation [2]) demonstrated mostly

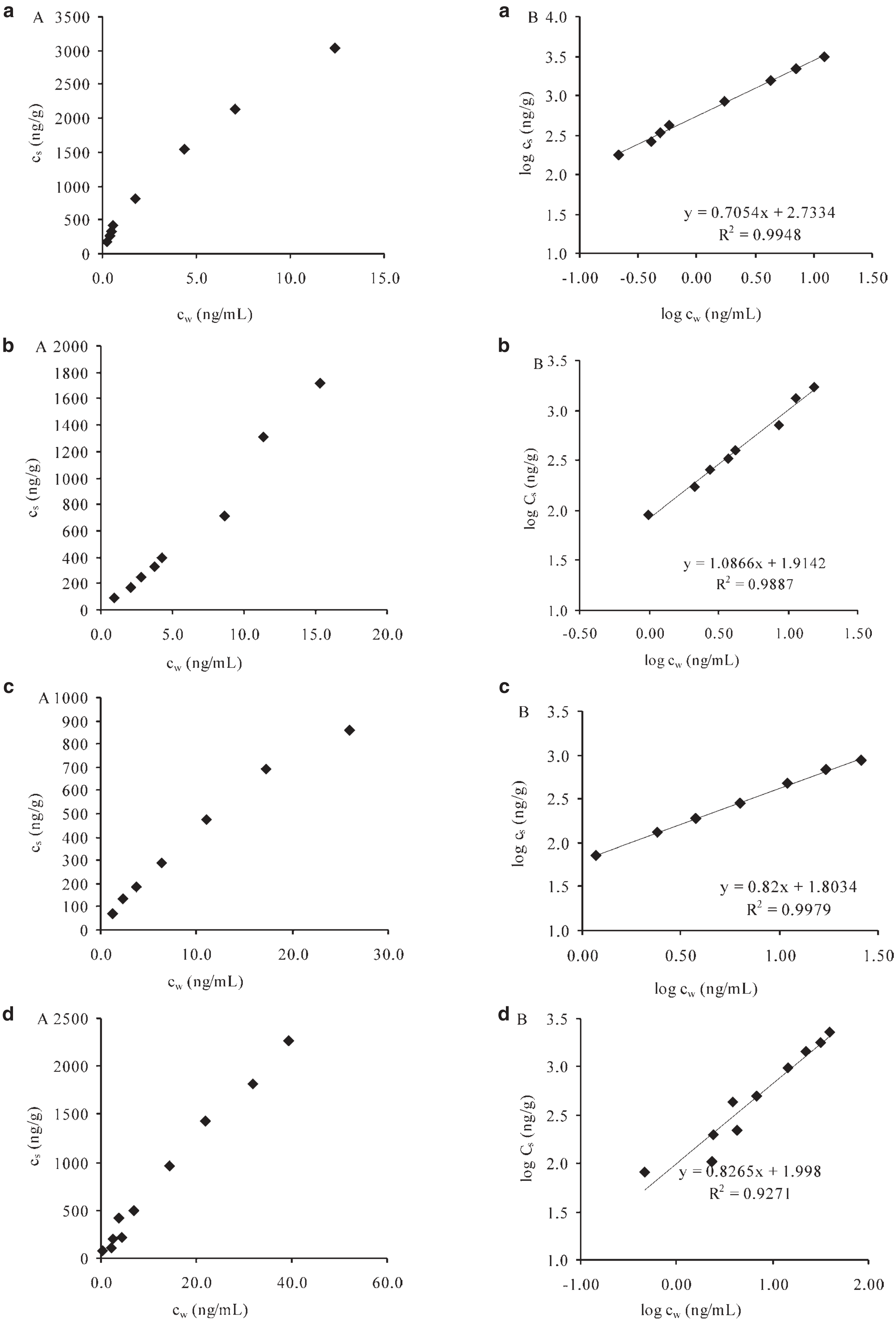

Fig. 6. Freundlich isotherms (in normal A and linearized B form) for the sorption of fluoranthene by natural sorbents a – H1 (f_{oc} = 0.0081); b – St2 (f_{oc}= 0.0078); c – R4 (f_{oc}= 0.0039); d – TvP5 (f_{oc}= 0.0028).

