

## Characteristics of organic matter and contents of some ubiquitous hydrophobic organic pollutants in selected soils and sediments

Zbyněk Boháček<sup>1</sup> – Josef Bezděk<sup>1</sup> – Miloslava Kovářová<sup>1</sup> – Jaromír Hanák<sup>2</sup> – Jan Toul<sup>1</sup> – Pavel Müller<sup>1</sup>

<sup>1</sup> Czech Geological Survey, Leitnerova 22, 658 69 Brno, Czech Republic. E-mail: bohacek@cgu.cz, bezdek@cgu.cz

<sup>2</sup> Lelekovice 370, 664 31. E-mail: hanaks@volny.cz

**Abstract.** Compositions of organic matter in soil and sediment samples were analysed using standard geochemical analytical methods. The tested set contained 44 lake sediment samples from three depth profiles on the bottom of the Horní Bečva Reservoir and 14 samples of uncultivated soil from shallow profiles at the localities of interest: Potočník, Lelekovice and Červenohorské sedlo Saddle. Organic matter was characterised by determinations of individual carbon fractions/forms ( $C_{\text{tot}}$ ,  $C_{\text{org}}$ ,  $C_{\text{min}}$ ,  $C_{\text{HS}}$ ,  $C_{\text{HA}}$ ,  $C_{\text{FA}}$ ), by customary analyses of group parameters (Hum, EOM, TES, NES, AOX-S) and also by multicomponent analyses of the contents and distributions of individual selected hydrophobic organic pollutants – normal and isoprenoid alkanes ( $\text{SH}_{n+i}$ ), polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and organochlorinated pesticides (OCP).

Reliability of data, characterising organic compositions of the tested samples, was guaranteed by certified analytical methods and consequently verified by statistical evaluations of correlations between the values of definitionally related quantities. Characteristics of the organic matter were then used in a parallel investigation of sorption properties of some of the samples. Results of pollutant analyses were also evaluated and discussed with respect to the Czech national legislation limits for permissible pollution of the environment; they proved, in general, a significant and widespread background distribution of some of these xenobiotics in the examined rock environments. Characteristic distributions of individual alkanes determined by multicomponent analyses also helped to distinguish external hydrocarbon contaminations from the natural background as well as to estimate a probable source of contamination.

**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

Parameters describing and quantifying equilibrium distribution of chemical compounds among individual phases of environmental systems belong to significant physical and chemical quantities characterising properties and behaviour of these compounds as potential pollutants of the environment. Quantities describing the behaviour of chemical components in equilibrium between gas and liquid phase (such as boiling point, melting point, vapour pressure, solubilities, diffusion coefficients and partition coefficients for more simple two-phase systems, e.g. water – air or n-octanol – water) are specific for every single compound and their values for common pollutants can be found in various monographs and data bases (e.g., Koch 1986, Sax 1984, Schwarzenbach et al. 1993, Mackay et al. 1999). In contrast, the equilibrium distribution of organic pollutants in systems such as water – natural sorbent (e.g., rock, soil, sediment or, generally, geosorbent) depends much more on the nature and composition of the solid phase in the sorption system.

A sum of processes leading to a decrease in sorbate concentration in solutions by fixation onto solid phase of a sorbent is often referred to as “sorption”. The mass or concentration balance of the final sorbate content in phases of the tested system is usually referred to as “partition” or, nowadays more frequently, “distribution”. In general, the basic processes and mechanisms, which may participate in the distribution of a sorbate between water and solid phase, can include adsorption, partition, chemisorption, absorption, ion exchange and molecular exclusion. An experi-

mental assessment of contribution of individual model mechanisms to the overall sorbate fixation by the solid phase is often rather complicated, even in the case of well-defined synthetic (chromatographic) sorbents. This is even more the case of natural materials of much more complicated matrix character (possessing miscellaneous and variable mineral and organic compositions and structural arrangements of the solid phase).

Equilibrium distribution of the sorbed component (sorbate) between solid (s) and water (w) phase is generally characterised by the distribution (sorption) coefficient  $K_D$ , defined by an equation:  $K_D = c_s / c_w$ , where  $c_s$  and  $c_w$  stand for overall analytical sorbate concentrations in the sorption system phase in question. The distribution coefficient  $K_D$  is a commonly used measure of a sorption affinity of the given sorbate (pollutant) with the investigated sorbent.

Hydrophobic properties are typical for many organic sorbates, comprising a class of highly toxic and relatively persistent environmental pollutants. This class of compounds is represented, e.g., by aromatic hydrocarbons (especially PAH), their halogenated derivatives (e.g., chlorinated biphenyls, benzenes, toluenes, naphthalenes), saturated and unsaturated aliphatic and alicyclic chlorinated hydrocarbons, various organochlorinated pesticides and a great deal of other compounds. The incidence of prior hydrophobic pollutants and studies of regularities controlling their capture, migration and fate in various environmental constituents/spheres therefore remain subjects of intense interest of environmentally and ecotoxicologically oriented research.

Studies of abundant neutral and hydrophobic pollutants' sorption onto various natural sorbents (see, e.g., Karickhoff et al. 1979, Hasset et al. 1980 or Schwarzenbach and Westall 1981) proved that distribution coefficient values  $K_D$  grow with an increasing hydrophobicity of sorbate molecules and also with an increasing content of sorbent organic matter. The measure of hydrophobicity (lipophilicity) is evaluated by the partition coefficient for a two-phase system n-octanol – water,  $K_{OW}$ , defined as a ratio of the overall equilibrium concentration of the given compound in organic (o) and water (w) phase:  $K_{OW} = c_o / c_w$ . For these purposes, the organic matter content is usually expressed in the form of organic carbon mass fraction,  $f_{OC}$ . If the organic carbon content is expressed in percentage  $C_{org} = p_{OC}$  (wt%), then  $f_{OC} = p_{OC} / 100$ . Mutual relationship between  $K_D$ ,  $K_{OW}$  and  $f_{OC}$  can then be represented by an equation:  $K_D = f_{OC} \cdot K_{OC} = f_{OC} \cdot b \cdot K_{OW}^a$ , where  $K_{OC}$  stands for a normalised distribution coefficient of a sorbate, calculated by the relation of an experimentally obtained  $K_D$  value to a hypothetical 100% organic carbon content in the solid phase (i.e., by a recalculation for a hypothetical sorbent of  $f_{OC} = 1$ ). Parameters a and b are empirically determined constants, which are, to a certain extent, characteristic for individual categories or groups of structurally similar pollutants and for various types of natural sorbents.

A model of hydrophobic sorption, based on the aforementioned relationships, is frequently cited in monographs (Smith et al. 1988, Schwarzenbach et al. 1993, Yaron et al. 1996, Domenico and Schwartz 1998) and used in practice. However, some more recent publications point out its limitations (see, e.g., Luthy et al. 1997). The complications associated with practical applications of this model can be indirectly demonstrated by the fact that the values of individual normalised sorption coefficients ( $K_{OC}$ ) published by various authors and compiled in a respected database of environmental parameters of organic pollutants (Mackay et al. 1999) are often significantly different (in extreme cases even by orders of magnitude). The inconsistency of published data is both due to different methods used for their determination and specific differences in the properties of investigated natural materials.  $K_D$  and  $f_{OC}$  parameters should therefore be determined using methods which are sufficiently reliable and properly validated for given purposes. Considering the important role played by organic matter in the processes of hydrophobic sorption of organic pollutants, it is also necessary to draw the attention to a more detailed characterisation of organic composition of natural sorbents.

The above mentioned conclusions and recommendations were considered in our experimental study of sorption interactions between hydrophobic organic pollutants and some natural sorbents within the grant project VaV/630/3/00 "Complex geochemical research on interactions and migration of organic and inorganic chemicals in rock environment", allocated by the Ministry of the Environment of the Czech Republic. In the present paper, results of a more detailed chemical characterization of organic matter in all studied natural materials are summa-

rised. A wider set of the tested samples comprised rocks, soils and sediments with different contents and compositions of organic matter, which were collected at the sites of current exploratory projects of the Czech Geological Survey (CGS). Compositions of all samples were characterised by a set of standard geochemical and environmental analytical methods, including multicomponent analyses of significant and widespread hydrophobic pollutants (PAH, PCB, OCP).

A limited selection of the examined natural sorbents was then tested for their sorption interactions with model hydrophobic organic pollutants (sorbates). Results of this sorption study are published in a separate article (Toul et al. 2003).

## Samples and methods

### Tested samples

A set of the examined natural sorbents included soil and sediment samples collected and investigated in a scope of a complex project solution. The majority of materials were represented by reservoir sediments collected from three depth profiles excavated on the bottom of the Horní Bečva Reservoir. The rest of the samples were collected from shallow depth profiles of uncultivated fields at the localities of interest: Potočník (P), Lelekovice (Le) and Červenohorské sedlo Saddle (SCS). The origin/location and mineral matrix properties (mineralogy, petrography and inorganic geochemistry) of the samples are described in detail by Koubová et al. (2003). Identification data of the samples analysed for their organic composition are presented in Tab. 1.

### Sample preparations

The applied procedure was in full compliance with the ISO/DIS 11 464 (1992) standard for initial preparation of soil samples for chemical analyses. The collected soil samples were dried freely at ambient temperature and then ground and sieved through a 2 mm sieve. The main fraction of particles which penetrated the sieve was then kept at 5 °C in hermetically sealed glass jars. Dry mass was determined in aliquot parts of this way prepared analytical samples using standard procedures (drying at 105 °C until a constant weight is reached).

### Analysis of organic matter

The investigated samples were, first of all, analysed using standard methods of geochemical and environmental organic analysis, which are used for the determination of various group parameters. In addition to analyses of proportional shares of individual carbon forms (total carbon  $C_{tot}$ , mineral carbon  $C_{min}$ , organic carbon  $C_{org}$ , carbon of soluble humic substance  $C_{HS}$ , carbon of humic acids  $C_{HA}$ , carbon of fulvic acids  $C_{FA}$ ), several other common parameters were

Tab. 1. Identification and granulometry of the examined soil and sediment samples

Sample No.	Sample type	Location	Depth interval	Contents (% , m/m) of grain size fractions (mm)			
			[cm]	< 0.002	0.002–0.063	0.063–2.0	> 2.0
P 1	soil	Potočník	0–6	nd	nd	nd	nd
P 2	soil	Potočník	6–12	nd	nd	nd	nd
P 3	soil	Potočník	12–18	nd	nd	nd	nd
P 4	soil	Potočník	18–23	nd	nd	nd	nd
SCS 1	forest soil	Červenohorské sedlo	0–8	3	13	61	23
SCS 2	forest soil	Červenohorské sedlo	8–16	3	10	63	29
SCS 3	forest soil	Červenohorské sedlo	16–24	3	15	36	46
SCS 4	forest soil	Červenohorské sedlo	24–32	3	12.5	48	36.5
SCS 5	forest soil	Červenohorské sedlo	32–42	3.5	17	39	40.5
Le 1	soil	Lelekovice	0–5	11	56	11.5	21.5
Le 2	soil	Lelekovice	5–15	13.5	66	13.5	7
Le 3	soil	Lelekovice	15–27	15	64	14.5	6.5
Le 4	soil	Lelekovice	27–37	15	63.5	13	8.5
Le 5	soil	Lelekovice	37–48	14.5	59	11.5	15
HBK 1	bottom sediment	Horní Bečva	0–12	nd	nd	nd	nd
HBK 2	bottom sediment	Horní Bečva	12–22	nd	nd	nd	nd
HBK 3	bottom sediment	Horní Bečva	22–34	nd	nd	nd	nd
HBK 4	bottom sediment	Horní Bečva	34–46	nd	nd	nd	nd
HBK 5	bottom sediment	Horní Bečva	46–50	nd	nd	nd	nd
HBK 6	bottom sediment	Horní Bečva	50–54	nd	nd	nd	nd
HBK 7	bottom sediment	Horní Bečva	54–67	nd	nd	nd	nd
HBK 8	bottom sediment	Horní Bečva	67–76	nd	nd	nd	nd
HBK 9	bottom sediment	Horní Bečva	76–83	nd	nd	nd	nd
HBK 10	bottom sediment	Horní Bečva	83–91	nd	nd	nd	nd
HBK 11	bottom sediment	Horní Bečva	91–100	nd	nd	nd	nd
HBK 12	bottom sediment	Horní Bečva	100–109	nd	nd	nd	nd
HBK 13	bottom sediment	Horní Bečva	109–116	nd	nd	nd	nd
HBK 14	bottom sediment	Horní Bečva	116–130	nd	nd	nd	nd
HBK 15	bottom sediment	Horní Bečva	130–135	nd	nd	nd	nd
HBK 16	bottom sediment	Horní Bečva	135–145	nd	nd	nd	nd
HBK 17	bottom sediment	Horní Bečva	145–155	nd	nd	nd	nd
HBK 18	bottom sediment	Horní Bečva	155–166	nd	nd	nd	nd
HBK 19	bottom sediment	Horní Bečva	166–175	nd	nd	nd	nd
HBK 20	bottom sediment	Horní Bečva	175–182	nd	nd	nd	nd
HBK 21	bottom sediment	Horní Bečva	182–189	nd	nd	nd	nd
HBK 22	bottom sediment	Horní Bečva	189–199	nd	nd	nd	nd
HBK 23	bottom sediment	Horní Bečva	199–204	nd	nd	nd	nd
HBK 24	bottom sediment	Horní Bečva	204–214	nd	nd	nd	nd
HBK 25	bottom sediment	Horní Bečva	214–225	nd	nd	nd	nd
HBK 26	bottom sediment	Horní Bečva	225–230	nd	nd	nd	nd
HBK 27	bottom sediment	Horní Bečva	230–235	nd	nd	nd	nd
HBK 28	bottom sediment	Horní Bečva	235–245	nd	nd	nd	nd
HBK 29	bottom sediment	Horní Bečva	245–253	nd	nd	nd	nd
HBK 30	bottom sediment	Horní Bečva	235–268	nd	nd	nd	nd

Tab. 1, continued

Sample No.	Sample type	Location	Depth interval	Contents (% m/m) of grain size fractions (mm)			
			[cm]	< 0.002	0.002–0.063	0.063–2.0	> 2.0
HBS 1	bottom sediment	Horní Bečva	0–12	0	2	93	5
HBS 2	bottom sediment	Horní Bečva	12–21	1	2	74.5	22.5
HBS 3	bottom sediment	Horní Bečva	21–33	1.5	3	53.5	42
HBS 4	bottom sediment	Horní Bečva	33–49	12	76	12	0
HBS 5	bottom sediment	Horní Bečva	49–53	13.5	72	13.5	1
HBS 6	bottom sediment	Horní Bečva	53–57	8.5	40	51	0.5
HBS 7	bottom sediment	Horní Bečva	57–85	2.5	3.5	88	4
HBS 8	bottom sediment	Horní Bečva	85–107	5	17	72	4
HBS 9	bottom sediment	Horní Bečva	107–127	7	41	50	2
HBS 10	bottom sediment	Horní Bečva	127–148	15	78	7	0
HBV 1	bottom sediment	Horní Bečva	0–6	15	81	4	0
HBV 2	bottom sediment	Horní Bečva	6–13	13.5	81.5	5	0
HBV 3	bottom sediment	Horní Bečva	13–19	16	81	3	0
HBV 4	bottom sediment	Horní Bečva	19–26	18.5	80.5	1	0

Note: nd – value not determined

Tab. 2. Chemical group parameters used to characterise organic matter of the examined soils and sediments

Symbol	Parameter	Unit	LOD (unit)	RSTDEV (%)	Method code <sup>a</sup>	SOP code
C <sub>tot</sub>	Total carbon	% (m/m)	0.05	5	EA	H-1
C <sub>min</sub>	Inorganic (carbonate) carbon	% (m/m)	0.05	5	EA	H-1
C <sub>org</sub>	Organic carbon (= C <sub>tot</sub> – C <sub>min</sub> )	% (m/m)	0.05	5	EA	H-1
S	Total sulphur	% (m/m)	0.02	5	EA	H-1
Hum	Total humic (= organic) matter	% (m/m)			OxT	
C <sub>HS</sub>	Carbon of soluble humic substance	% (m/m)			SE+OxT	
C <sub>HA</sub>	Carbon bonded in humic acids	% (m/m)			SE+OxT	
C <sub>FA</sub>	Carbon bonded in fulvic acids	% (m/m)			SE+OxT	
EOM	Extractable organic matter	%	0.003	10	SE+G	
AOX-S	Adsorbed organic bonded halogens	mg/kg	5	7	EA	Z-4
TES	Total extractable substances (IR)	mg/kg	5	6	SE+IR	Z-1
NES	Nonpolar extractable substances (IR)	mg/kg	5	6	SE+IR	Z-1
TSH <sub>n+i</sub>	Total normal (C <sub>10-38</sub> ) and isoprenoid (C <sub>13-20</sub> ) alkanes	mg/kg	see text	see text	SE + HRGC/FID	H-3
PCB(14)	Total polychlorinated biphenyls (sum of all 14 determined congeners)	mg/kg	see text	see text	SE + HRGC/ECD	Z-2
PCB(6)	Sum of 6 PCB congeners (Ballschmitter's set)	mg/kg	see text	see text	SE + HRGC/ECD	Z-2
PAH(15)	Total polycyclic aromatic hydrocarbons (sum of all 15 determined components)	mg/kg	see text	see text	SE + HPLC/FLD	Z-3
PAH(9)	Sum of 9 individual PAHs (as required by MP MŽP CR, 1996)	mg/kg	see text	see text	SE + HPLC/FLD	Z-3
OCP(8)	Sum of 8 organochlorine pesticides (as required by MP MŽP CR, 1996)	mg/kg	see text	see text	SE + HRGC/ECD	Z-2

Abbreviations: LOD – limit of detection; RSTDEV – relative standard deviation.

<sup>a</sup> Method code: EA – elemental analysis; OxT – oxidimetric titration; SE – solvent extraction; G – gravimetry; IR – infrared spectrophotometry; HRGC – high resolution gas chromatography FID – flame ionisation detection; ECD – electron capture detection; HPLC – high performance liquid chromatography; FLD – fluorescence detection; SOP – standard operation procedure (CGS Brno).

assessed (total humic matter Hum, extractable organic matter EOM, total extractable substance TES, non-polar extractable substance NES, adsorbed organic halogens AOX-S). The overview of all examined parameters with methodology citations, approximate limits of detection (LOD) and relative standard deviations (RSTDEV) are presented in Tab. 2.

Organic composition of the tested soils and sediments was also characterised by the determination of a proportional share (distribution) of individual geologically and environmentally relevant constituents – normal and isoprenoid alkanes ( $\text{SH}_{n+i}$ ), polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and organochlorinated pesticides (OCP). Designations of all individual analytes and their abbreviations used in this text are presented together with basic parameters of individual analyses (LOD, RSTDEV) in the descriptive characteristics of the individual methods.