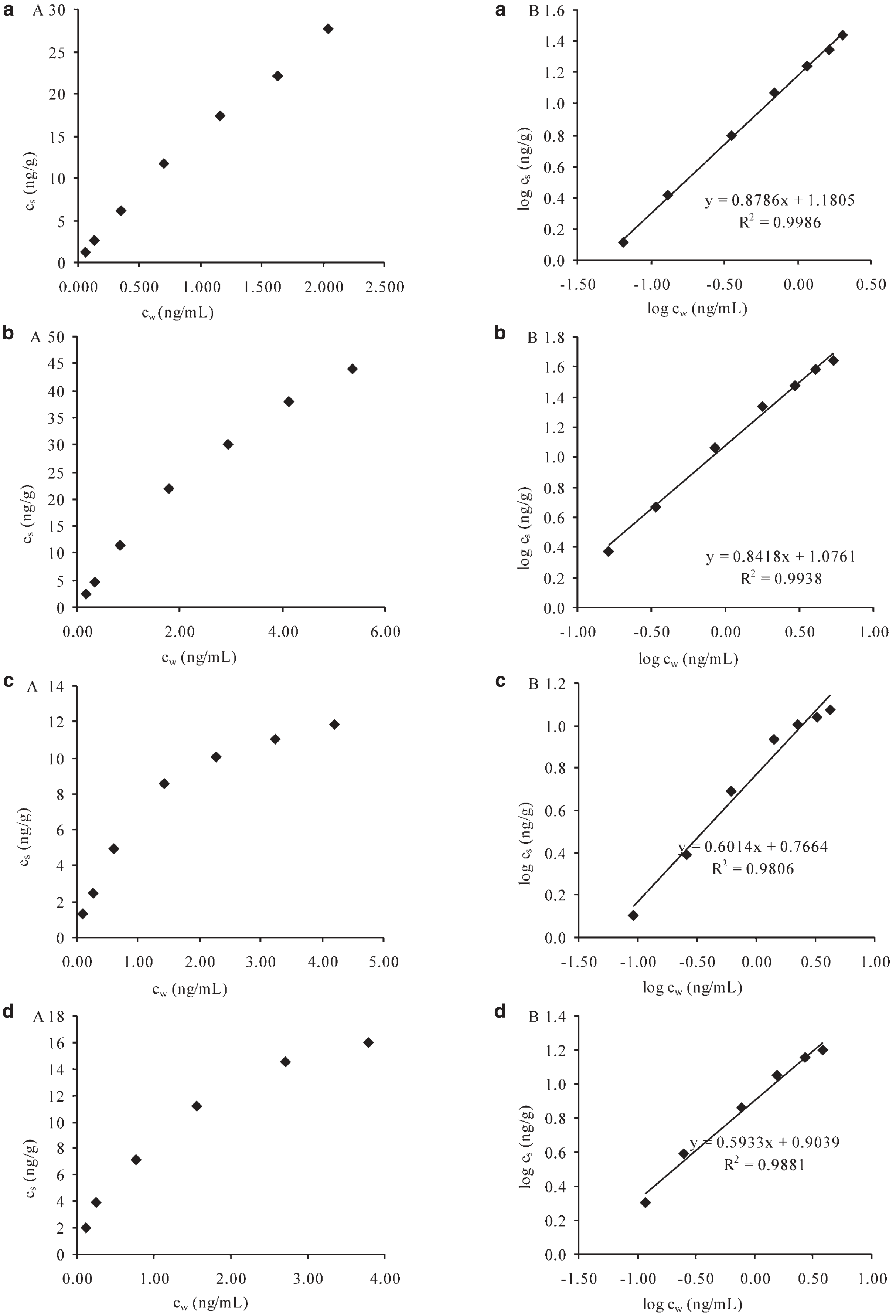

Fig. 7. Freundlich isotherms (in normal A and linearized B form) for the sorption of lindane by natural sorbents a – H1 (f_{oc} = 0.0081); b – St2 (f_{oc}= 0.0078); c – R4 (f_{oc}= 0.0039); d – TvP5 (f_{oc}= 0.0028).

slightly non-linear convex shapes in the tested concentration intervals (Figs 6 and 7, Graphs A), which could be made linear by plotting logarithms of concentration values according to equation (3) (Graphs B).

Freundlich sorption coefficients K_F, obtained via linear regression analysis of variables in the logarithmic shape of the Freundlich isotherm equation, do not differ significantly from average K_D values calculated from the ratios of equilibrium sorbate concentrations in individual experimental points of isotherms (see Tab. 5). Slightly convex shapes of sorption isotherms also agree with the exponent values 1/n (ranging from 0.6 to 1), equal to the slopes of linearised sorption isotherms. The coefficient of determination R^2 (similarly to the correlation coefficient R) indicates the reliability of K_F and 1/n values, obtained by the regression analysis of the Freundlich equation in a logarithmic shape for particular sorption systems.

Data in Tab. 5 and Fig. 8 also indicate that the distribution coefficients $K_{OC(F)}$ of fluoranthene and lindane found in this way correspond relatively well to the average values of log K_{OC} calculated for individual experimental points in the investigated concentration ranges. The measurement of sorption isotherms of both sorbates by H 1 sorbent from Hevlín provided the values of $K_{OC(F)}$ (or K_{OC}, respectively), which were virtually identical to those suggested by the literature (4.83 for fluoranthene and 3.31 for lindane – see Tabs 5 and 6). Measurements of fluoranthene sorption on H 1 and St 2 also corroborated the average values of log K_{OC}, acquired from the analyses of coarser-grained preparations (series A) of the samples (see Tab. 4 and Fig. 8).

Most sorption measurements of all tested sorbates as well as the measurements of fluoranthene and lindane on differently pretreated sample charges of siltstone from Hevlín (H 1, H 1 A) indicate that organic matter of this sample possesses properties predicted by the hydrophobic sorption model. Therefore, this sorbent can serve as an internal reference material for experimental studies of sorption of organic pollutants by natural sorbents. Comparable sorption efficiences for the majority of tested model pollutants can also be observed in the case of lake bottom sediment HBS A. Even though the other tested natural sorbents contain the organic matter in concentrations corresponding to the presumptive dominance of hydrophobic sorptions ($f_{OC} > 0.001$), experimental distribution coefficients K_{OC} of these materials with most tested sorbates are significantly lower than the expected K_{OC} values. According to data in Table 4 (see also Fig. 5), sandstone Žd A exhibited the smallest sorption affinity with all sorbates (corresponding to 7 % of the presumptive K_{OC} value in the case of naphthalene, 9 % in the case of anthracene and 2 % in the case of methoxychlor).

Variability in sorption parameter values of hydrophobic organic pollutants

Distribution coefficient K_{OC} is the main output parameter in measurements of sorption interactions between organic sorbates and natural sorbents containing organic matter.

Tab. 5. Freundlich distribution coefficients K_F and $K_{OC(F)}$ and respective K_D and K_{OC} mean values for the sorption of fluoranthene and lindane by natural sorbents H 1, St 2, R 4 and TvP 5 in comparison with published reference data (Mackay et al. 1999)

Sorbate	Sorbent	Organic carbon content	Data derived from linearized plot of Freundlich equation $\log c_s = \log K_F + (1/n) * \log c_w$						Calculated as $K_D \approx c_s/c_w$ for each point of the plot		
			intercept	slope	coefficient of determination	Freundlich distribution coefficients			distribution coefficients (mean)		RSTDEV
		f_{OC}	log K_F	1/n	R^2	K_F	$K_{OC(F)}$	log $K_{OC(F)}$	log K_{OC}	K_{OC}	%
Fluoranthene	H 1	0.0081	2.733	0.705	0.995	541.25	66821	4.82	4.82	65362	40
	St 2	0.0078	1.914	1.087	0.989	82.07	10522	4.02	4.08	12059	13
	R 4	0.0039	1.803	0.820	0.998	63.59	16306	4.21	4.08	11967	19
	TvP 5	0.0028	1.998	0.827	0.927	99.54	35550	4.55	4.45	27993	47
	Mackay et al.							(4.83)	(4.83)		
Lindane	H 1	0.0081	1.181	0.879	0.999	15.15	1871	3.27	3.32	2096	16
	St 2	0.0078	1.076	0.842	0.994	11.92	1528	3.18	3.18	1523	18
	R 4	0.0039	0.766	0.601	0.981	5.84	1497	3.18	3.23	1692	53
	TvP 5	0.0028	0.904	0.593	0.988	8.01	2862	3.46	3.54	3487	50
	Mackay et al.							(3.31)	(3.31)		