The majority of chemical characterisations of organic matter were accomplished in the testing laboratory of the Czech Geological Survey in Brno, using certified methods described in the references CGS Brno (1999a–g). Humus analyses were carried out in a laboratory of the Institute of Soil Science and Microbiology associated with Mendel University of Agriculture and Forestry (MZLU) in Brno. Particle-size analyses were accomplished in a laboratory of Geodril Brno, Ltd.

#### Methods, instrumentation and experimental arrangements

The overview contains only basic characteristics of the used methods. Detailed information on materials, experimental arrangements, instrumentation and methodologies is included in standard operation procedures (SOP) of individual analytical methods cited in Tab. 2 (see also the set of references CGS Brno 1999a–g).

Elementary analyses (EA) for carbon and sulphur contents were performed by using the METALYT CS 100/1000 analyser (ELTRA, FRG). For the  $C_{\text{tot}}$  and S determinations, the samples were combusted in oxygen at 1200 °C, the mineral (carbonate bonded) carbon ( $C_{\text{min}}$ ) was assessed via sample decomposition in orthophosphoric acid. The content of organic carbon was in all cases determined indirectly by a calculation from the difference of parallel analyses as  $C_{\text{org}} = C_{\text{tot}} - C_{\text{min}}$ .

The total amount of humus (Hum) and carbon bonded in its acidic constituents ( $C_{\text{HL}}$ ,  $C_{\text{HA}}$ ,  $C_{\text{FA}}$ ) were assessed using traditional methods based on volumetric bichromatometric determinations of oxidizable organic soil matter and its alkaline aqueous leachates (Kononova and Belchikova 1961). Thus, in addition to the overall content of organic humic matter (Hum), fractions of carbon bonded in acidic humic substances ( $C_{\text{HS}}$ ), humic acids ( $C_{\text{HA}}$ ) and fulvic acids ( $C_{\text{FA}}$ ) were determined.

Non-polar (NES) and total (TES) extractable substances were determined using a standard IR spectrophotometric method complying with the ISO TR 11 046 (1994)

standard. The analysis is based on a solvent extraction of extractable organic substances by 1,1,2-trichlorotrifluoroethane and on a measurement of absorption intensities of aliphatic extract constituents in the wavenumber range of 3200–2600  $\text{cm}^{-1}$ . The NES parameter is a measure of the content of non-polar extractable substances in extracts, which were purified via sorption of co-extracted more polar compounds on silica gel. The TES parameter is determined in the same way as NES but indicates the overall amount of compounds extracted by chlorofluorocarbon (i.e., unpurified extract). Owing to a problematic calibration of the method in the case of natural sample analysis, the relevance of TES is just tentative, and it can generally be stated that  $\text{TES} \geq \text{NES}$ . Absorption spectra were measured on Perkin-Elmer 783 IR spectrophotometer and interpreted using SPECTACLE/IR 1.50 application software (LabControl, Germany).

Total adsorbed organically bonded halogens in solid samples (AOX-S) were determined using method complying with the DIN 38 414 S18 (1989) norm. Samples, dried at 105 °C and free of soluble halogens after water extraction, were burned at 950 °C in a stream of oxygen. The sum of halogenated hydrocarbons in the products of burning was determined using coulometric argentometric titration on COULOMAT 7020 CL apparatus (Ströhlein, Germany) with CLMAT operation program.

Extractable organic matter (EOM) was extracted by agitation with a mixture of n-hexane and acetone (1 : 1, v/v), supported by an ultrasound. The EOM content in evaporation residues of the extracts was determined gravimetrically; constant weights of the evaporation residues were measured using BP 210 D semimicrobalance instrument (Sartorius, Germany).

Evaporation residues of EOM were also used for the determination of the organochlorinated pollutants of interest (PCB, OCP). Hexane leachates of EOM evaporation residues were chromatographically purified on a column with silica gel, impregnated with concentrated  $\text{H}_2\text{SO}_4$ , NaOH and  $\text{AgNO}_3$ . Pentane eluates, concentrated using TurboVap evaporator (Zymark, USA), were analysed on HP 5890 (Hewlett-Packard, USA) gas chromatograph, equipped with an electron capture detector (ECD) and HP ChemStation software package. Basic parameters of the HRGC experimental arrangement for analysis of halogenated substances were: capillary column HP-5 (length 60 m, inner diameter 0.25 mm, phase film thickness 0.25  $\mu\text{m}$ ), hydrogen as carrier gas, automated pulsed splitless sample injection. This way, altogether 14 components (congeners) of PCB and 8 components of OCP were determined, with LOD values of about 0.0001 mg/kg for the majority of analysed analytes (except 0.0003 mg/kg for o,p'-DDE and p,p'-DDE and 0.0005 mg/kg for p,p'-DDT) and with relative standard deviations of about 15 %.

Symbols (names) of the individual PCB congeners: CB8 (2,4'-dichlorobiphenyl); CB18 (2,2',5-trichlorobiphenyl); CB28 (2,4,4'-trichlorobiphenyl); CB31 (2,4',5-trichlorobiphenyl); CB31 (2,4',5-trichlorobiphenyl); CB44 (2,2',3,5'-tetrachlorobiphenyl); CB52



Tab. 3 Organic composition of soils and sediments – data of group parameter analyses  
Abbreviations and symbols are explained in Tabs 1 and 2, percentages given in wt%; nd – value not determined.

Sample	EOM (mg/g)	C <sub>min</sub> (%)	C <sub>org</sub> (%)	C <sub>tot</sub> (%)	S (%)	Hum (%)	C <sub>HS</sub> (%)	C <sub>HA</sub> (%)	C <sub>FA</sub> (%)	AOX-S (mg/kg)	TES (mg/kg)	NES (mg/kg)	TSH <sub>n+i</sub> (mg/kg)	PCB(14) (mg/kg)	PCB(6) (mg/kg)	PAH(15) (mg/kg)	PAH(9) (mg/kg)	PAH(7) (mg/kg)	OCP(8) (mg/kg)
P 1	0.720	<0.05	4.61	4.61	0.05	nd	nd	nd	nd	56	36	12	11.77	0.0082	0.0055	5.45	4.68	3.32	0.0030
P 2	0.270	<0.05	2.01	2.01	0.05	nd	nd	nd	nd	29	22	7	4.26	0.0067	0.0043	2.18	1.88	1.24	0.0060
P 3	0.220	<0.05	1.53	1.53	0.04	nd	nd	nd	nd	42	19	8	2.19	0.0047	0.0028	2.86	2.51	1.71	0.0021
P 4	0.260	<0.05	1.48	1.48	0.04	nd	nd	nd	nd	26	19	8	3.35	0.0047	0.0029	2.80	2.46	1.62	0.0022
SCS 1	6.920	<0.05	13.00	13.00	0.15	17.60	4.48	2.80	1.68	76	128	35	30.98	0.0281	0.0177	2.19	1.65	0.87	0.0661
SCS 2	8.570	<0.05	16.50	16.50	0.19	14.40	6.04	4.31	1.73	85	122	27	38.20	0.0247	0.0159	3.13	2.29	1.17	0.0581
SCS 3	4.430	<0.05	8.79	8.79	0.09	14.70	7.55	5.10	2.45	49	61	14	14.31	0.0277	0.0195	0.72	0.50	0.24	0.0143
SCS 4	3.130	<0.05	7.97	7.97	0.08	8.97	2.00	1.08	0.92	59	23	8	8.43	0.0886	0.0644	0.36	0.24	0.11	0.0096
SCS 5	1.610	<0.05	5.40	5.40	0.06	6.18	1.13	0.13	1.00	48	40	11	4.35	0.0052	0.0031	0.26	0.19	0.08	0.0055
Le 1	0.670	0.48	4.47	4.95	0.01	6.17	0.93	0.44	0.50	20	97	20	13.49	0.0138	0.0100	1.78	1.58	1.01	0.0092
Le 2	0.170	0.49	2.47	2.96	<0.02	3.44	0.59	0.30	0.29	17	34	6	3.08	0.0133	0.0094	1.16	1.02	0.62	0.0125
Le 3	0.230	0.57	2.02	2.59	<0.02	2.79	0.42	0.19	0.23	14	206	47	3.00	0.0141	0.0098	1.09	0.96	0.59	0.0118
Le 4	0.180	0.60	1.68	2.28	<0.02	2.05	0.39	0.17	0.22	13	14	6	2.50	0.0089	0.0059	3.63	3.25	2.21	0.0067
Le 5	0.130	0.58	1.35	1.93	<0.02	1.71	0.28	0.12	0.16	12	27	5	1.71	0.0056	0.0038	1.13	1.00	0.65	0.0040
HBK 1	0.390	<0.05	0.36	0.36	0.12	nd	nd	nd	nd	8	11	<3	5.36	0.0058	0.0040	18.87	16.50	11.56	0.0020
HBK 2	0.260	<0.05	0.28	0.28	0.12	nd	nd	nd	nd	8	10	<3	5.64	0.0102	0.0068	5.05	4.34	3.13	0.0023
HBK 3	0.450	<0.05	0.29	0.29	0.08	nd	nd	nd	nd	<8	10	<3	5.78	0.0097	0.0068	8.95	7.71	5.44	0.0025
HBK 4	0.490	<0.05	0.32	0.32	0.12	nd	nd	nd	nd	<8	41	18	6.42	0.0165	0.0112	12.26	10.48	7.49	0.0038
HBK 5	0.610	<0.05	0.38	0.38	0.10	nd	nd	nd	nd	8	26	8	6.40	0.0082	0.0053	13.81	11.79	8.25	0.0048
HBK 6	0.710	<0.05	1.67	1.67	0.15	nd	nd	nd	nd	15	50	19	9.70	0.0135	0.0091	11.69	10.10	6.87	0.0060
HBK 7	0.100	<0.05	0.17	0.17	0.15	nd	nd	nd	nd	<8	6	<3	3.58	0.0035	0.0022	5.80	5.01	3.48	0.0014
HBK 8	0.340	<0.05	0.28	0.28	0.11	nd	nd	nd	nd	<8	12	<3	5.56	0.0052	0.0036	8.16	6.95	4.88	0.0020
HBK 9	0.730	0.05	0.38	0.43	0.13	nd	nd	nd	nd	8	21	8	6.59	0.0064	0.0045	24.12	20.60	14.33	0.0033
HBK 10	0.390	0.06	0.29	0.35	0.16	nd	nd	nd	nd	<8	19	7	6.80	0.2516	0.1844	11.16	9.62	6.83	0.0004
HBK 11	0.650	<0.05	0.49	0.49	0.14	nd	nd	nd	nd	<8	50	23	7.12	0.0094	0.0064	16.87	14.54	10.02	0.0036
HBK 12	0.670	0.06	0.68	0.74	0.18	nd	nd	nd	nd	<8	37	17	6.77	0.0086	0.0059	21.75	18.55	13.32	0.0037
HBK 13	0.430	<0.05	0.36	0.36	0.16	nd	nd	nd	nd	<8	15	6	6.68	0.0044	0.0028	13.13	11.42	7.78	0.0018
HBK 14	0.630	0.10	0.48	0.58	0.16	nd	nd	nd	nd	<8	30	13	8.93	0.0097	0.0064	36.64	31.49	21.54	0.0045
HBK 15	0.470	0.09	0.58	0.67	0.20	nd	nd	nd	nd	<8	26	10	10.05	0.0170	0.0114	20.97	18.14	12.79	0.0063
HBK 16	0.230	0.09	0.27	0.36	0.14	nd	nd	nd	nd	<8	15	4	6.19	0.0045	0.0030	6.15	5.36	3.58	0.0018
HBK 17	0.370	<0.05	0.38	0.38	0.13	nd	nd	nd	nd	5	64	19	5.32	0.0043	0.0029	11.08	9.64	6.77	0.0018
HBK 18	0.990	0.05	1.73	1.78	0.16	nd	nd	nd	nd	14	73	23	10.02	0.0191	0.0134	10.26	8.95	5.96	0.0051
HBK 19	1.380	0.05	2.54	2.59	0.09	nd	nd	nd	nd	15	116	35	17.20	0.0048	0.0031	4.99	4.34	2.66	0.0118
HBK 20	1.190	<0.05	1.96	1.96	0.05	nd	nd	nd	nd	14	53	9	9.55	0.0047	0.0028	1.10	0.92	0.63	0.0049
HBK 21	0.980	<0.05	1.94	1.94	0.05	nd	nd	nd	nd	17	40	3	6.16	0.0036	0.0021	0.34	0.24	0.16	0.0013

Tab. 3, continued

Sample	EOM (mg/g)	C <sub>min</sub> (%)	C <sub>org</sub> (%)	C <sub>tot</sub> (%)	S (%)	Hum (%)	C <sub>HS</sub> (%)	C <sub>HA</sub> (%)	C <sub>FA</sub> (%)	AOX-S (mg/kg)	TES (mg/kg)	NES (mg/kg)	TSH <sub>HTI</sub> (mg/kg)	PCB(14) (mg/kg)	PCB(6) (mg/kg)	PAH(15) (mg/kg)	PAH(9) (mg/kg)	PAH(7) (mg/kg)	OCP(8) (mg/kg)
HBK 22	0.320	<0.05	0.83	0.83	0.03	nd	nd	nd	nd	12	11	< 3	1.95	0.0025	0.0015	0.07	0.02	0.02	0.0002
HBK 23	0.520	<0.05	1.08	1.08	0.03	nd	nd	nd	nd	12	21	< 3	3.27	0.0028	0.0015	0.14	0.08	0.05	0.0009
HBK 24	1.740	<0.05	2.27	2.27	0.06	nd	nd	nd	nd	13	103	13	14.65	0.0035	0.0021	0.65	0.50	0.31	0.0004
HBK 25	0.980	<0.05	0.95	0.95	0.04	nd	nd	nd	nd	8	29	5	10.31	0.0054	0.0034	0.24	0.21	0.16	0.0004
HBK 26	0.550	<0.05	0.73	0.73	0.09	nd	nd	nd	nd	8	38	4	7.25	0.0024	0.0013	0.21	0.17	0.14	0.0001
HBK 27	2.760	<0.05	1.97	1.97	0.07	nd	nd	nd	nd	13	261	22	23.25	0.0044	0.0027	0.39	0.34	0.28	0.0008
HBK 28	1.280	<0.05	1.81	1.81	0.05	nd	nd	nd	nd	10	87	11	7.99	0.0057	0.0038	0.19	0.05	0.10	0.0010
HBK 29	0.320	<0.05	0.61	0.66	0.02	nd	nd	nd	nd	8	19	4	5.48	0.0044	0.0028	0.12	0.10	0.08	0.0004
HBK 30	0.920	<0.05	1.25	1.25	0.04	nd	nd	nd	nd	7	47	8	9.11	0.0029	0.0017	0.15	0.12	0.10	0.0002
HBS 1	3.970	<0.05	0.74	0.74	0.09	0.83	0.05	0.02	0.03	8	63	32	8.67	0.0669	0.0478	80.40	69.68	50.53	0.0080
HBS 2	0.110	<0.05	0.22	0.22	0.07	0.31	0.02	0	0.02	5	14	12	4.05	0.0053	0.0035	3.55	3.07	2.17	0.0018
HBS 3	0.060	<0.05	0.23	0.23	0.08	0.52	0.05	0.01	0.04	7	18	13	5.51	0.0072	0.0046	9.86	8.70	5.97	0.0027
HBS 4	1.340	<0.05	2.53	2.53	0.16	2.44	0.45	0.18	0.27	21	158	92	12.67	0.0537	0.0378	32.26	28.30	18.38	0.0096
HBS 5	1.450	<0.05	2.16	2.16	0.18	2.96	0.62	0.31	0.31	17	194	138	13.98	0.0788	0.0542	26.61	23.32	14.82	0.0126
HBS 6	0.920	<0.05	1.58	1.58	0.10	0.77	0.25	0.12	0.13	13	93	61	11.90	0.0312	0.0219	20.72	18.08	12.02	0.0071
HBS 7	0.270	<0.05	0.29	0.29	0.08	0.39	0.07	0.03	0.04	6	25	17	5.09	0.0043	0.0028	5.20	4.52	3.16	0.0031
HBS 8	0.630	<0.05	0.63	0.63	0.08	1.67	0.22	0.06	0.17	7	32	21	7.92	0.0068	0.0047	42.66	36.64	26.85	0.0044
HBS 9	2.200	<0.05	1.88	1.88	0.13	3.49	0.54	0.33	0.21	13	298	111	19.77	0.1159	0.0807	37.87	32.63	22.51	0.0168
HBS 10	2.190	<0.05	2.78	2.78	0.18	3.31	0.51	0.30	0.21	19	238	168	16.86	0.0662	0.0510	29.57	25.79	15.85	0.0169
HBV 1	2.360	0.07	2.63	2.70	0.15	4.22	0.50	0.30	0.20	22	118	69	12.88	0.0331	0.0232	26.01	22.79	14.39	0.0090
HBV 2	1.160	<0.05	1.66	1.66	0.18	3.74	0.43	0.24	0.19	12	78	44	8.20	0.0208	0.0145	16.51	14.39	9.36	0.0061
HBV 3	0.990	<0.05	2.63	2.63	0.19	4.30	0.51	0.32	0.19	21	103	56	12.77	0.0647	0.0449	21.12	18.38	11.80	0.0092
HBV 4	3.590	<0.05	3.54	3.54	0.28	4.81	0.68	0.43	0.25	28	416	198	23.59	0.0970	0.0666	44.87	39.13	24.24	0.0136

(2,2',5,5'-tetrachlorobiphenyl); CB101 (2,2',4,5,5'-pentachlorobiphenyl); CB118 (2,3',4,4',5-pentachlorobiphenyl); CB138 (2,2',3,4,4',5'-hexachlorobiphenyl); CB149 (2,2',3,4',5',6'-hexachlorobiphenyl); CB153 (2,2',4,4',5,5'-hexachlorobiphenyl); CB180 (2,2',3,4, 4',5,5'-heptachlorobiphenyl); CB194 (2,2',3,3',4,4',5,5'-octachlorobiphenyl); CB203 (2,2',3,4,4',5,5',6-octachlorobiphenyl).

Symbols (names) of the OCP pollutants: HCB (hexachlorobenzene);  $\gamma$ -HCH ( $\gamma$ -hexachlorocyclohexane); o,p'-DDE [1,1-dichloro-2,2-bis(2-chlorophenyl)ethylene]; p,p'-DDE [1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene]; o,p'-DDD [1,1-dichloro-2,2-bis(2-chlorophenyl)ethane]; p,p'-DDD [1,1-dichloro-2,2-bis(4-chlorophenyl)ethane]; o,p'-DDT [1,1,1-trichloro-2,2-bis(2-chlorophenyl)ethane]; p,p'-DDT [1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane].

Analyses of all hydrocarbon constituents were accomplished using leachates from extractions with a mixture of n-hexane and methanol (97:3, v/v). Extract evaporation residues were separated and divided on a silica gel column into two fractions: saturated hydrocarbons (SH or TSH) and polycyclic aromatic hydrocarbons (PAH). Before the final analysis, the fraction eluates were also concentrated using TurboVap evaporator (Zymark, USA).

Alkane fractions were analysed on HP 6890 (Hewlett-Packard, USA) gas chromatograph, equipped with flame ionisation detector (FID) and a data station with HP ChemStation software package. Basic parameters of the HRGC experimental arrangement for alkane analysis: capillary column HP-5MS (length 30 m, inner diameter 0.25 mm, phase film thickness 0.25  $\mu$ m); other parameters were the same as were for PCB and OCP analyses.

By using this method, 29 individual n-alkanes (in the range n-C<sub>10-38</sub>) and 6 isoprenoid alkanes (in the range i-C<sub>13-20</sub>) could be determined, with the LOD values within 0.006–0.010 mg/kg for individual components and the relative standard deviations (RSTDEV) near 15 %.

Tab. 4. Concentrations of individual polycyclic aromatic hydrocarbons in the examined soil and sediment samples  
See Table 1 for sample identification and description of HPLC/FLD method (in text) for symbols of component names.

PAH Sample	N (mg/kg)	Acten (mg/kg)	Fluoren (mg/kg)	Fen (mg/kg)	A (mg/kg)	F (mg/kg)	P (mg/kg)	B(a)A (mg/kg)	Ch (mg/kg)	B(b)F (mg/kg)	B(k)F (mg/kg)	B(a)P (mg/kg)	DB(ab)A (mg/kg)	B(ghi)Pe (mg/kg)	I(123-cd)P (mg/kg)
P 1	0.019	0.018	0.041	0.502	0.230	1.089	0.844	0.478	0.534	0.401	0.211	0.465	0.068	0.240	0.312
P 2	< 0.001	0.006	0.008	0.145	0.048	0.417	0.319	0.192	0.227	0.188	0.097	0.205	0.041	0.117	0.164
P 3	< 0.001	< 0.001	0.012	0.247	0.075	0.575	0.419	0.258	0.297	0.220	0.121	0.258	0.039	0.141	0.193
P 4	< 0.001	< 0.001	< 0.001	0.157	0.056	0.567	0.418	0.267	0.299	0.249	0.129	0.274	0.040	0.147	0.202
SCS 1	< 0.001	< 0.001	< 0.001	0.102	0.010	0.281	0.204	0.086	0.261	0.489	0.140	0.128	0.046	0.182	0.262
SCS 2	< 0.001	< 0.001	< 0.001	0.133	0.015	0.363	0.274	0.123	0.360	0.760	0.217	0.174	0.062	0.250	0.395
SCS 3	< 0.001	0.016	< 0.001	0.037	0.003	0.066	0.053	0.024	0.071	0.177	0.048	0.036	0.020	0.065	0.101
SCS 4	< 0.001	0.012	< 0.001	0.025	0.001	0.028	0.020	0.008	0.033	0.091	0.023	0.014	0.011	0.034	0.059
SCS 5	< 0.001	0.007	< 0.001	0.019	0.001	0.019	0.017	0.006	0.022	0.056	0.017	0.013	0.006	0.026	0.054
Le 1	< 0.001	0.005	0.007	0.120	0.025	0.335	0.245	0.157	0.183	0.166	0.090	0.193	< 0.001	0.109	0.147
Le 2	< 0.001	< 0.001	< 0.001	0.056	0.010	0.228	0.173	0.096	0.108	0.108	0.058	0.121	0.019	0.079	0.106
Le 3	< 0.001	< 0.001	< 0.001	0.058	0.010	0.212	0.156	0.090	0.104	0.102	0.053	0.117	0.021	0.069	0.102
Le 4	< 0.001	< 0.001	< 0.001	0.404	0.053	0.831	0.544	0.273	0.330	0.284	0.152	0.320	0.039	0.163	0.234
Le 5	< 0.001	< 0.001	< 0.001	0.065	0.014	0.234	0.161	0.106	0.112	0.097	0.054	0.116	0.019	0.058	0.095
HBK 1	< 0.001	0.114	0.202	1.724	0.697	4.436	2.831	1.608	1.471	1.141	0.845	1.628	0.211	0.860	1.099
HBK 2	0.012	0.036	0.077	0.566	0.239	1.175	0.728	0.357	0.356	0.303	0.170	0.421	0.051	0.254	0.308
HBK 3	0.003	0.129	0.182	0.842	0.324	2.299	1.477	0.658	0.647	0.512	0.288	0.664	0.092	0.363	0.472
HBK 4	0.012	0.162	0.203	1.204	0.531	2.812	1.876	0.967	0.985	0.749	0.432	0.979	0.129	0.536	0.684
HBK 5	0.010	0.243	0.283	1.437	0.494	3.162	2.165	1.039	1.014	0.853	0.471	1.096	0.142	0.635	0.766
HBK 6	0.013	0.138	0.174	1.083	0.359	2.599	1.908	0.929	0.900	0.775	0.427	0.992	0.131	0.548	0.711
HBK 7	< 0.001	0.093	0.117	0.672	0.199	1.293	0.942	0.446	0.415	0.326	0.193	0.454	0.061	0.272	0.320
HBK 8	0.009	0.095	0.127	0.694	0.393	1.724	1.359	0.681	0.694	0.498	0.289	0.683	0.088	0.370	0.451
HBK 9	0.009	0.502	0.526	2.493	0.864	5.419	4.049	1.907	1.741	1.365	0.790	1.901	0.246	1.054	1.251
HBK 10	< 0.001	0.117	0.161	1.265	0.503	2.442	1.800	0.867	0.836	0.645	0.380	0.913	0.111	0.511	0.603
HBK 11	< 0.001	0.279	0.323	1.941	0.560	3.792	2.878	1.136	1.270	0.988	0.556	1.318	0.172	0.764	0.889
HBK 12	< 0.001	0.412	0.492	3.295	0.880	4.536	3.398	1.461	1.497	1.209	0.691	1.653	0.211	0.939	1.079
HBK 13	< 0.001	0.217	0.262	1.426	0.390	3.093	2.373	0.973	0.922	0.715	0.408	0.976	0.125	0.592	0.659
HBK 14	< 0.001	0.796	0.829	3.318	0.934	8.685	5.866	2.934	2.629	2.185	1.247	3.039	0.402	1.703	2.073
HBK 15	< 0.001	0.244	0.334	2.540	0.864	4.686	3.493	1.632	1.434	1.195	0.674	1.639	0.201	0.970	1.067
HBK 16	< 0.001	0.064	0.097	0.552	0.180	1.346	1.076	0.499	0.474	0.392	0.219	0.532	0.060	0.314	0.349
HBK 17	< 0.001	0.110	0.138	1.217	0.452	2.481	1.938	0.894	0.849	0.633	0.363	0.875	0.102	0.479	0.548
HBK 18	< 0.001	0.121	0.157	0.972	0.277	2.339	1.818	0.733	0.819	0.653	0.356	0.824	0.106	0.519	0.566
HBK 19	< 0.001	0.036	0.054	0.475	0.077	0.885	0.851	0.297	0.483	0.429	0.208	0.441	0.060	0.350	0.346
HBK 20	0.012	0.003	0.013	0.179	0.015	0.201	0.123	0.034	0.115	0.119	0.041	0.074	0.020	0.072	0.075
HBK 21	0.008	0.024	0.003	0.036	0.003	0.053	0.030	0.010	0.032	0.053	0.012	0.019	0.005	0.022	0.028



Tab. 4, continued

PAH Sample	N (mg/kg)	Acten (mg/kg)	Fluoren (mg/kg)	Fen (mg/kg)	A (mg/kg)	F (mg/kg)	P (mg/kg)	B(a)A (mg/kg)	Ch (mg/kg)	B(b)F (mg/kg)	B(k)F (mg/kg)	B(a)P (mg/kg)	DB(ah)A (mg/kg)	B(ghi)Pe (mg/kg)	I(1,2,3-cd)P (mg/kg)
HBK 22	0.004	0.041	< 0.001	0.010	< 0.001	0.004	0.002	< 0.001	0.002	0.003	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
HBK 23	0.007	0.030	< 0.001	0.013	< 0.001	0.016	0.010	< 0.001	0.011	0.018	0.004	0.004	0.001	0.010	0.012
HBK 24	0.018	0.003	0.008	0.073	0.003	0.114	0.054	0.010	0.067	0.102	0.026	0.029	0.010	0.059	0.069
HBK 25	0.003	< 0.001	0.010	0.088	0.002	0.025	0.014	0.006	0.027	0.019	0.004	0.009	< 0.001	0.023	0.011
HBK 26	< 0.001	< 0.001	0.010	0.082	0.002	0.020	0.011	0.007	0.022	0.013	0.002	0.007	0.013	0.015	0.007
HBK 27	< 0.001	0.002	0.008	0.198	0.001	0.025	0.012	0.009	0.041	0.027	0.004	0.007	0.014	0.024	0.019
HBK 28	< 0.001	0.027	0.002	0.004	0.081	0.002	0.013	0.005	0.003	0.013	0.010	0.001	0.017	< 0.001	0.009
HBK 29	< 0.001	< 0.001	0.005	0.045	0.002	0.015	0.006	0.003	0.014	0.009	0.001	0.005	0.003	0.009	< 0.001
HBK 30	< 0.001	< 0.001	0.010	0.046	0.002	0.020	0.009	0.002	0.023	0.009	0.002	0.006	0.008	0.009	0.007
HBS 1	< 0.001	1.444	1.660	9.639	3.222	20.593	13.845	5.246	6.914	3.577	2.137	4.919	0.817	3.030	3.357
HBS 2	< 0.001	0.028	0.043	0.380	0.132	0.827	0.598	0.283	0.260	0.217	0.122	0.285	0.062	0.138	0.178
HBS 3	< 0.001	0.077	0.096	0.919	0.329	2.397	1.756	0.789	0.744	0.553	0.330	0.791	0.103	0.440	0.537
HBS 4	< 0.001	0.271	0.314	2.359	0.717	7.414	5.275	2.486	2.453	2.238	1.303	2.947	0.416	1.835	2.225
HBS 5	< 0.001	0.144	0.206	1.453	0.561	5.941	4.288	2.148	2.144	2.011	1.164	2.568	0.362	1.631	1.988
HBS 6	0.019	0.079	0.145	1.654	0.559	4.292	3.082	1.815	1.670	1.532	0.906	2.007	0.307	1.179	1.477
HBS 7	< 0.001	0.031	0.058	0.520	0.185	1.181	0.851	0.391	0.441	0.331	0.198	0.440	0.078	0.215	0.279
HBS 8	< 0.001	0.725	0.827	3.124	1.823	10.455	6.698	2.963	5.357	2.260	1.381	3.128	0.388	1.563	1.973
HBS 9	< 0.001	0.296	0.365	2.015	0.682	9.871	3.369	3.792	1.868	3.294	1.962	4.285	0.602	2.407	3.063
HBS 10	< 0.001	0.087	0.117	1.543	0.417	5.616	4.207	2.550	2.573	2.719	1.556	3.151	0.440	2.095	2.501
HBV 1	< 0.001	0.149	0.177	1.384	0.407	5.652	4.020	2.264	2.100	2.077	1.175	2.588	0.413	1.606	2.000
HBV 2	< 0.001	0.124	0.156	1.182	0.352	3.566	2.522	1.367	1.330	1.238	0.700	1.564	0.257	0.950	1.165
HBV 3	< 0.001	0.212	0.191	1.437	0.401	4.544	3.280	1.727	1.686	1.614	0.901	2.004	0.322	1.245	1.558
HBV 4	< 0.001	0.375	0.456	2.540	0.582	10.015	7.221	3.327	3.596	3.685	1.976	4.181	0.642	2.781	3.492

PAH fractions were dissolved in acetonitrile and analysed using HP 1100 (Hewlett-Packard, USA) liquid chromatograph equipped with HP 1046A fluorescence detector (FLD) and a data station with HP ChemStation software package. Experimental HPLC arrangement for PAH analysis: LiChroCART 250-3 LiChrospher PAH column with LiChroCART 4-4 LiChrospher PAH precolumn (Merck, Germany), gradient elution by mobile phases of acetonitrile/water (beginning) → acetonitrile (end). The response of the fluorescence detector was measured at various excitation and emission wavelengths, which were optimal and specific for individual PAH components. By using this method, usually 15 individual PAH components were determined with LOD values of about 0.002 mg/kg and relative standard deviations (RSTDEV) of about 10 %.

Symbols (names) of the quantified PAH components: N [naphthalene]; Acten [acenaphthene]; Fluoren [fluorene]; Fen [phenanthrene]; A [anthracene]; F [fluoranthene]; P [pyrene]; B(a) [benzo(a)anthracene]; Ch [chrysene]; B(b)F [benzo(b)fluoranthene]; B(k)F [benzo(k)fluoranthene]; B(a)P [benzo(a)pyrene]; DB(ah)A [dibenz(a,h)anthracene]; B(ghi)Pe [benzo(ghi)perylene]; I(1,2,3-cd)P [indeno(1,2,3-cd)pyrene].

## Results and discussion

### Composition of organic matter in examined soils and sediments

The soil samples collected at the localities of Potočník (P), Lelekovice (Le), Červenohorské sedlo Saddle (SCS) and sediments from three different sampling sites (HBK, HBS, HBV) on the bottom of the Horní Bečva Reservoir were analysed using various methods for some group parameters characterizing their organic matter. Results of these analyses are summarized in Tab. 3. Identification data relating to the analysed samples are presented in Tab. 1, definitions and symbols of the investigated quantities and basic parameters of

Tab. 5. Concentrations of individual polychlorinated biphenyls (PCB) in the examined soils and sediments  
See Tab. 1 for sample identification and description of the HRGC/ECD method (in text) for symbols of component names.

Sample	CB8 (mg/kg)	CB18 (mg/kg)	CB28 (mg/kg)	CB31 (mg/kg)	CB44 (mg/kg)	CB52 (mg/kg)	CB101 (mg/kg)	CB118 (mg/kg)	CB138 (mg/kg)	CB149 (mg/kg)	CB153 (mg/kg)	CB180 (mg/kg)	CB194 (mg/kg)	CB203 (mg/kg)
P 1	0.0002	0.0002	0.0003	0.0003	0.0002	0.0004	0.0010	0.0002	0.0015	0.0012	0.0015	0.0008	0.0002	0.0002
P 2	0.0002	0.0003	0.0004	0.0003	0.0002	0.0004	0.0008	0.0001	0.001	0.0010	0.0011	0.0006	0.0001	0.0002
P 3	0.0002	0.0002	0.0002	0.0002	0.0002	0.0005	0.0006	< 0.0001	0.0006	0.0010	0.0007	0.0002	< 0.0001	0.0001
P 4	0.0002	0.0003	0.0003	0.0003	0.0002	0.0003	0.0007	0.0001	0.0006	0.0006	0.0007	0.0003	< 0.0001	0.0001
SCS 1	0.0003	0.0007	0.0008	0.0006	0.0005	0.0008	0.0028	0.0018	0.0054	0.0038	0.0049	0.0030	0.0010	0.0017
SCS 2	0.0003	0.0006	0.0007	0.0006	0.0005	0.0006	0.0026	0.0016	0.0050	0.0036	0.0045	0.0025	0.0005	0.0011
SCS 3	0.0003	0.0006	0.0006	0.0005	0.0004	0.0008	0.0033	0.0009	0.0058	0.0042	0.0057	0.0033	0.0004	0.0009
SCS 4	0.0005	0.0015	0.0008	0.0007	0.0011	0.0019	0.0110	0.0030	0.0194	0.0141	0.0194	0.0119	0.0014	0.0019
SCS 5	0.0002	0.0003	0.0004	0.0003	0.0002	0.0003	0.0007	0.0002	0.0007	0.0006	0.0007	0.0003	0.0001	0.0002
Le 1	0.0001	0.0002	0.0003	0.0002	0.0003	0.0002	0.0010	0.0003	0.0030	0.0020	0.0033	0.0022	0.0003	0.0004
Le 2	0.0001	0.0002	0.0003	0.0002	0.0001	0.0003	0.0009	0.0002	0.0025	0.0019	0.0028	0.0026	0.0006	0.0006
Le 3	0.0002	0.0002	0.0003	0.0003	0.0002	0.0003	0.0011	0.0002	0.0026	0.0020	0.0028	0.0027	0.0006	0.0006
Le 4	0.0002	0.0003	0.0003	0.0003	0.0002	0.0002	0.0007	0.0002	0.0015	0.0011	0.0017	0.0015	0.0003	0.0004
Le 5	0.0002	0.0002	0.0001	0.0001	0.0002	0.0005	0.0006	0.0001	0.0009	0.0007	0.0010	0.0007	0.0001	0.0002
HBK 1	< 0.0001	0.0002	0.0003	0.0002	0.0001	0.0003	0.0008	0.0002	0.0010	0.0009	0.0011	0.0005	0.0001	0.0001
HBK 2	0.0002	0.0003	0.0005	0.0004	0.0002	0.0004	0.0015	0.0004	0.0018	0.0017	0.0019	0.0007	0.0001	0.0001
HBK 3	0.0001	0.0003	0.0005	0.0003	0.0002	0.0004	0.0016	0.0004	0.0017	0.0014	0.0019	0.0007	0.0001	0.0001
HBK 4	0.0002	0.0003	0.0006	0.0004	0.0006	0.0008	0.0020	0.0006	0.0029	0.0027	0.0033	0.0016	0.0002	0.0003
HBK 5	< 0.0001	0.0002	0.0004	0.0003	0.0002	0.0002	0.0008	0.0005	0.0015	0.0014	0.0015	0.0009	0.0001	0.0002
HBK 6	< 0.0001	0.0002	0.0003	0.0003	0.0002	0.0003	0.0010	0.0004	0.0026	0.0023	0.0027	0.0022	0.0004	0.0006
HBK 7	0.0001	0.0002	0.0003	0.0002	0.0001	0.0002	0.0003	0.0001	0.0005	0.0005	0.0006	0.0003	< 0.0001	0.0001
HBK 8	0.0001	0.0002	0.0002	0.0002	0.0001	0.0002	0.0005	0.0001	0.0010	0.0007	0.0010	0.0007	0.0001	0.0001
HBK 9	< 0.0001	0.0001	0.0003	0.0002	0.0001	0.0002	0.0005	0.0002	0.0013	0.0010	0.0013	0.0009	0.0001	0.0002
HBK 10	0.0004	0.0002	0.0003	0.0003	0.0002	0.0008	0.0160	0.0049	0.0559	0.0383	0.0535	0.0579	0.0106	0.0123
HBK 11	0.0001	0.0002	0.0003	0.0002	0.0003	0.0003	0.0009	0.0002	0.0018	0.0015	0.0019	0.0012	0.0002	0.0003
HBK 12	< 0.0001	0.0001	0.0004	0.0002	0.0003	0.0001	0.0009	0.0002	0.0017	0.0015	0.0017	0.0011	0.0002	0.0002
HBK 13	0.0001	0.0002	0.0003	0.0002	0.0002	0.0002	0.0004	0.0001	0.0007	0.0006	0.0008	0.0004	0.0001	0.0001
HBK 14	0.0001	0.0002	0.0004	0.0003	0.0003	0.0002	0.0008	0.0002	0.0018	0.0016	0.0019	0.0013	0.0003	0.0003
HBK 15	0.0002	0.0002	0.0005	0.0004	0.0008	0.0007	0.0015	0.0005	0.0032	0.0028	0.0035	0.0020	0.0003	0.0004
HBK 16	0.0001	0.0001	0.0002	0.0002	0.0001	0.0002	0.0004	0.0001	0.0008	0.0007	0.0009	0.0005	0.0001	0.0001
HBK 17	0.0001	0.0001	0.0002	0.0002	0.0001	0.0002	0.0004	0.0001	0.0008	0.0007	0.0009	0.0004	< 0.0001	0.0001
HBK 18	< 0.0001	0.0007	0.0004	0.0003	0.0002	0.0004	0.0018	0.0005	0.0039	0.0029	0.0041	0.0028	0.0004	0.0007
HBK 19	0.0001	0.0001	0.0002	0.0002	0.0002	0.0001	0.0005	0.0002	0.0009	0.0006	0.0009	0.0005	0.0001	0.0002
HBK 20	0.0001	0.0001	0.0003	0.0002	0.0004	0.0001	0.0004	0.0002	0.0008	0.0005	0.0008	0.0004	0.0001	0.0003
HBK 21	0.0001	0.0001	0.0002	0.0002	0.0002	0.0001	0.0003	0.0001	0.0006	0.0004	0.0006	0.0003	0.0001	0.0003