Tab. 6. Variability of published values of distribution coefficients K_{OC} (data compiled in the cited databases/handbooks)

Sorbate	Statistic parameter	US EPA (1996)			Mackay et al. (1999)		
		n	K_{OC}	log K_{OC}	n	K_{OC}	log K_{OC}
			(mL/g)			(mL/g)	
Naphthalene	number of publications	20			26		
	arithmetic mean		1231	3.09			
	reference value (geomean)		1191	3.08		961	2.98
	minimal value		830	2.92		240	2.38
	maximal value		1950	3.29		100000	5
Anthracene	evaluated publications	9			24		
	arithmetic mean		24362	4.39			
	reference value (geomean)		23493	4.37		24547	4.39
	minimal value		14500	4.16		912	2.96
	maximal value		33884	4.53		57544	5.76
Fluoranthene	evaluated publications	3			8		
	arithmetic mean		49433	4.69			
	reference value (geomean)		49096	4.69		68043	4.83
	minimal value		41687	4.62		10000	4
	maximal value		54954	4.74		2398833	6.38
Methoxychlor	evaluated publications	1			30		
	arithmetic mean						
	reference value (geomean)		80000	4.9		79433	4.9
	minimal value					617	2.79
	maximal value					1096478	6.04
Hexachlorobenzene	evaluated publications	1			19		
	arithmetic mean						
	reference value (geomean)		80000	4.9		129653	5.11
	minimal value					363	2.56
	maximal value					1995262	6.3
Lindane	evaluated publications	65			39		
	arithmetic mean		1477	3.17			
	reference value (geomean)		1352	3.13		2054	3.31
	minimal value		731	2.86		15	1.18
	maximal value		3249	3.51		43652	4.64

The ASTM E 1195 – 01 (2001) standard denotes the K_{OC} parameter as a sorption constant of the given chemical compound in soils and sediments. This designation is somewhat misleading because both published and experimentally obtained K_{OC} values for sorbate interactions with various types of natural sorbents are far from having a nature of universally valid constants. Even though our study is methodically based on the ASTM guideline, this report designates the K_{OC} quantity solely as a distribution/sorption coefficient instead of a sorption constant.

The limited reliability of scatteredly published values of normalised distribution coefficients K_{OC} was already mentioned in the introductory section of this study. The variability of data found in the literature is indicated by the overview of average, minimal and maximal log K_{OC} values for our selection of model hydrophobic sorbates, presented in Tab. 6. Data in the table were taken from two recognized databases, compiling relevant published data on properties of organic pollutants (US EPA 1996; Mackay et al. 1999). Though the average and/or recommended reference K_{OC} values (used also in our study) are of the highest significance for practical applications, substantial differences in the published parameter values cannot be ignored.

Another characteristic example of real variability in experimental K_{OC} values can be illustrated on results of interlaboratory comparative tests presented in the appendix to the standard ASTM E 1195 – 2001. Measurements of sorption of trifluraline (herbicide) on 13 soils of different type (with f_{OC} ranging from 0.0041 to 0.0337) provided a data set of K_{OC} measurements with an average value of 5730, standard deviation of 2150 and relative standard deviation (variation coefficient) of 38 %. The standard also generally presumes and accepts a divergence in analogous K_{OC} measurements with various natural sorbents, characterised by relative standard deviations between 20 and 50 % of the average value.