Tab. 5, continued

Sample	CB8 (mg/kg)	CB18 (mg/kg)	CB28 (mg/kg)	CB31 (mg/kg)	CB44 (mg/kg)	CB52 (mg/kg)	CB101 (mg/kg)	CB118 (mg/kg)	CB138 (mg/kg)	CB149 (mg/kg)	CB153 (mg/kg)	CB180 (mg/kg)	CB194 (mg/kg)	CB203 (mg/kg)
HBK 22	0.0001	0.0001	0.0003	0.0002	0.0002	0.0001	0.0002	0.0001	0.0003	0.0002	0.0004	0.0002	< 0.0001	0.0001
HBK 23	0.0002	0.0001	0.0003	0.0002	0.0003	0.0001	0.0002	0.0001	0.0003	0.0003	0.0004	0.0002	< 0.0001	0.0001
HBK 24	0.0001	0.0002	0.0003	0.0002	0.0002	0.0002	0.0004	0.0001	0.0005	0.0004	0.0005	0.0002	< 0.0001	0.0002
HBK 25	0.0001	0.0001	0.0003	0.0002	0.0005	0.0004	0.0005	0.0002	0.0009	0.0008	0.0010	0.0003	< 0.0001	0.0001
HBK 26	0.0001	0.0001	0.0002	0.0002	0.0002	0.0001	0.0002	0.0001	0.0003	0.0003	0.0004	0.0001	< 0.0001	0.0001
HBK 27	0.0002	0.0002	0.0004	0.0003	0.0002	0.0002	0.0004	0.0001	0.0007	0.0005	0.0007	0.0003	< 0.0001	0.0002
HBK 28	0.0001	0.0001	0.0002	0.0002	0.0003	0.0004	0.0006	0.0001	0.0010	0.0009	0.0011	0.0005	< 0.0001	0.0002
HBK 29	< 0.0001	0.0001	0.0002	0.0001	0.0004	0.0004	0.0005	0.0001	0.0007	0.0007	0.0008	0.0002	< 0.0001	0.0002
HBK 30	0.0001	0.0001	0.0002	0.0002	0.0002	0.0002	0.0003	0.0001	0.0004	0.0003	0.0004	0.0002	0.0001	0.0001
HBS 1	0.0002	0.0005	0.0009	0.0010	< 0.0001	0.0010	0.0070	0.0020	0.0140	0.0120	0.0150	0.0100	0.0020	0.002
HBS 2	0.0001	0.0002	0.0003	< 0.0001	< 0.0001	< 0.0001	0.0010	< 0.0001	0.0010	0.0010	0.0010	< 0.0001	< 0.0001	< 0.0001
HBS 3	< 0.0001	0.0002	0.0003	0.0002	0.0003	0.0007	0.0007	< 0.0001	0.0011	0.0017	0.0012	0.0006	0.0001	0.0001
HBS 4	0.0001	0.0003	0.0007	0.0004	0.0004	0.0007	0.0041	0.0012	0.0107	0.0091	0.0115	0.0101	0.0020	0.0024
HBS 5	0.0030	< 0.0001	0.0118	0.0065	< 0.0001	0.0033	0.0034	0.0016	0.0123	0.0092	0.0128	0.0106	0.0020	0.0023
HBS 6	< 0.0001	0.0002	0.0004	0.0003	0.0002	0.0003	0.0020	0.0005	0.0061	0.0052	0.0065	0.0066	0.0013	0.0016
HBS 7	0.0001	0.0001	0.0003	0.0002	0.0002	0.0002	0.0005	0.0001	0.0007	0.0006	0.0007	0.0004	0.0001	0.0001
HBS 8	< 0.0001	0.0002	0.0003	0.0002	0.0001	0.0002	0.0008	0.0002	0.0013	0.0011	0.0013	0.0008	0.0001	0.0002
HBS 9	0.0004	0.0007	0.0013	0.0009	0.0008	0.0023	0.0110	0.0033	0.0226	0.0202	0.0232	0.0203	0.0037	0.0052
HBS 10	0.0055	< 0.0001	0.0217	< 0.0001	< 0.0001	0.0052	0.0021	0.0013	0.0079	0.0056	0.0077	0.0064	0.0013	0.0015
HBV 1	0.0002	0.0003	0.0007	0.0005	0.0004	0.0005	0.0028	0.0008	0.0068	0.0056	0.0070	0.0054	0.0009	0.0012
HBV 2	0.0002	0.0002	0.0005	0.0004	0.0002	0.0003	0.0018	0.0005	0.0042	0.0034	0.0044	0.0033	0.0006	0.0008
HBV 3	0.0002	0.0003	0.0006	0.0005	0.0003	0.0006	0.0052	0.0012	0.0125	0.0116	0.0134	0.0126	0.0025	0.0032
HBV 4	0.0030	< 0.0001	0.0068	0.0038	0.0003	< 0.0001	0.0060	0.0020	0.0182	0.0144	0.0193	0.0163	0.0033	0.0036

their determination are summarized in Tab. 2.

Individual environmentally relevant hydrophobic organic compounds, 35 SH<sub>n+1</sub>, 15 PAH, 14 PCB and 8 OCP components (for their specifications see method descriptions in text), were determined by multicomponent analytical methods (HRGC and HPLC). The results of these analyses were used for calculations of various summational group parameters ( $\Sigma$  TSH,  $\Sigma$  PAH,  $\Sigma$  PCB and  $\Sigma$  OCP) shown in Tab. 3 and displayed graphically. Contents of individual PAH, PCB and OCP components are shown in Tabs 4–6. The overall data set for aliphatic hydrocarbons could not be, due to its extent, included in this text and can be found only in the research report of the project (Bezděk et al. 2002).

Appraisal of the quality of results and relations between investigated quantities

The required quality of data, characterising the composition of organic matter in analysed soils and sediments, was guaranteed predominantly by usage of certified methods with both internal and external check of analytical reliability of obtained results. Moreover, the accuracy of achieved results was consecutively checked by statistical regression analysis and by correlations between definitionally related quantities, which were determined using different methods or completed in different laboratories, participating in the project.

The presumptive relation between the values of two qualitatively related analyte concentration parameters is, in practice (in ideal case), often a simple linear dependence. The relationship between the two compared quantities X and Y was therefore gained through plotting the pairs of values of both quantities on an X-Y point graph. The values of a and b parameters in a linear regression equation  $Y = b \cdot X + a$  as well as the determination coefficient  $R^2$  for linear trend line of the plot were calculated using the least square method in MS Excel

Tab. 6. Concentrations of individual organochlorine pesticides (OCPs) in the examined soils and sediments  
See Tab. 1 for sample identification and HRGC/ECD method (in text) for symbols of component names.

	HCB	γ-HCH	o,p'-DDE	p,p'-DDE	o,p'-DDD	p,p'-DDD	o,p'-DDT	p,p' DDT
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Sample								
P 1	0.0004	< 0.0001	< 0.0001	0.0015	< 0.0003	< 0.0003	0.0001	0.0010
P 2	0.0004	0.0001	< 0.0001	0.0040	< 0.0003	< 0.0003	0.0001	0.0014
P 3	0.0003	0.0001	< 0.0001	0.0017	< 0.0003	< 0.0003	< 0.0001	< 0.0005
P 4	0.0003	0.0001	< 0.0001	0.0018	< 0.0003	< 0.0003	< 0.0001	< 0.0005
SCS 1	0.0031	0.0001	0.0003	0.0265	< 0.0003	0.0007	0.0068	0.0286
SCS 2	0.0033	0.0001	0.0002	0.0292	< 0.0003	0.0006	0.0052	0.0195
SCS 3	0.0010	0.0001	< 0.0001	0.0069	< 0.0003	0.0004	0.0010	0.0049
SCS 4	0.0006	0.0001	< 0.0001	0.0032	< 0.0003	0.0008	0.0005	0.0044
SCS 5	0.0004	0.0001	< 0.0001	0.0024	< 0.0003	< 0.0003	0.0003	0.0023
Le 1	0.0068	0.0001	< 0.0001	0.0011	< 0.0003	< 0.0003	0.0001	0.0011
Le 2	0.0101	< 0.0001	< 0.0001	0.0010	< 0.0003	< 0.0003	0.0001	0.0013
Le 3	0.0093	< 0.0001	< 0.0001	0.0010	< 0.0003	< 0.0003	0.0001	0.0014
Le 4	0.0046	0.0001	0.0001	0.0007	< 0.0003	< 0.0003	0.0001	0.0011
Le 5	0.0025	0.0001	< 0.0001	0.0004	< 0.0003	< 0.0003	< 0.0001	0.0010
HBK 1	0.0004	< 0.0001	0.0001	0.0005	< 0.0003	< 0.0003	0.0001	0.0009
HBK 2	0.0004	0.0001	0.0001	0.0006	< 0.0003	< 0.0003	0.0001	0.0010
HBK 3	0.0004	0.0001	0.0002	0.0007	< 0.0003	< 0.0003	0.0001	0.0010
HBK 4	0.0007	0.0002	0.0001	0.0013	< 0.0003	< 0.0003	0.0002	0.0013
HBK 5	0.0006	0.0001	0.0001	0.0019	< 0.0003	0.0004	0.0003	0.0014
HBK 6	0.0006	0.0001	0.0002	0.0028	< 0.0003	0.0003	0.0003	0.0017
HBK 7	0.0003	< 0.0001	0.0001	0.0003	< 0.0003	< 0.0003	< 0.0001	0.0007
HBK 8	0.0004	< 0.0001	0.0001	0.0006	< 0.0003	< 0.0003	0.0001	0.0008
HBK 9	0.0006	< 0.0001	0.0001	0.0011	< 0.0003	< 0.0003	0.0003	0.0012
HBK 10	0.0004	< 0.0001	< 0.0001	< 0.0001	< 0.0003	< 0.0003	< 0.0001	< 0.0005
HBK 11	0.0008	< 0.0001	0.0001	0.0013	< 0.0003	< 0.0003	0.0002	0.0012
HBK 12	0.0008	< 0.0001	0.0001	0.0012	< 0.0003	0.0003	0.0002	0.0011
HBK 13	0.0005	< 0.0001	< 0.0001	0.0005	< 0.0003	< 0.0003	0.0001	0.0007
HBK 14	0.0009	< 0.0001	< 0.0001	0.0017	< 0.0003	< 0.0003	0.0003	0.0016
HBK 15	0.0010	0.0002	0.0005	0.0022	< 0.0003	< 0.0003	0.0004	0.0020
HBK 16	0.0004	< 0.0001	< 0.0001	0.0005	< 0.0003	< 0.0003	0.0001	0.0008
HBK 17	0.0004	< 0.0001	< 0.0001	0.0005	< 0.0003	< 0.0003	0.0001	0.0008
HBK 18	0.0005	0.0001	0.0001	0.0022	< 0.0003	0.0004	0.0002	0.0016
HBK 19	0.0004	< 0.0001	0.0003	0.0042	0.0010	0.0016	0.0007	0.0036
HBK 20	0.0002	0.0001	0.0001	0.0020	< 0.0003	0.0003	0.0005	0.0017
HBK 21	0.0001	< 0.0001	0.0001	0.0004	< 0.0003	< 0.0003	0.0001	0.0006
HBK 22	0.0001	< 0.0001	< 0.0001	0.0001	< 0.0003	< 0.0003	< 0.0001	< 0.0005
HBK 23	0.0001	0.0001	0.0001	0.0001	< 0.0003	< 0.0003	< 0.0001	0.0005
HBK 24	0.0002	< 0.0001	0.0001	0.0001	< 0.0003	< 0.0003	< 0.0001	< 0.0005
HBK 25	0.0001	0.0001	< 0.0001	0.0001	< 0.0003	< 0.0003	0.0001	< 0.0005
HBK 26	0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0003	< 0.0003	< 0.0001	< 0.0005
HBK 27	0.0002	< 0.0001	< 0.0001	< 0.0001	< 0.0003	< 0.0003	0.0001	0.0005
HBK 28	0.0001	0.0001	0.0001	0.0001	< 0.0003	< 0.0003	0.0001	0.0005
HBK 29	0.0001	0.0001	< 0.0001	0.0001	< 0.0003	< 0.0003	0.0001	< 0.0005
HBK 30	0.0001	< 0.0001	< 0.0001	0.0001	< 0.0003	< 0.0003	< 0.0001	< 0.0005
HBS 1	0.0010	< 0.0001	< 0.0001	0.0016	< 0.0003	< 0.0003	0.0013	0.0041
HBS 2	0.0006	< 0.0001	< 0.0001	0.0005	< 0.0003	< 0.0003	0.0001	0.0006

Tab. 6, continued

	HCB	$\gamma$ -HCH	o,p'-DDE	p,p'-DDE	o,p'-DDD	p,p'-DDD	o,p'-DDT	p,p'-DDT
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Sample								
HBS 3	0.0008	0.0001	< 0.0001	0.0005	< 0.0003	0.0003	0.0002	0.0008
HBS 4	0.0012	< 0.0001	0.0001	0.0038	< 0.0003	0.0006	0.0005	0.0034
HBS 5	0.0028	0.0011	< 0.0001	0.0046	< 0.0003	0.0005	0.0003	0.0033
HBS 6	0.0015	< 0.0001	0.0002	0.003	< 0.0003	< 0.0003	0.0002	0.0022
HBS 7	0.0013	< 0.0001	0.0001	0.0008	< 0.0003	< 0.0003	0.0001	0.0008
HBS 8	0.0015	< 0.0001	0.0001	0.0018	< 0.0003	< 0.0003	0.0001	0.0009
HBS 9	0.0032	0.0001	0.0002	0.0051	< 0.0003	0.0008	0.0005	0.0069
HBS 10	0.0036	0.0005	0.0003	0.0080	< 0.0003	0.0003	0.0007	0.0035
HBV 1	0.0024	0.0001	0.0001	0.0037	< 0.0003	< 0.0003	< 0.0001	0.0027
HBV 2	0.0013	< 0.0001	0.0001	0.0028	< 0.0003	< 0.0003	0.0002	0.0017
HBV 3	0.0013	0.0001	0.0001	0.0033	< 0.0003	< 0.0003	0.0004	0.004
HBV 4	0.0016	0.0021	0.0001	0.0054	< 0.0003	< 0.0003	0.0002	0.0042

spreadsheet processor. The coefficient of determination  $R^2$  indicates (similarly to the correlation coefficient  $R$ ) a measure of connectedness between the compared quantities.

Results of correlation evaluations between couples of chosen quantities are, for various series of investigated samples, summarized in Tab. 7. A wider selection of tested

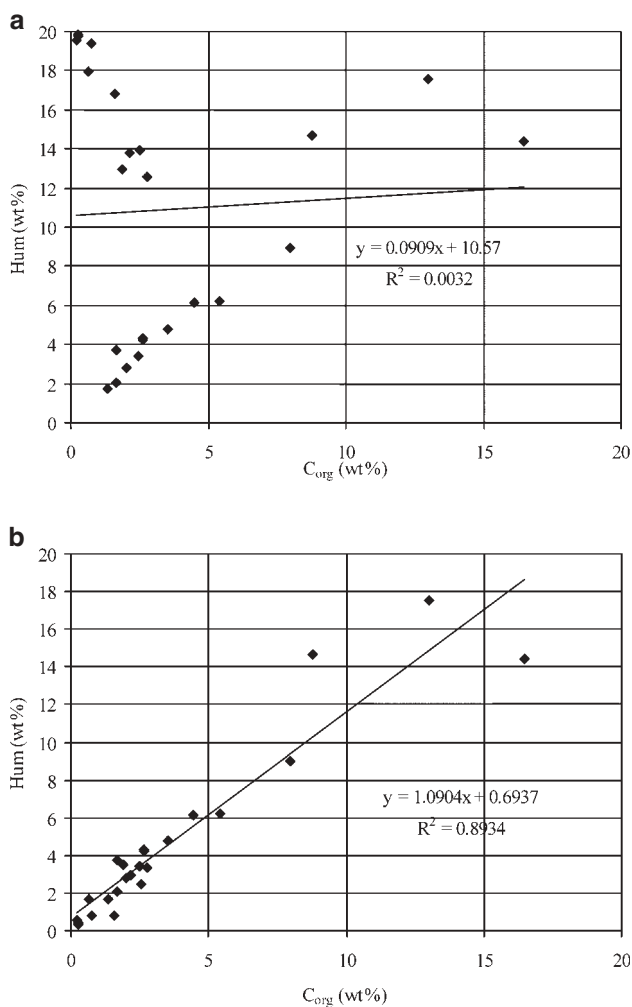


Fig. 1. Plot of Hum versus  $C_{org}$  values for all samples from the profiles (HBS + HBV + Le + SCS); a – with outlying Hum values for HBS data set (due to a calculation error), b – after correction of the erroneous HBS data.

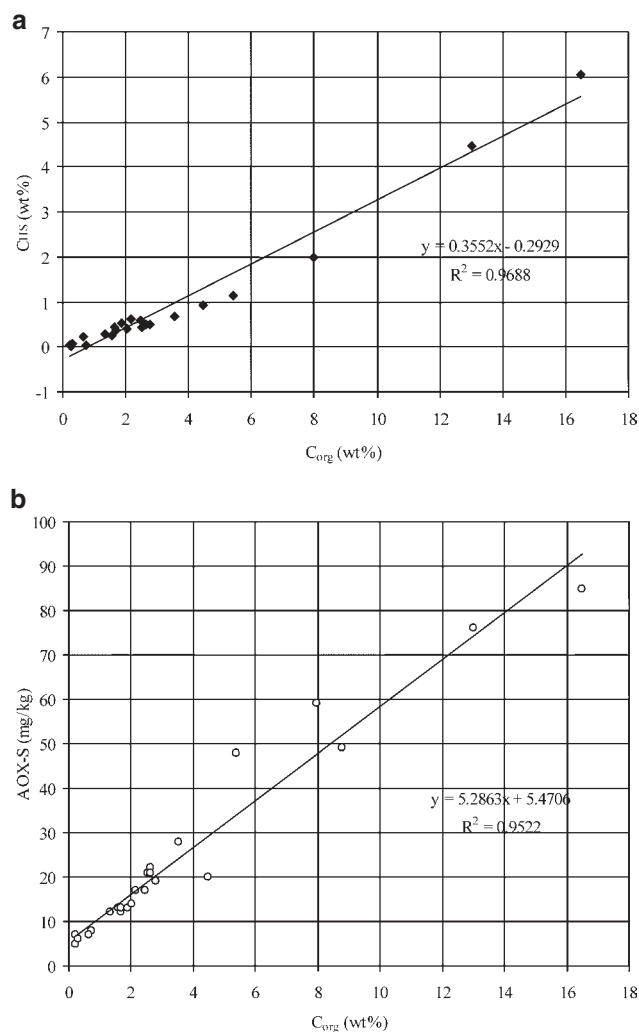


Fig. 2. Plots of  $C_{HS}$  (a) and AOX-S (b) versus  $C_{org}$  values for all samples from the profiles (HBS + HBV + Le + SCS).



Tab. 7. Relationships between different analytical parameters characterising the organic composition of soils and sediments. See Tab. 1 for identification of sample sets from different depth profiles and Tab. 2 for symbols of the variables (methods); b is the coefficient (slope) of the linear regression equation  $Y = a + b \cdot X$  and  $R^2$  the coefficient of determination, found by testing relations between pairs of experimental variables Y-X for various sets and subsets of the samples.

Sample set (subset)	HBS + HBV + Le + SCS	HBK	HBS	HBV	Le	SCS	P
Number of samples	24	30	10	4	5	5	4
Evaluated variables							
Y	b	b	b	b	b	b	b
X	$R^2$	$R^2$	$R^2$	$R^2$	$R^2$	$R^2$	$R^2$
Hum	1.09	nd	1.1	0.57	1.44	0.8	nd
C <sub>org</sub>	0.36	nd	0.23	0.14	0.21	0.35	nd
C <sub>HS</sub>	0.47	0.59	0.51	1.3	0.17	0.64	0.16
EOM	1.6	46.1	88.4	177	14	9.7	5.5
TES	-1.51	6.2	54	80	2.4	2.13	1.4
NES	5.29	3.75	5.72	8.53	2.55	3.56	7.68
AOX-S	1.67	3.96	4.62	8.13	3.07	3.29	2.89
TSH <sub>n+1</sub>	-1.72	-5.8	4.43	15	0.23	0.28	0.91
PAH	13.3	84.7	40.9	118	139	15.6	24.1
TES	3.5	3.9	66.4	54.1	28.1	3.5	9
NES	9.13	2.59	5.78	4.35	12.2	5.36	47.4
AOX-S	3.74	6.99	3.55	4.78	21.9	5.16	18.3
TSH <sub>n+1</sub>	1.01	-4.6	16.3	9.77	1.27	0.44	5.9
PAH	0.013	0.108	0.788	0.899	0.95	0.842	0.92

samples, comprising soils and reservoir sediments (HBS+HBV+Le+SCS series), provided valuable and remarkable correlations, e.g., in parameter couples of Hum / C<sub>org</sub> (Fig. 1); C<sub>HS</sub> / C<sub>org</sub> and AOX-S / C<sub>org</sub> (Fig. 2); TES / EOM (Fig. 3); and TSH(n,ip) / EOM (Fig. 4). Data in Tab. 7 further imply that there are close correlations in limited soil subsets (coming from various collection sites/profiles of individual localities) between a series of some more compared quantities. This inference can be concluded for almost all analysed subsets of soil samples collected at the localities of Potočnick (P), Červenohorské sedlo Saddle (SCS) and Lelekovice (Le) (see Figs 5 and 6). In the case of subsets comprising sediment samples from the bottom of the Horní Bečva Reservoir, the strength of the correlations found increases in a profile series HBK < HBS < HBV for most of the compared couples of variables.

The main cause of the increased correlations between compared parameters of individual soil sample subsets is probably a genetically conditioned similarity of organic matter composition in examined layers of the same sampling profile. Differences and trends in values of the coefficient of determination for reservoir sample collections (as shown in Table 7) can be explained in a similar way. In this case, certain worsening of the correlations between the compared quantities in sediment subsets can be observed. This is probably due to the increasing heterogeneity of organic matter phase and chemical composition along a line from the dam (HBV series) across the centre of the reservoir (HBV series) to its end (HBK series).

Variances in organic matter compositions of samples coming from different localities imply different coefficients of linear regressions in Table 7 and also affect “b” coefficient values (slopes) of lines in XY diagrams for individual subsets of analysed samples (see, e.g., Figs 5 and 6).

The convenience of the described statistical testing of acquired data files can be demonstrated on its serviceability for simpler identification of distinct or anomalous results and revelation of a systematic error in the whole series of humus analyses in some reservoir sediment samples (see Fig. 1).

#### Environmental interpretation of the results of pollutant analyses

The contents of organic priority pollutants of the environment acquired from analyses of all tested sediments and soils were also confronted with criteria and limits of acceptable pollutant concentrations, defined by the national environmental legislation.

The acquired values of summary parameters NES, Σ PAH (9) and Σ PCB (6) are shown in Figs 7-14 and compared with A, B and C criteria for evaluation of soil contamination in accordance with the national directive now in effect (MP MŽP ČR 1996). In addition to established I<sub>ST</sub> values of C criterion (for standard soils containing 10 % of organic matter or 5 % C<sub>org</sub>, respectively), actual values of I<sub>C</sub> criterion for all tested sam-

ples are also plotted in graphs. The  $I_C$  values are calculated according to the equation adduced in the aforementioned systematic directive:  $I_C = I_{ST} \cdot (\% \text{ of organic matter} / 10) \approx I_{ST} \cdot (\% C_{org} / 5)$ .

NES contents in sediments of the Horní Bečva Reservoir (see Fig. 7) do not exceed concentration limits of B and C criteria; A criterion for natural background is exceeded only in some cases and the contravention is virtually negligible (A, B and C criterion values of  $I_{ST}$  and  $I_C$  are plotted in graph). PAH (9) values in all samples (Fig. 8) exceeded, in accordance with our expectations, the background criterion A (1 mg/kg). The concentrations in about 60 % of samples significantly (in the case of HBS 1 abnormally) exceeded even the  $I_C$  criterion limit calculated for known  $C_{org}$  contents in analysed samples. It is worth to notice that the PAH(9) contents found in the surficial layers of the bottom sediment samples HBK 1 and HBV 1 from the Horní Bečva Reservoir (18.8 and 26.8 mg/kg, respectively) are very close to the values reported by Fernandez et al. (1999) for analogous sediment samples from the lakes

of the High Tatra Mountains (Starolesnianské pleso and Dlugi Staw: 18.0 and 13.0 mg/kg, respectively).

The calculated  $I_C$  value of C criterion was, in the case of PCB (6), exceeded in one sediment sample only (Fig. 9). In most cases, the concentrations did not even reach the level set by A criterion; these limits were exceeded only at sampling sites in the vicinity of the reservoir outlet.

The evaluation of the aforementioned pollutant contents in samples from the localities of Lelekovice, Červenohorské sedlo Saddle and Potočník indicates that NES concentrations in all samples are far from reaching A criterion levels (Fig. 10), and  $\Sigma$  PAH (9) contents fluctuate around limits set by A criterion (Fig. 11).  $\Sigma$  PCB (6) contents are, except for one sample, lower than a hypothetical background concentration level given by A criterion (Fig. 12).

AOX-S values of all sediment samples from the Horní Bečva Reservoir (Fig. 13) are far from reaching the

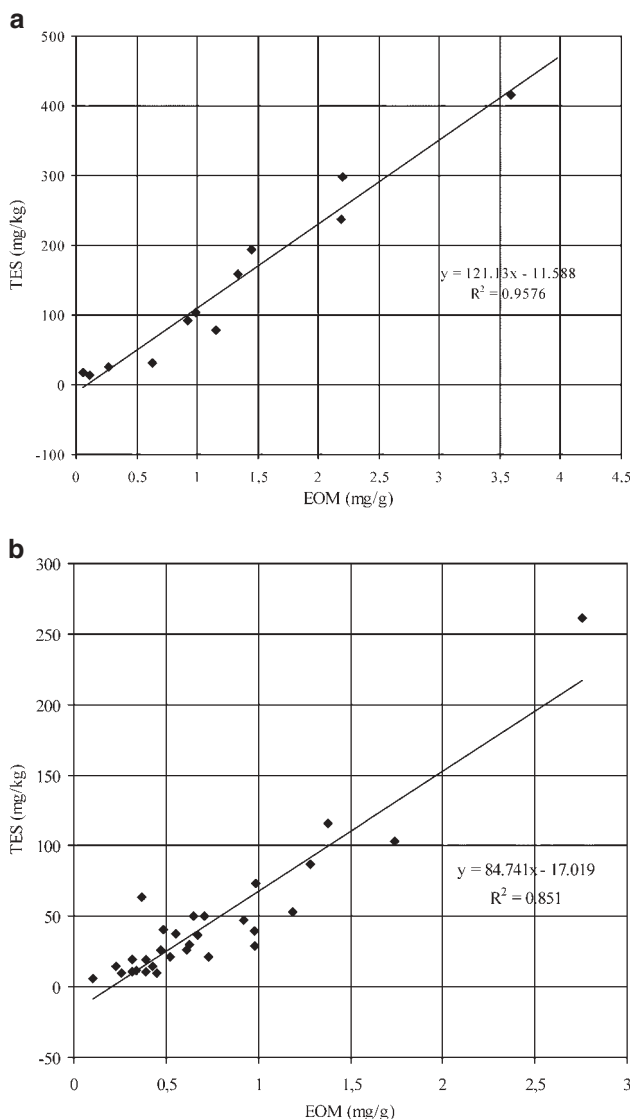


Fig. 3. Plots of TES versus EOM values for the sediment samples from profiles; a – HBS + HBV, b – HBK.

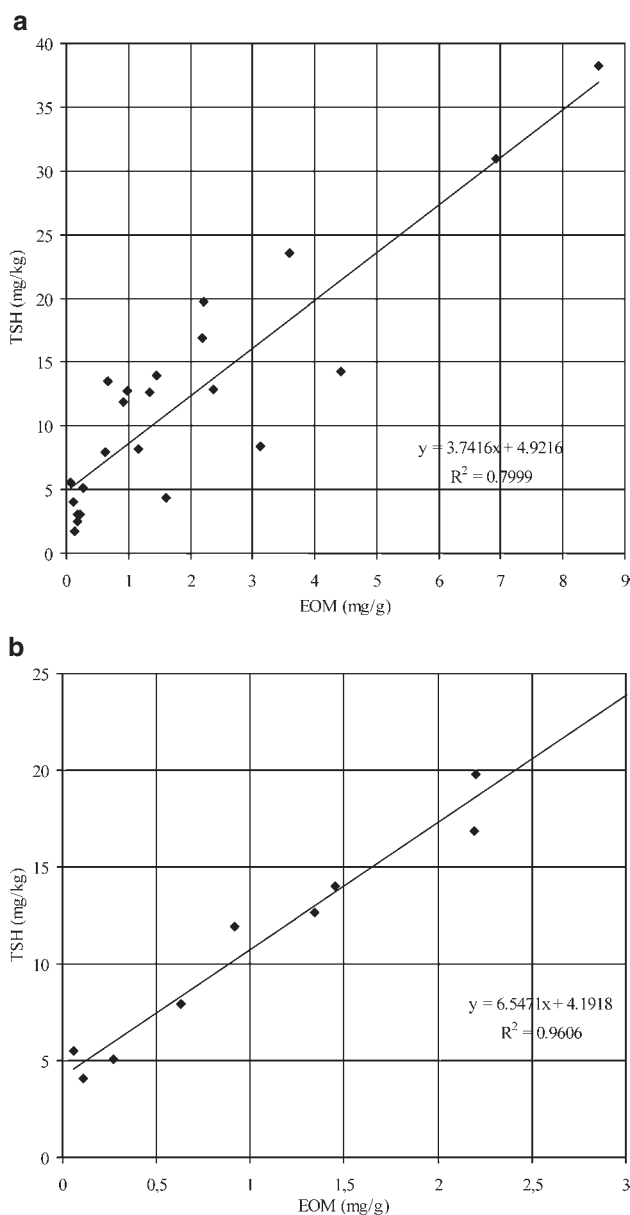


Fig. 4. Plots of TSH versus EOM values for samples; a – from profiles (HBS + HBV + Le + SCS), b – from HBS profile only.

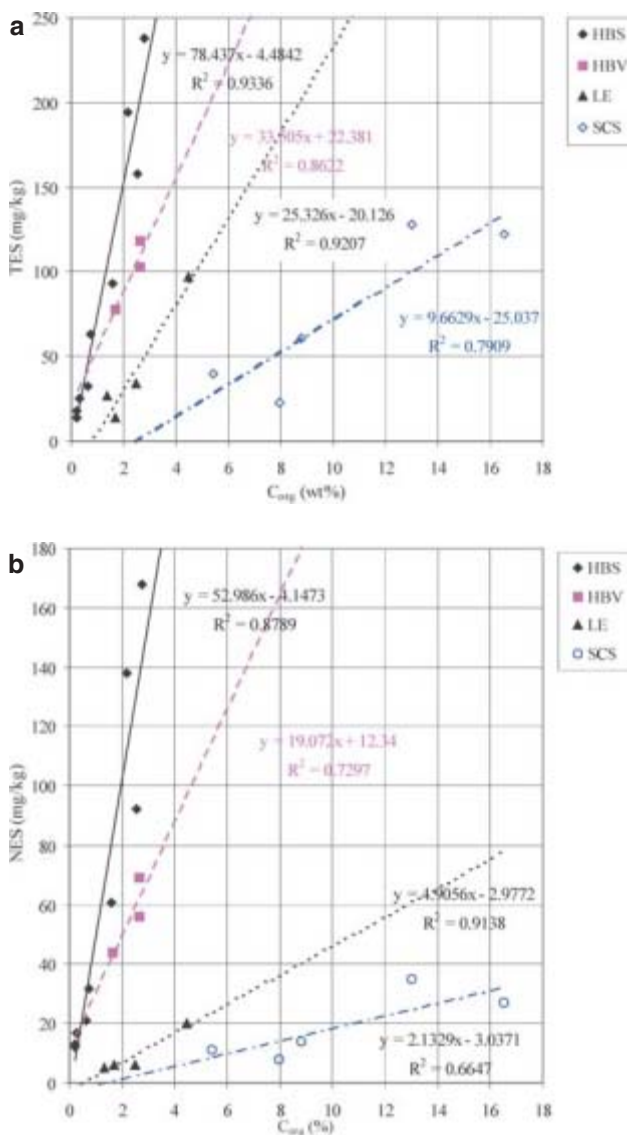


Fig. 5. Plots of TES (a) resp. NES (b) versus  $C_{org}$  values for sample subsets from individual profiles HBS, HBV, Le, SCS.

limiting concentration (500 mg AOX / kg of dry mass), set by the directive for evaluation of pond sediments and sludges (MŽP ČR 382/2001). A similar limit for soils has not yet been determined, however, if the AOX contents in investigated soils were compared by a value EOC1 indicator (= total extractable organically bonded chlorine) with limits acceptable for cultivated soils, the concentration level would be exceeded many times in all tested samples (Fig. 14). These concentration limits for farmlands, which are still valid according to the Directive MŽP 13/1994 (0.1 mg EOC1 / kg of dry mass), are very strict and unrealistic.

#### Distributions of individual pollutants in organic matter fractions

The contents of saturated hydrocarbons (alkanes), polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and organochlorinated pesticides (OCP), acqu-

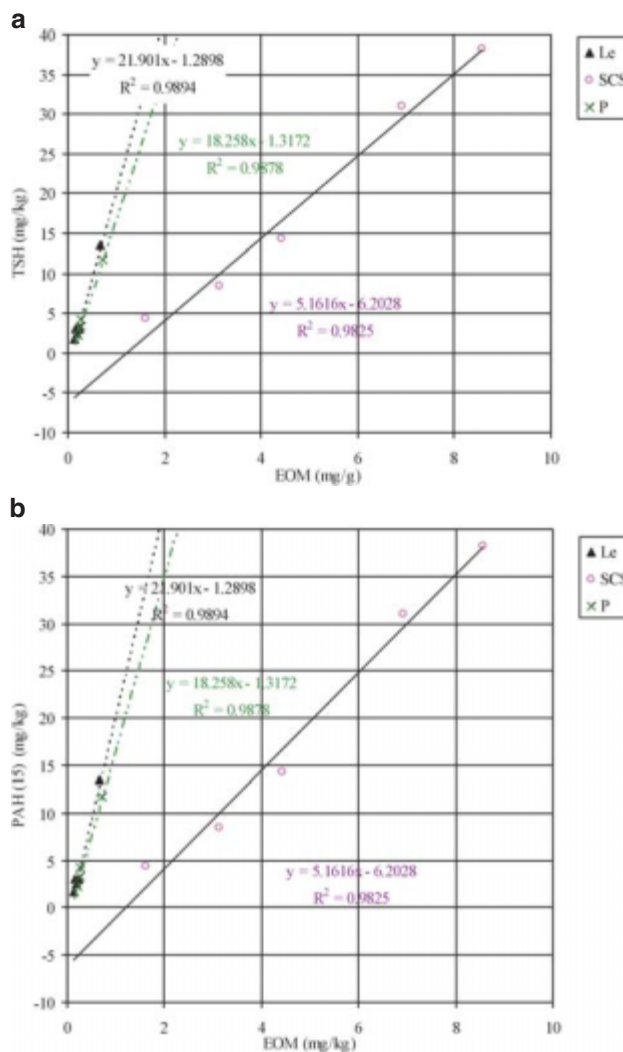


Fig. 6. Plots of THS (a) resp. PAH (15) (b) versus EOM values for soil samples from each of the profiles Le, SCS, P.

ired by means of highly efficient gas and liquid chromatography (HRGC, HPLC), offer very useful information on the proportions of individual components in the analysed organic matter fractions of the tested samples. The distributions of individual components (homologues) found by multicomponent analyses of the examined samples can be compared with known distribution patterns of these components, characteristic for natural background concentrations in given materials and/or for some potential sources of contamination. Anomalous distributions of individual compounds, differing both qualitatively and quantitatively from the natural background, reflect differences in composition and origin of organic matter in the sample and sensitively indicate possible external contamination by organic material of similar composition.