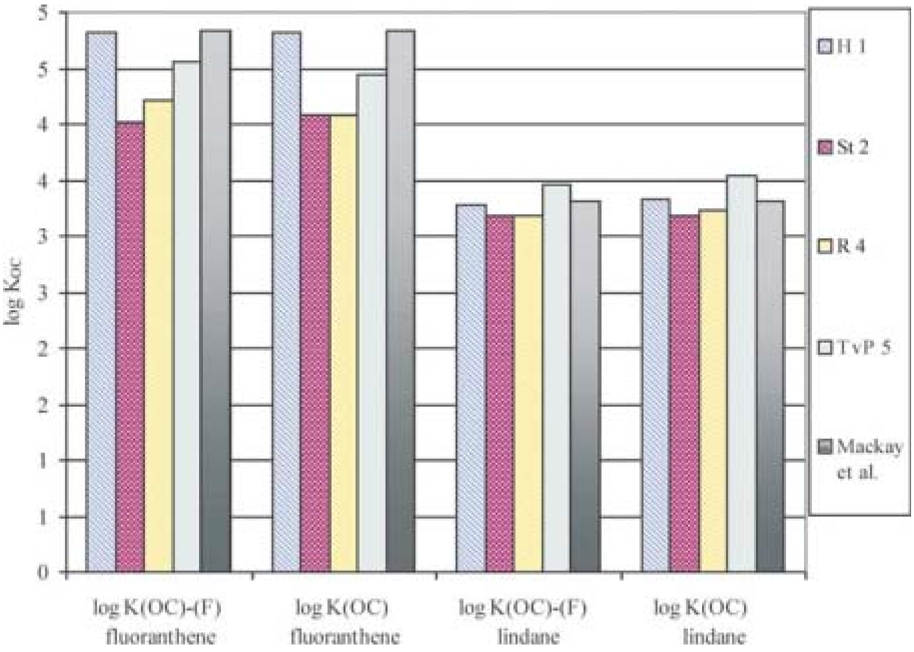

Fig. 8. Freundlich coefficients $K_{OC(F)}$ and mean distribution coefficients K_{OC} found for sorption of fluoranthene and lindane by natural sorbents H1, St2, R4 and TvP5 – in comparison with the respective reference K_{OC} values (Mackay et al. 1999).

The differences in experimentally acquired K_{OC} parameter values, observed even in our measurements employing the batch method, lead to considerations over possible sources of uncertainty in K_{OC} determinations. The overall uncertainty in K_{OC} assessments is largely due to the:

a) uncertainty in the determination of distribution coefficient K_D, defining the overall sorbate distribution between the phases of the investigated system,
b) uncertainty in the determination of the total organic carbon content (f_{OC} parameter),
c) uncertainty resulting from different sorption affinities of different structure types of organic matter (present in natural sorbents) with hydrophobic sorbates.

Ad a) Uncertainties covered by this point can be significantly reduced by applications of substantial recommendations and rules included in the above cited methodical standards and guidelines. According to our experience, operations affecting the reliability of experimental K_D determinations comprise, among others, the pretreatment procedures of the tested natural sorbents, the way of sorbate dosing into the investigated sorption systems and, of course, the overall analytical reliability of sorbate determinations in the water phase.

Ad b) The determination of the total organic carbon (C_{org}, f_{OC}) in the tested sorbents is usually carried out by the calculation from the difference in parallel determination of total and mineral (carbonate) carbon ($C_{org} = C_{tot} - C_{min}$) or directly by the analysis of C_{org} in the sample after a preceding acidic decomposition of carbonates. Organic carbon is oxidised to carbon dioxide either by burning in the oxygen atmosphere or by the excess of oxidative agents in solutions. Results of all methodical varieties are usually affected by specific errors, the relative extent of which (and thus their share on the distortion of f_{OC} and K_{OC}) depends on the nature of organic matter in the samples. Relative values of these errors generally grow with decreasing contents of organic matter in the samples. Provided that the lower limit of the concentration interval, in which hydrophobic sorptions of organic sorbates by organic matter sorbents predominate, is considered to be identical to the content of organic carbon of around 0.1–0.2 %, the limits of detection of the method used for the assessment of C_{org} or f_{OC} must be reasonably lower (at least by one order of magnitude). The scale of the used method must also guarantee that the results of the C_{org} determination cannot be affected by common compositional heterogeneity of the tested natural sorbents.