Distributions of normal ( $n-C_{10-38}$ ) and isoprene-like ( $i-C_{13-20}$ ) alkanes in the tested samples are demonstrated by selected examples of HRGC primary records. Chromatograms of all tested soils showed a characteristic predominance of hydrocarbons of higher molecular weights with odd number of carbon atoms, with maximal proportional share of  $n-C_{27}$  –  $n-C_{31}$  (see, e.g., Fig. 15a, b). Significant

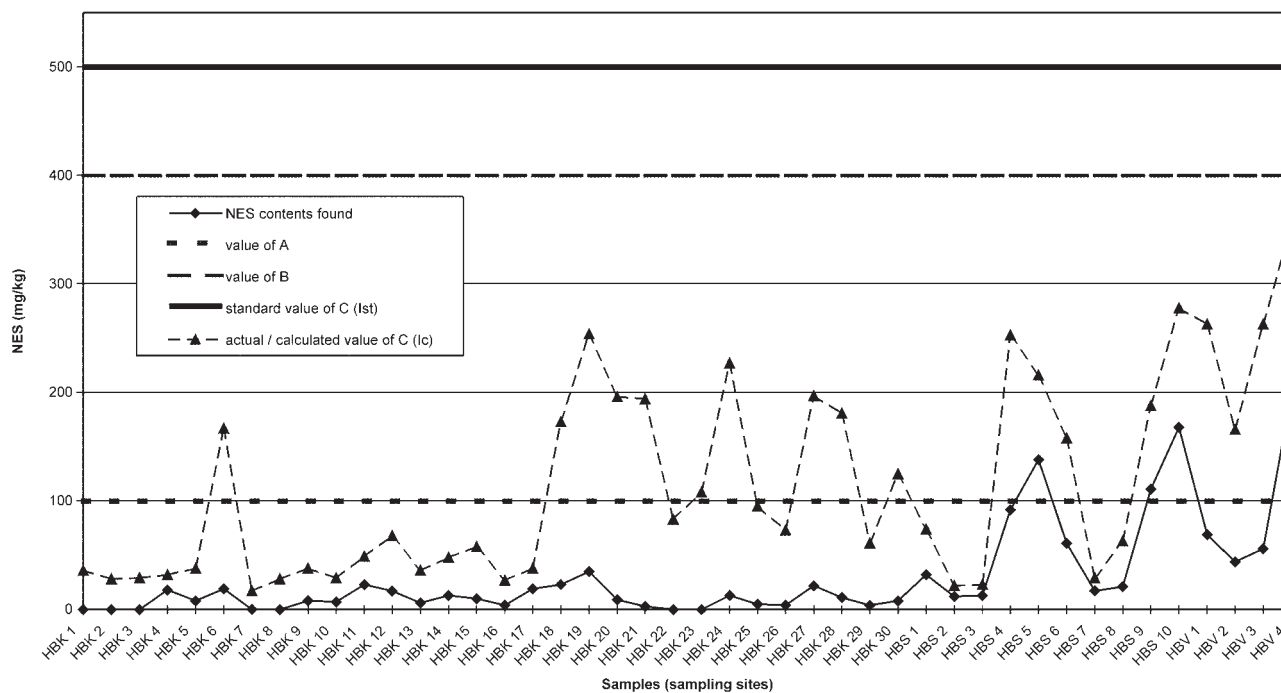


Fig. 7. Contents of NES in sediment samples from the Horní Bečva River basin, in confrontation with accepted national limits (criteria A, B, C) of admissible soil contamination.

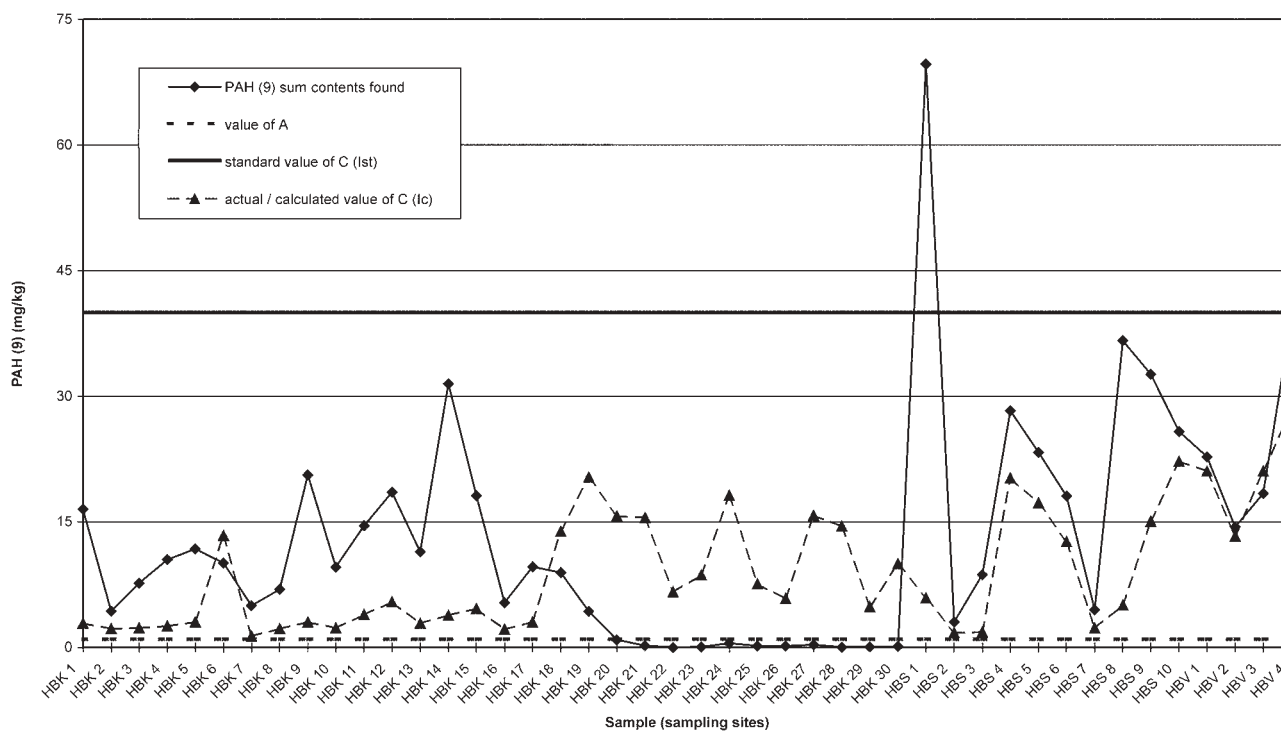


Fig. 8. Contents of the PAH (9) sum in sediment samples from the Horní Bečva River basin, in confrontation with national limits (criteria A, C) of admissible soil contamination.

predominance of odd n-alkanes indicates their biological origin and the maximum suggests the likely source of these hydrocarbons – vegetal organic matter containing higher lipids (waxes) with long fatty acid chains. n-Alkanes with shorter chains ( $n\text{-C}_{10}$  –  $n\text{-C}_{20}$ ), which originate from algae or microbial activity, are present only in negligible amounts.

A chromatographic record of n-alkane distribution in sediments of the Horní Bečva Reservoir is more complicated. A significant predominance of higher homologues with odd number of carbon atoms in chain is preserved only in the lowermost layers of profile HBK (approximately in the interval of HBK 18–30 – see, e.g., Fig. 15c). The amounts of odd and even alkanes in upper parts are

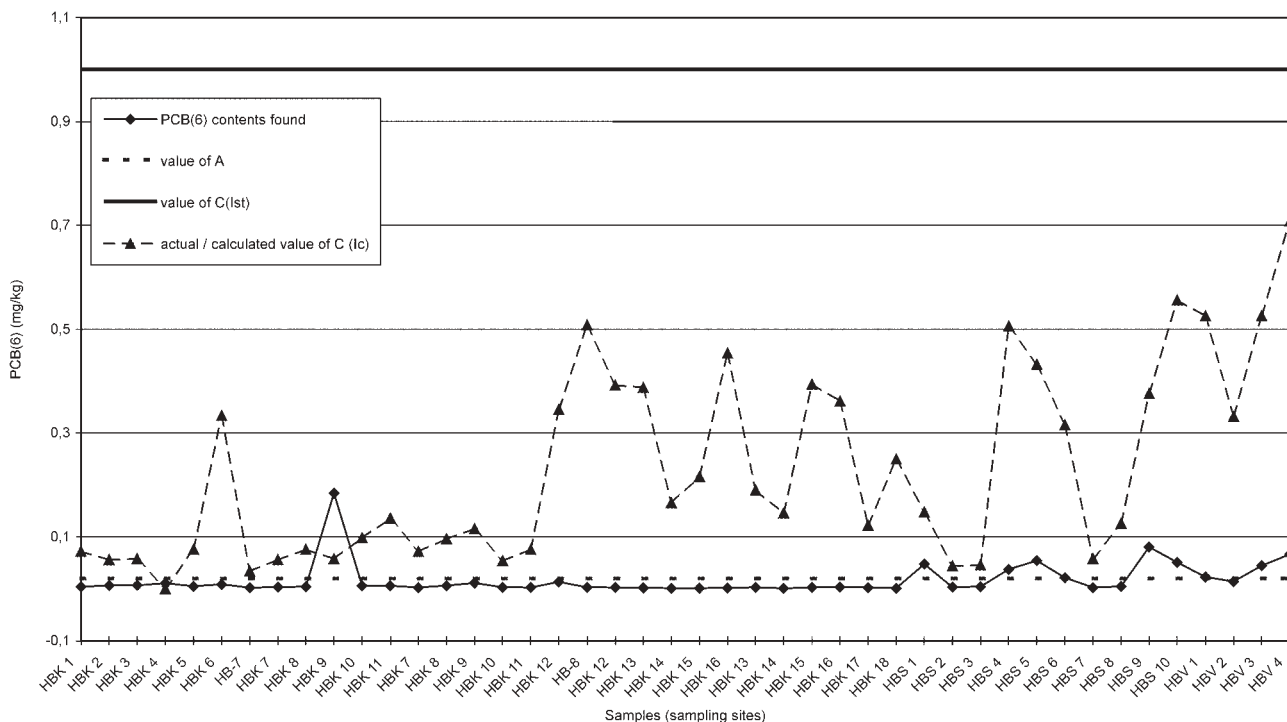


Fig. 9. Contents of the PCB (6) sum in sediment samples from the Horní Bečva River basin, in confrontation with national limits (criteria A, C) of admissible soil contamination.

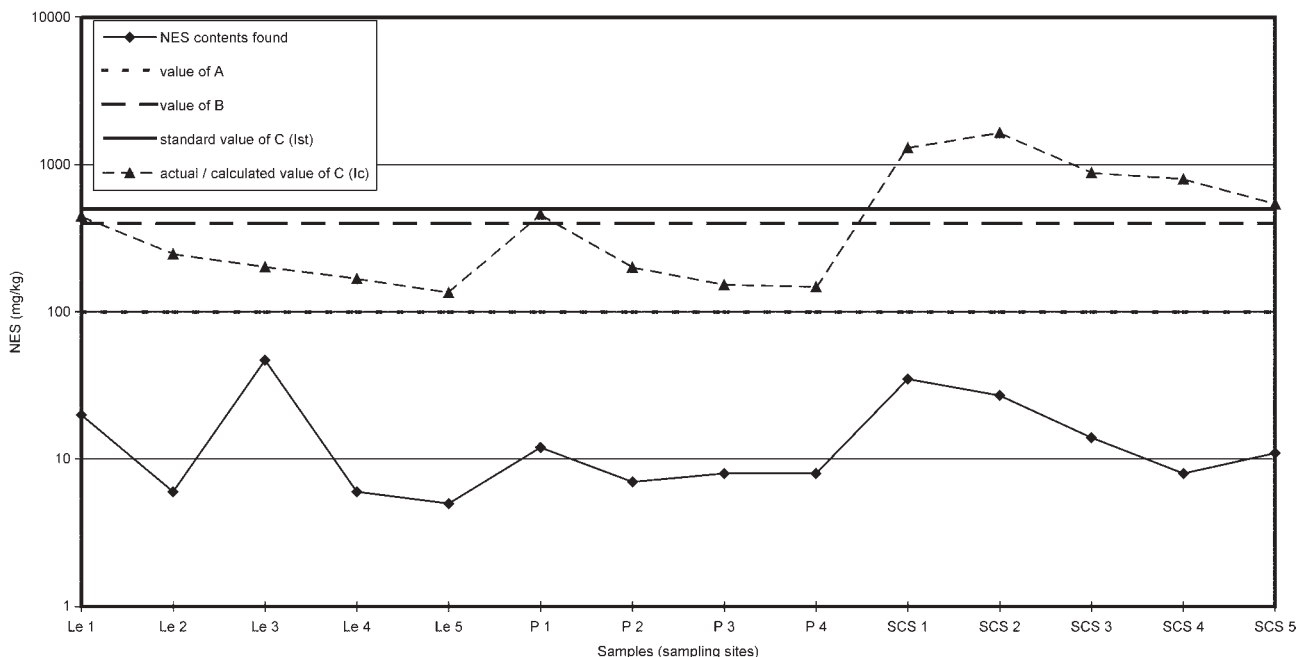


Fig. 10. Contents of NES in soils from localities Le, P, SCS in confrontation with national limits (criteria A, B, C) of admissible soil contamination.

more or less equivalent, which indicates an external sediment contamination by oil derivatives. The most contaminated samples contain an alkane distribution corresponding to distillation fractions of fuel oil/diesel oil (many samples in the interval of HBK 1–17 – see, e.g., Fig. 15d for HBK 1). The maximum in a distribution diagram is then shifted to lower n-alkanes, characteristic for the contaminating oil derivative. External contamination often masks the contribution of lower biogenic alkanes, which originate

from sapropelic organic matter and form a second maximum (around n-C<sub>15</sub>) in bimodal-shaped distribution diagrams of similar but unpolluted sediment samples.

The most highly contaminated HBS samples are HBS 2 and HBS 3 (Fig. 15e). Moreover, in samples HBS 4–HBS 10, a broad elution zone assigned to an unresolved complex mixture (UCM) of branched saturated hydrocarbons was observed. Such zone is characteristic for paraffinic lubricant oils and is present especially in sample HBS 5



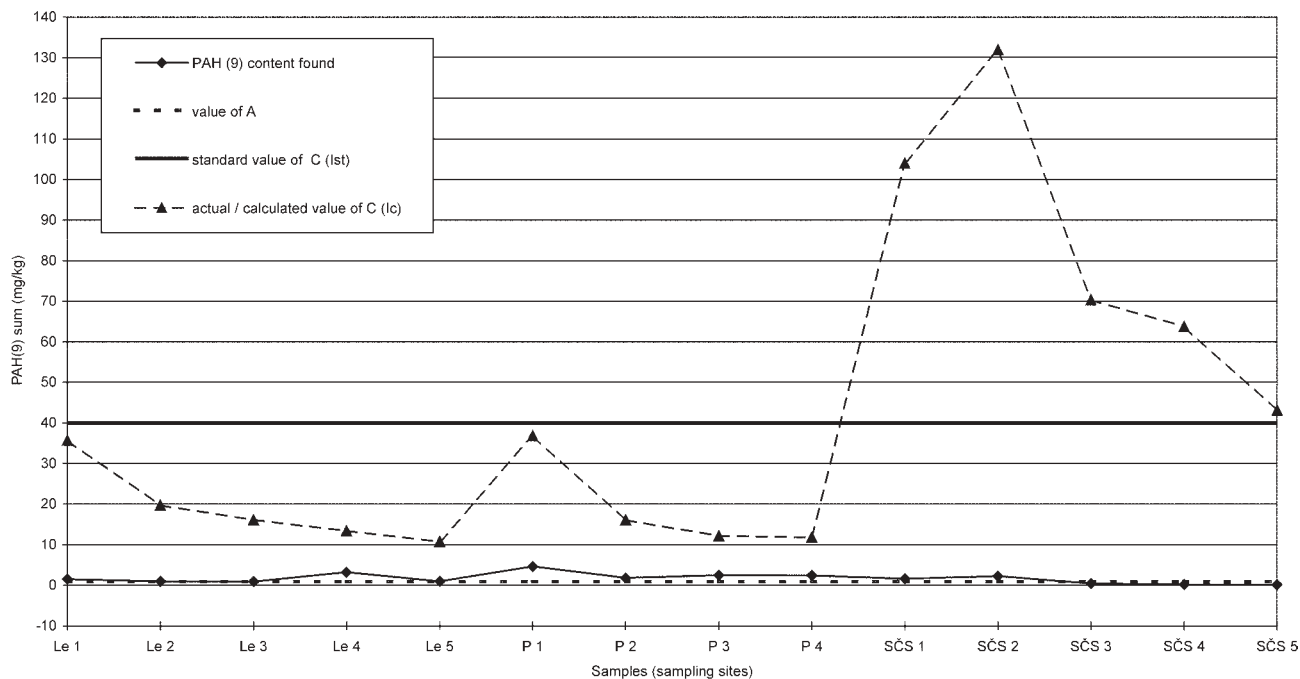


Fig. 11. Contents of the PAH (9) sum in soils from localities Le, P, and SCS in confrontation with national limits (criteria A, C) of admissible soil contamination.

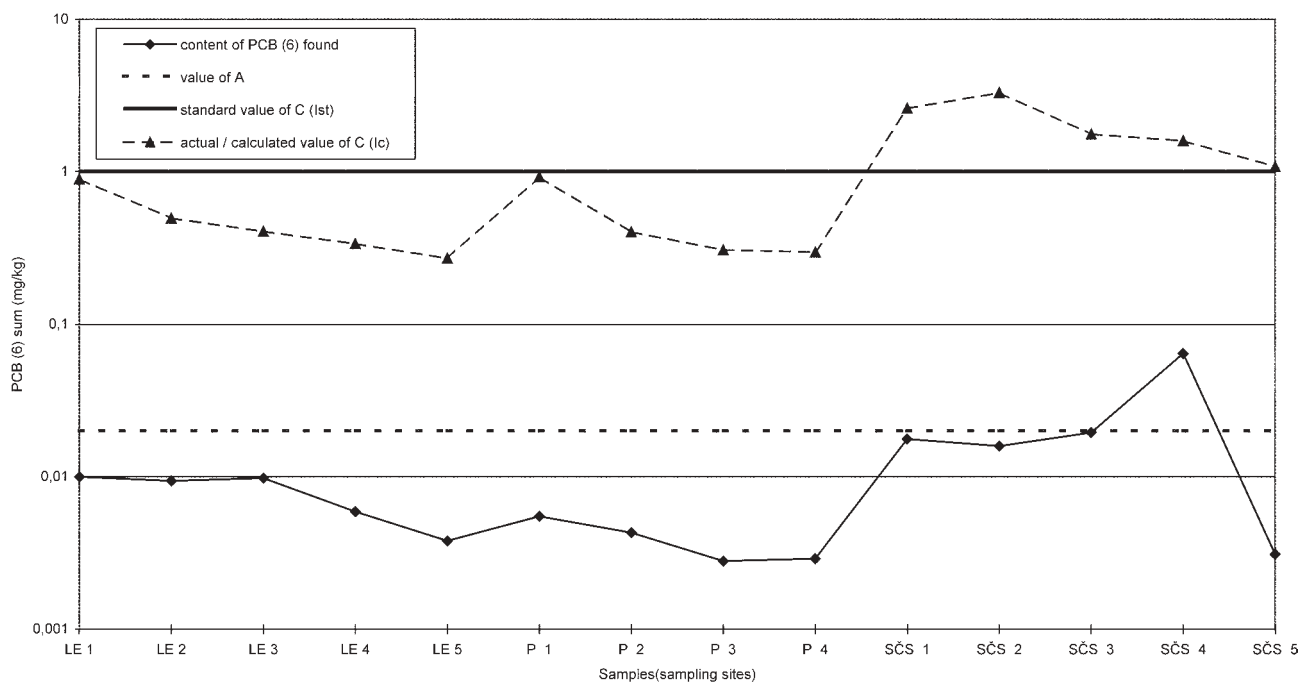


Fig. 12. Contents of PCB (6) sum in soil from localities Le, P, and SCS in confrontation with national limits (criteria A, C) of admissible soil contamination.

(Fig. 15f). The UCM contamination is, to a certain extent, also present in the samples of profile HBV (see, e.g., Fig. 15g). The contribution of lower oil derivatives to the equalization of the predominance and distribution of n-alkanes is, however, not as significant as in case of profiles HBS or HBK.

The recognition and assessment of differences in the contents and distribution of individual constituents determined by means of multicomponent analysis can be facilitated by a collective diagram representation incorporating

3-D graphs of results acquired from analyses of monitored compounds for a set of tested samples. This can be illustrated on a series of 3-D column graphs (see Figs 16–18) showing the distributions of individual PAH and PCB concentrations in sample sets from particular profiles at the localities of interest. A comparison of these figures positively implies that 3-D result presentations of multicomponent analyses can significantly contribute to the complex evaluation and better utilisation of data, acquired using these methods.

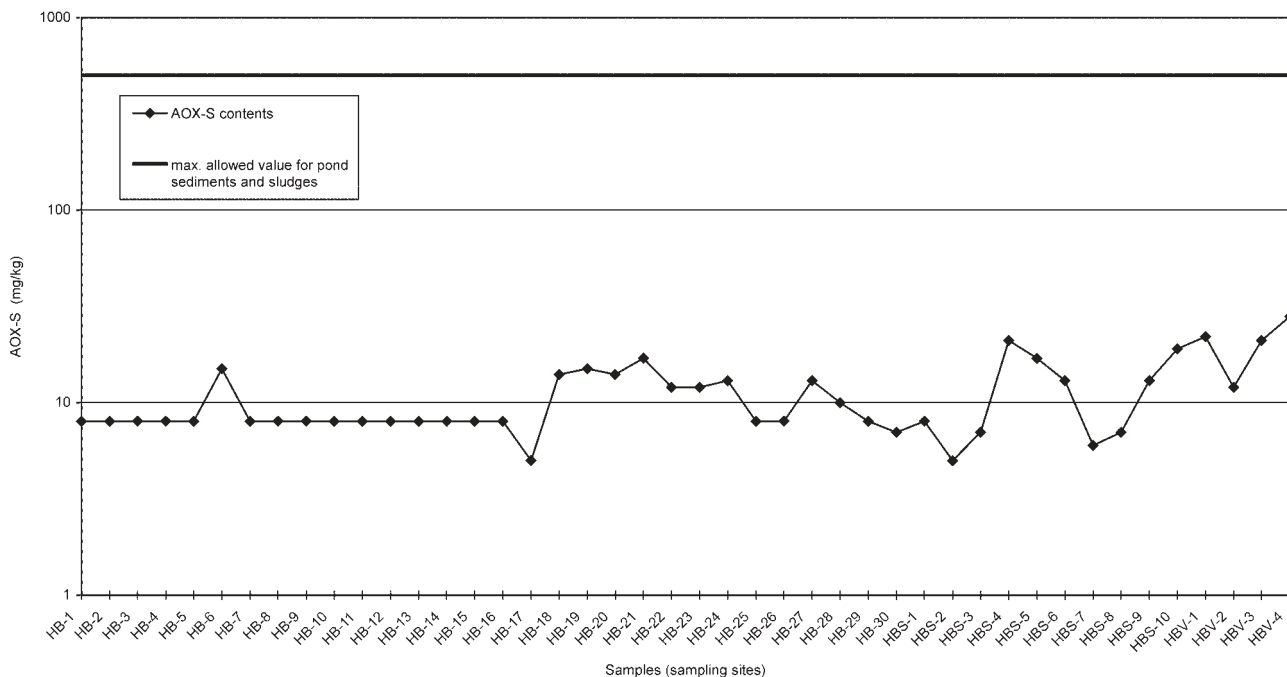


Fig. 13. Contents of AOX-S in sediments of the Horní Bečva River basin, in comparison with the accepted limit value for pond sediments and sludges.

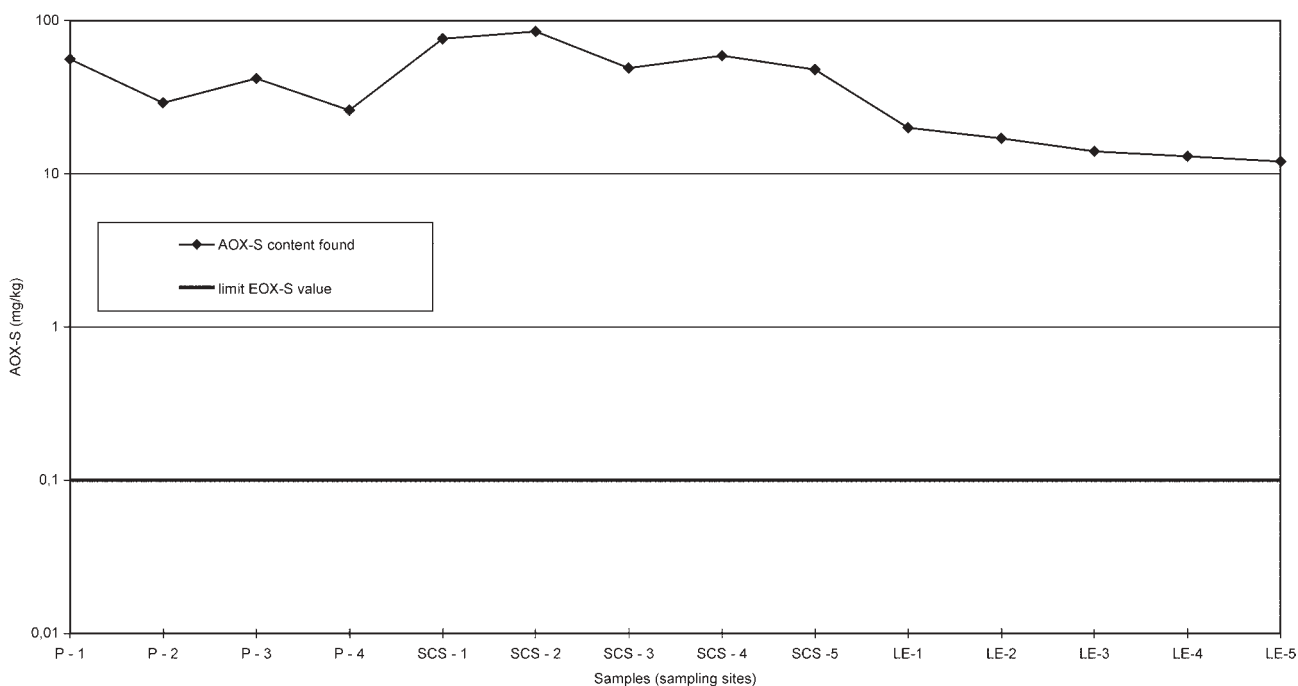


Fig. 14. Contents of AOX-S in soils from profiles Le, P and SCS in comparison with a limit EOX-S value for agricultural soils.

### Conclusions

With respect to the important role played by the sorbent organic matter in the processes of sorption of hydrophobic pollutants, the primary attention in this paper was paid to a more detailed characterisation of organic compounds in the tested natural materials – samples of uncultivated soils from the localities of Potočník, Lelekovice, Červenohorské sedlo Saddle and sediments from the bottom of the Horní Bečva Reservoir. Organic matter in these materials was

characterised using standard and certified methods of geochemical and environmental organic analysis. In addition to the determination of proportional shares of various carbon forms (mineral, organic and various fractions of humic carbon), the organic composition of samples was also characterised by customary determinations of other significant category parameters (humic organic matter, extractable organic matter, total and non-polar extractable substances, total adsorbed halogens) and by multicomponent analyses of distribution (individual content) of significant hydrocar-

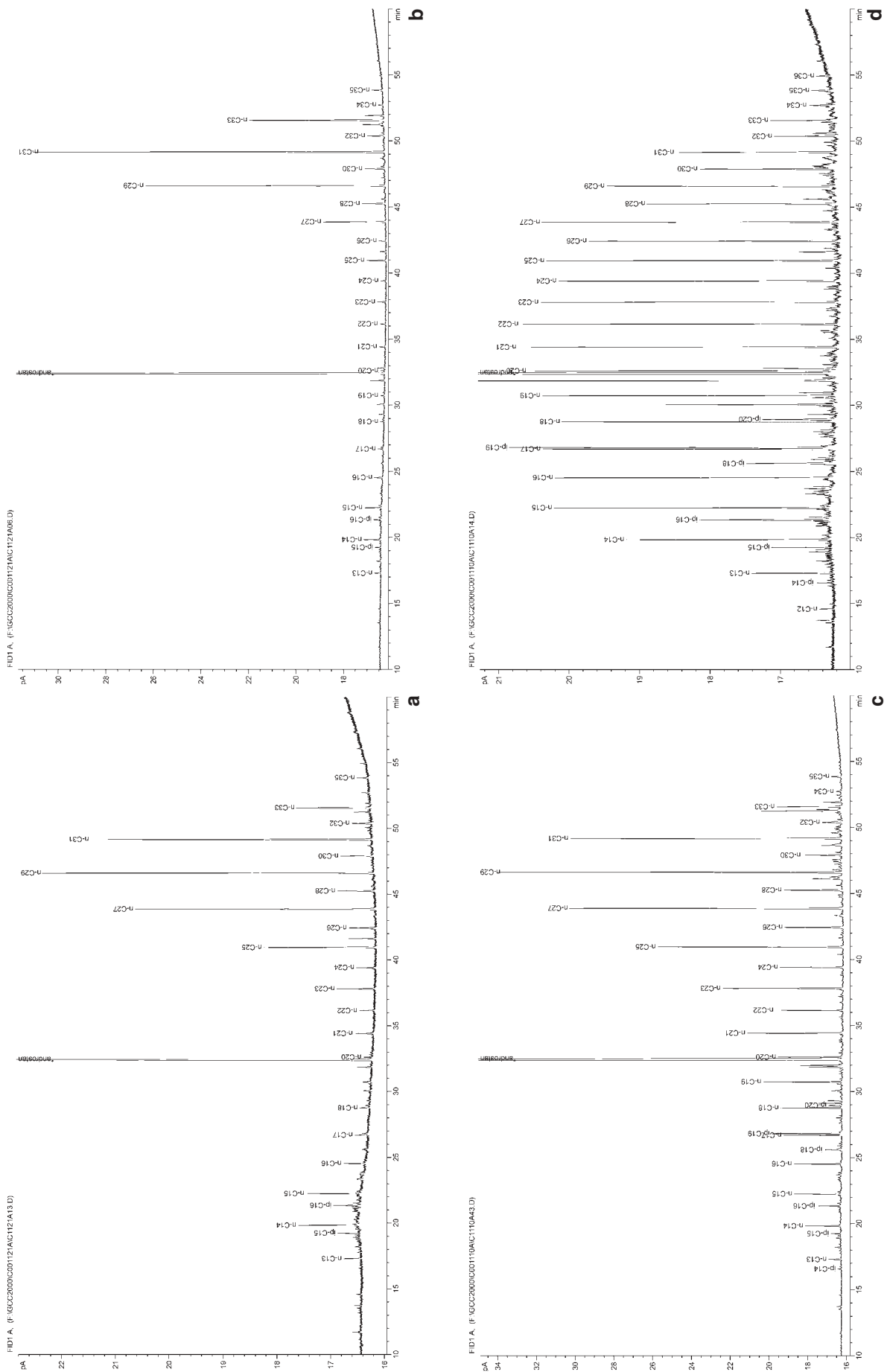


Fig. 15a–d. HRGC chromatograms showing characteristic distribution patterns of individual alkane components in selected soil and sediment samples: a – P 3, b – Le 3, c – HBK 28, d – HBK 1.

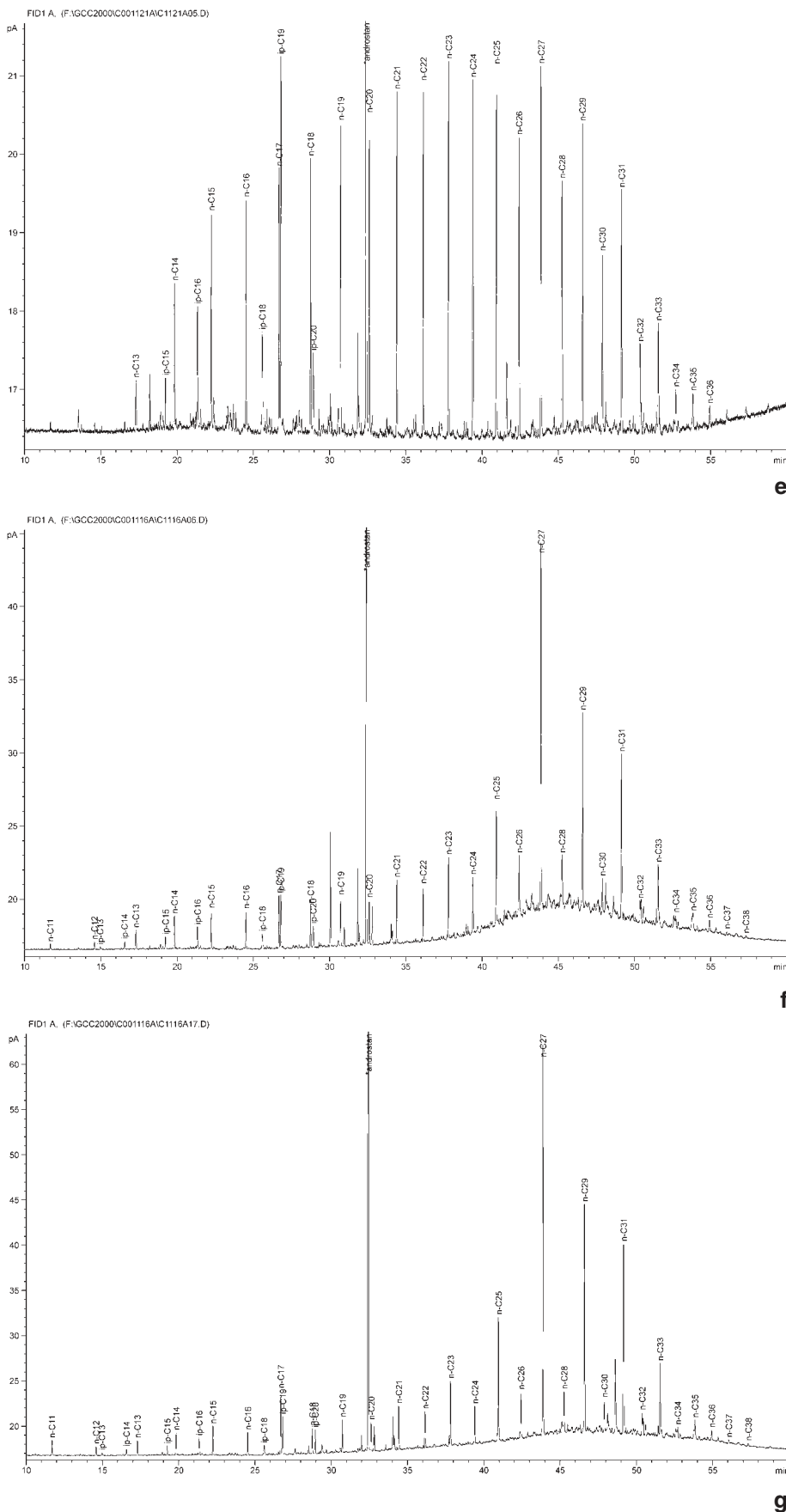


Fig. 15e–g. HRGC chromatograms showing characteristic distribution patterns of individual alkane components in selected soil and sediment samples: e – HBS 3, f – HBS 5, g – HBV 4.

bons and prior organic pollutants (normal and isoprene-like alkanes, PAH, PCB and OCP).

Statistical testing of analytical data files by means of evaluation of correlations between results of definitionally or quantitatively related quantities, proved valuable mutual correlations between a high number of quantities, applicable for environmentally geochemical interpretations. The interrelationships among the detected correlations increase significantly in sample subsets from individual profiles and localities. This trend apparently reflects the similarity in compositions or genetic cognition of organic matter and rock matrix in these sample subsets. Statistical audit of the quality of results also facilitated the identification and exclusion of outlying or anomalous results, not in line with the correlations found among the tested quantities.

The contents of monitored pollutants in the investigated sediment and soil samples were also evaluated with respect to valid criteria and limits set by the national environmental legislation, defining the degree of permissible pollution of individual environmental components.