Ad c) The original linear model of hydrophobic sorption assumed that sorption of non-polar solutes is predominantly controlled by the distribution of hydrophobic sorbate molecules between water and relatively homogeneous and highly amorphous gelatinous humic matrix. However, further research proved that the affinity of organic matter with non-polar organic compounds can be affected by its nature, origin and geological and geochemical history. For example, organic matter in unweathered shales and coals with higher degrees of carbonisation provides up to one order of magnitude higher sorption capacities than organic matter in Recent soils, geologically immature or intensely weathered materials (Grathwohl 1990, Weber et al. 1992). On the other hand, humic acids sorb under comparable conditions almost 30-times more trichloroethylene than the native cellulose having approximately identical elementary composition and atomic ratios ($O/C \approx 0.8$ and $H/O \approx 2.0$) (Grathwohl 1990). Primary knowledge of the different sorption of hydrophobic organic compounds on different fractions of natural organic matter (Garbarini and Lion 1986, Gauthier et al. 1987) was affirmed by some other authors (results and bibliography are presented, e.g., by Mackay et al. 1999). There are also experimentally founded hypotheses (Holmén and Gschwend 1997), according to which the lowered sorption affinities of organic matter with organic sorbates might be, in some cases, caused by a deposition of organic matter in hardly accessible positions of the rock matrix (e.g., by its encapsulation in the mineral phase). Polarity and the aromatic carbon content (Kile et al. 1995, Perminova et al. 1999) are regarded as important general structure parameters of organic matter in natural sorbents with positive correlations to the intensity of hydrophobic sorption interactions, however, the development of methods used for structural characterisation of geosorbent organic matter with respect to hydrophobic sorptions of organic sorbates has not yet (for various reasons) made a significant progress.

In any case, during the study of geosorbent sorption properties, it is advisable to pay much more attention to different composition and sorption properties of organic matter of distinct origin (natural, anthropogenic, Recent and fossil) as well as to other factors which have not been taken into account yet in the simple model of hydrophobic sorption.

Conclusions

Fairly universal batch (static) methods used for the determinations of equilibrium distribution coefficients K_D (K_F) are of paramount importance for sorption studies of hydrophobic organic pollutants. These methods are less affected by different nature and properties of both investigated natural materials and pollutants/sorbates. The reliability of results acquired by means of batch methods is significantly enhanced by their recent standardization. According to our experience, the latest version of an ASTM E 1195 – 01 (2001) standard well meets the practical requirements of environmental and geochemical determination of sorption parameters for various natural sorbents.

Column (dynamic) methods in a simple elution arrangement with gravitational elution by water clearly show the differences in distributions of different hydrophobic pollutants between the phases of the given sorption system on one hand, but, on the other hand, they are inefficient and (for various reasons) generally unsuitable for the measurements of distribution coefficients. They fail especially in sorption studies of strongly hydrophobic, volatile and less persistent pollutants and in gauging of sorbents possessing very fine granularity and/or higher organic matter contents.

Experimentally determined K_D (K_F) values and retentions of tested sorbates generally grow with their increasing hydrophobicity, the variability of results fluctuates in the case of repeated measurements of these parameters within the limits tolerated by the cited ASTM standard.

The normalised distribution coefficient K_{OC} and $K_{OC(F)}$ values for some of the examined sorption systems, calculated by introduction of experimental K_D and f_{OC} values into equations (5) and (5a), are in a good agreement with the published reference values of these parameters; some other sorbents demonstrate significantly lower values. Systematic decrease in K_{OC} ($K_{OC(F)}$) values (proportional for most sorbates) is probably caused by the different nature (structural type, composition or phase heterogeneity) of organic matter and/or by its limited accessibility in matrixes of the tested sorbents.

The aforementioned conclusions further imply that the potential of natural sorbents to sorb hydrophobic sorbates should always be tested by direct measurements of sorption interactions of these materials with suitable model sorbates. Estimation of K_D values for sorption of hydrophobic pollutants on a sorbent of interest, calculated by the introduction of its actual organic carbon content f_{OC} and the respective known (reference, overtaken) K_{OC} values of the sorbates into the definitional relationship $K_D = K_{OC} . f_{OC}$, is improperly simplified application of the hydrophobic sorption model, which may (without a direct experimental check of sorption potential of the examined natural material) lead to questionable results.

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