The obtained values of total and non-polar extractable substances (TES and NES), polychlorinated biphenyls (PCB) and total absorbed organic halogens (AOX-S) category parameters of most soils fluctuated around background concentration levels given by A criterion, according to the systematic directive of the MŽP ČR. The detection limit and background AOX-S parameters for the tested sample collection indicate, at the same time, the unrealistic, very strict and even technically hardly detectable limit (0.1 mg EOX/kg) given for permissible EOX pollution on farmlands. In contrast, higher contents of  $\Sigma$  PAH found in bottom sediments of the Horní

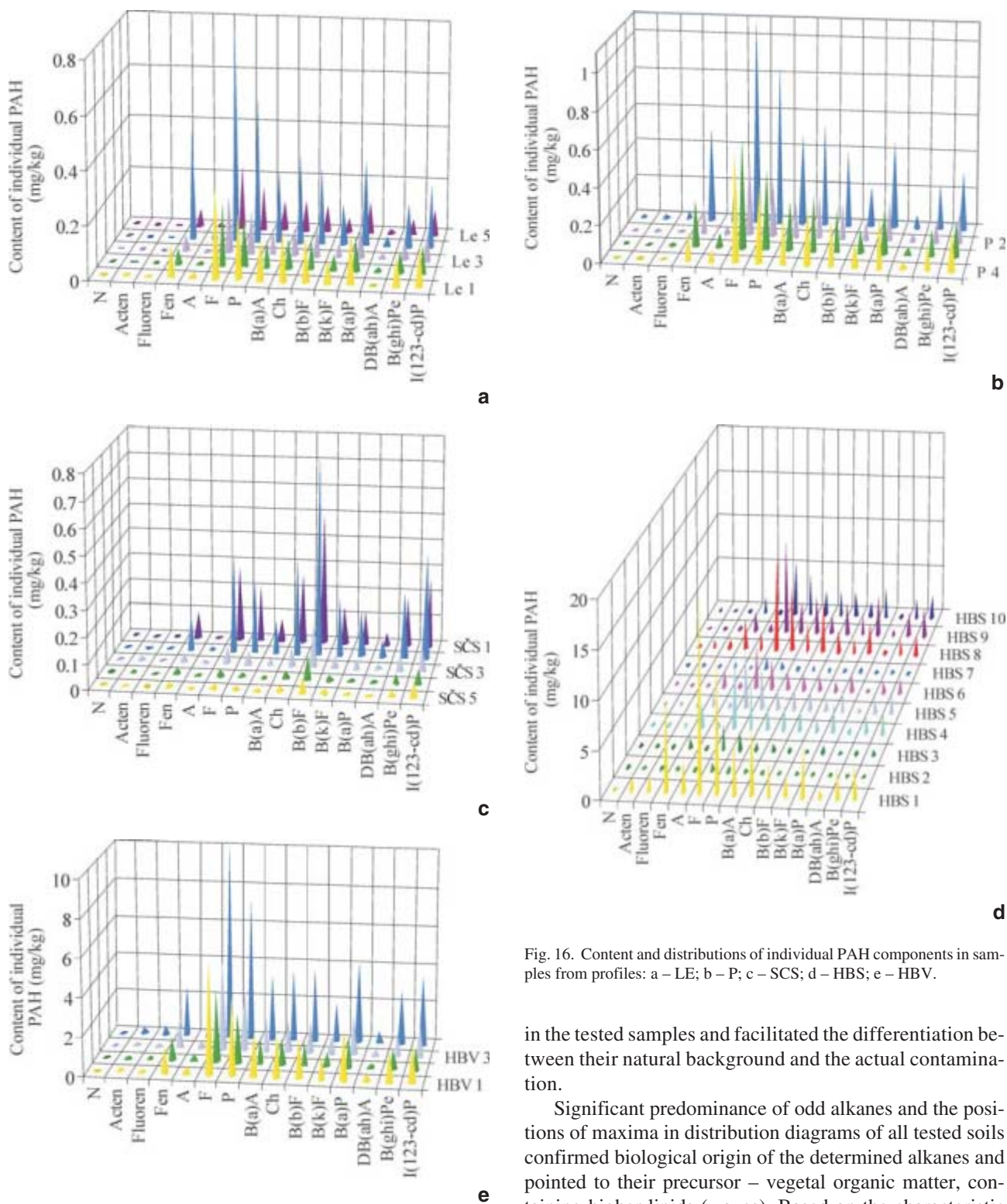


Fig. 16. Content and distributions of individual PAH components in samples from profiles: a – LE; b – P; c – SCS; d – HBS; e – HBV.

in the tested samples and facilitated the differentiation between their natural background and the actual contamination.

Significant predominance of odd alkanes and the positions of maxima in distribution diagrams of all tested soils confirmed biological origin of the determined alkanes and pointed to their precursor – vegetal organic matter, containing higher lipids (waxes). Based on the characteristic distributions of technical alkane mixtures (masking the typical background of natural hydrocarbons including lower biogenic alkanes), the positions (layers) externally contaminated by oil derivatives were identified in depth sediment profiles from the Horní Bečva Reservoir. Hydrocarbon contamination compositions corresponded to distillation fractions of diesel or fuel oils and also (at another sampling site) to complex mixtures of branched saturated hydrocarbons, typical for paraffinic lubrication oils. 3-D

Bečva Reservoir mostly exceeded actual limits set by the calculated values  $I_C$  of the C criterion.

Multicomponent determinations of alkanes, polycyclic aromatic hydrocarbons, polychlorinated biphenyls and organochlorinated pesticides, accomplished using highly efficient separation methods (gas and liquid chromatography), provided very useful information on the proportional share (distribution) of individual compounds



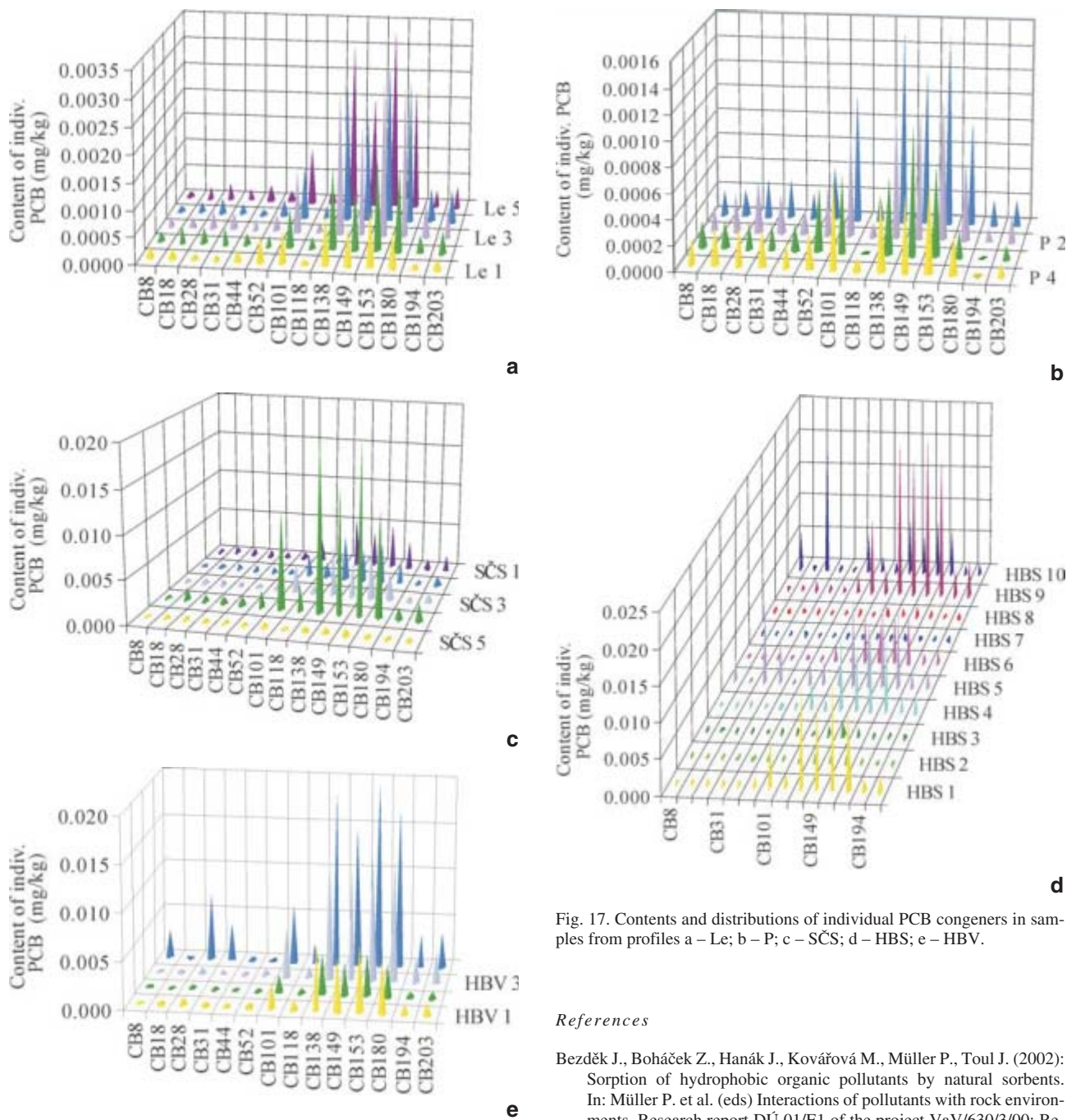


Fig. 17. Contents and distributions of individual PCB congeners in samples from profiles a – Le; b – P; c – SCS; d – HBS; e – HBV.

graphic presentations and comparisons of results significantly contribute to the complex evaluation and better utilisation of extensive data sets, obtained within multicomponent analyses.

**Acknowledgements.** This work has been performed within the state scientific program “Complex geochemical research of interaction and migration of organic and inorganic chemicals in the environment” supported by the Ministry of the Environment of the Czech Republic under grant project No. VaV/630/3/00.

Our special thanks are due to the staff of the geochemical laboratory of the CGS Brno for a huge amount of chemical analyses performed to characterize organic matter of the studied natural samples in a more complex manner. J. Jandák (Mendel Agriculture and Forest University, Brno) is thanked for the analyses on humic constituents.

*References*

Bezděk J., Boháček Z., Hanák J., Kovářová M., Müller P., Toul J. (2002): Sorption of hydrophobic organic pollutants by natural sorbents. In: Müller P. et al. (eds) Interactions of pollutants with rock environments. Research report DÚ 01/E1 of the project VaV/630/3/00; Report, Czech Geol. Surv., Brno (in Czech).

CGS Brno (1999a): SOP Z-1 Determination of nonpolar and total extractable compounds in soils. Standard operation procedure, Report, Czech Geol. Surv., Brno (in Czech).

CGS Brno (1999b): SOP Z-2 Determination of polychlorinated biphenyls and organochlorine pesticides in soils and solid materials. Standard operation procedure, Report, Czech Geol. Surv., Brno (in Czech).

CGS Brno (1999c): SOP H-1 Determination of mineral and organic carbon in rocks. Standard operation procedure, Report, Czech Geol. Surv., Brno (in Czech).

CGS Brno (1999d): SOP H-3 Determination of normal and isoprenoid aliphatic hydrocarbons in rocks and crude oils. Standard operation procedure, Report, Czech Geol. Surv., Brno (in Czech).

CGS Brno (1999e): SOP H-4 Determination of extractable organic matter in rocks and its component analysis. Standard operation procedure, Report, Czech Geol. Surv., Brno (in Czech).

CGS Brno (1999f): SOP Z-3 Determination of polycyclic aromatic fractions in soils and solid samples. Standard operation procedure, Report, Czech Geol. Surv., Brno (in Czech).

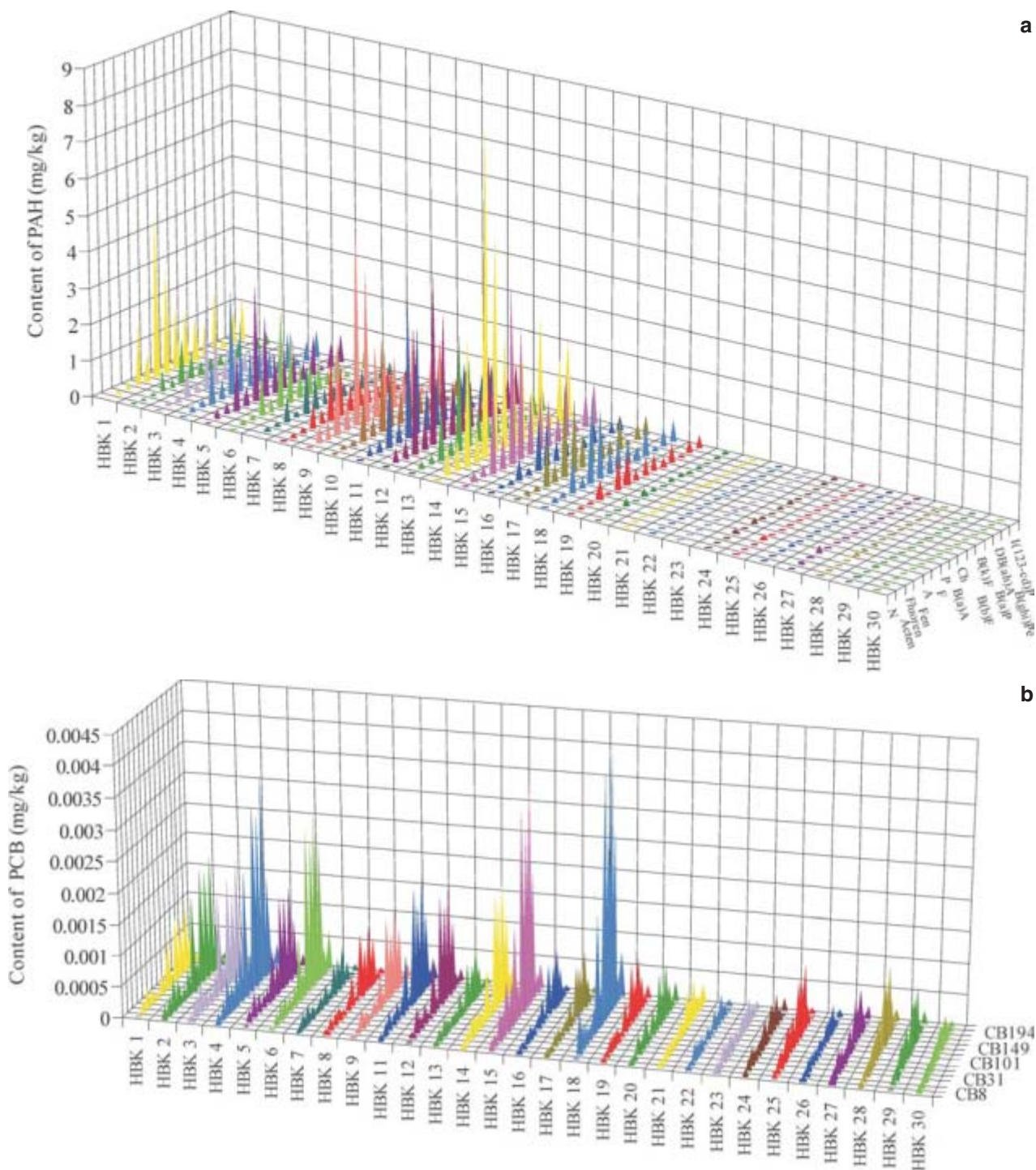


Fig. 18. Contents and distributions of individual PAH (18a) and PCB (18b) components in sediment samples from the profile HBK.

CGS Brno (1999g): SOP Z-4 Determination of adsorbed organic halogens in solid samples. Standard operation procedure, Report, Czech Geol. Surv., Brno (in Czech).

DIN 38 414 S 18 (1989): Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlamm-Untersuchung (Gruppe S – Schlämme und Sedimente), Teil 18: Bestimmung von adsorbierten organisch gebundenen Halogenen (AOX-S).

Domenico P. A., Schwartz F. W. (1998): Physical and chemical hydrogeology. 2nd ed., J.Wiley, New York.

Fernandez P., Vilanova R. M., Grimalt J. O. (1999): Sediment fluxes of polycyclic aromatic hydrocarbons in European high altitude mountain lakes. Environ. Sci. Technol. 33, 3716–3722.

Hassett J. J., Banwart W. L., Wood S. G. (1980): Sorption properties of

sediments and energy related pollutants. U.S. Environmental Protection Agency, EPA – 600/3-80-041.

ISO TR 11046 (1994): Soil quality – Determination of mineral oil content. – Method A by infrared spectrometry.

ISO/DIS 11464 (1992): Soil quality – Pretreatment of samples for physico-chemical analyses.

Karickhoff S. W., Brown D. S., Scott T. A. (1979): Sorption of hydrophobic pollutants on natural sediments. Water Res. 13, 241–248.

Koch R. (1986): Datenspeicher Umweltchemikalien. Eigenschaften – Toxizität – Umweltverhalten. VEB Verlag Volk und Gesundheit, Berlin.

Kononova M. M., Belchikova N. P. (1961): Uskorenyye metody opredeleniya sostava gumusa mineralnykh pochv. Pochvovedenie 10, 75–78.

- Koubová M., Zeman J., Müller P. (2003): Mineralogy, petrography and geochemistry of sediments used in pollutant sorption experiments. *Bull. Geosci.* 78, 3, 163–168.
- Luthy R. G., Aiken G. R., Brusseau M. L., Cunningham S. D., Gschwend P. M., Pignatello J. J., Reinhard M., Traina S. J., Weber W. J. Jr., Westall J. C. (1997): Sequestration of hydrophobic organic contaminants by geosorbents. *Environ. Sci. Technol.* 31, 3341–3347.
- Mackay D., Wan-Ying Shin, Kuo-Ching Ma (1999): Physical-chemical properties and environmental fate. Handbook / Database (CD-ROM form), CRC net Base 1999, CRC Press LLC.
- MP MŽP ČR (1996): Kriteria znečištění zeminy a podzemní vody – Postup zpracování analýzy rizika. Metodické pokyny Ministerstva životního prostředí ČR k zajištění procesu nápravy starých ekologických zátěží.
- MŽP ČR (13/1994): Vyhláška MŽP ČR čís. 13/1994 Sb., kterou se upravují některé podrobnosti ochrany zemědělského půdního fondu.
- MŽP ČR (382/2001): O podmínkách použití upravených kalů na zemědělské půdě. Vyhláška Ministerstva životního prostředí ČR čís. 382/2001.
- Sax N. I. (1984): Dangerous properties of industrial materials, 6th ed. Van Nostrand Reinhold, New York.
- Schwarzenbach R. P., Westall J. (1981): Transport of nonpolar organic compounds from surface water to ground water: Laboratory sorption studies. *Environ. Sci. Technol.* 15, 1360–1367.
- Schwarzenbach R. P., Gschwend P. M., Imboden D. M. (1993): Environmental organic chemistry. Wiley-Interscience, New York.
- Smith J. A., Witkowski P. J., Fusillo T. V. (1988): Manmade organic compounds in the surface waters of the United States – A review of current understanding. U. S. Geological Survey Circular 1007, Denver, Co.
- Toul J., Bezděk J., Kovářová M., Boháček Z., Hanák J., Milička J., Müller P. (2003): Sorption of hydrophobic organic priority pollutants on soils and sediments. *Bull. Geosci.* 78, 3, 205–223.
- Yaron B., Calvet R., Prost R. (1996): Soil Pollution – Processes and Dynamics. Springer Verlag, Berlin – Heidelberg – New York.

*Handling editor: Petr Dobeš*