OCCURRENCE OF DANGEROUS SUBSTANCES IN SUSPENDED SOLIDS AND RIVER SEDIMENTS OF THE MORAVA CATCHMENT ACCORDING TO CHMI MONITORING

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Abstract: The contribution quotes information on the occurrence of dangerous substances in solid matrices of water ecosystem, i.e. in suspended solids and sediments of the Morava catchment according to results of CHMI monitoring in the state network of water quality monitoring during 1999 – 2003 and results of research project VaV "Výskyt a pohyb nebezpečných látek v hydrosféře ČR" (Occurrence and movement of dangerous substances in the hydrosphere of the Czech Republic) (Rieder et al., 2003). The evaluated profiles belong to 45 profiles with extended monitoring of chemical state from the point of view of presence of dangerous and priority dangerous substances in the sense of the Directive of the Council 76/464/EHS and in the sense of Directive 2000/60/ES (Framework Directive) constituting framework for the activity of the Community in the area of water policy. Besides the overview of the occurrence of monitored chemical substances in both matrices on the individual profiles, comparison of the measure of contamination with limits valid in the Czech Republic (CR) is made. The temporal-spatial development of contamination by selected substances is evaluated. The bond to possible sources of pollution is considered. For information on quantitative parameters of pollution transported by the Morava River, detailed balance of runoff of priority pollutants in suspended solids is quoted.
Key words: dangerous substances, suspended solids, sediments, COMMPS procedure, loading, pollutant runoff.

1. Introduction

As dangerous substances are denoted those chemical substances in the water environment, that show toxicity for water organisms, bioaccumulation, persistence, carcinogenity, mutagenity and teratogenity. Their extent is defined by directives 76/464/EHS and daughter directives, directives 80/68/EHS, 96/91/EH, 2000/60/ES and in appendix no. 1 to Law no. 20/2004 Sb (amendment of the Water Act). Significance of monitoring of dangerous substances in the water environment and in the individual components of the hydrosphere is at the present time gaining in importance also in connection with the implementation of requirements of European directives for the area of water industry formulated in the Framework Directive.

The purpose is the gradual ceasing of pollution and elimination of dangerous substances, so as to achieve required immission standards and quality goals. Sensitive indicators of the pollution of surface waters are solid matrices of the hydrosphere – suspended solids and sediments. Many dangerous substances (pollutants) are bonded to them, which can be detected here even when their concentration in the water phase is under the limit of detection. Monitoring of qualitative state of solid matrices contributes to the overall evaluation of the immission situation of surface waters.

2. Monitoring of dangerous substances in the CHMI state network

CHMI monitores dangerous substance content in suspended solids and sediments since 1999, when monitoring with extended observation of chemical state within the framework of the so called complex water quality monitoring on streams began on 20 pilot profiles in agreement with EU requirements. Since 2000, the monitoring has been extended to altogether 45 profiles situated on the streams of Labe, Vltava, Morava, Odra, Dyje and on their significant tributaries. In the Morava catchment they are the profiles of Raškov, Olomouc, Kroměříž, Spytihněv and Lanžhot on the stream of Morava, and profiles on tributaries Bečva River – Dluhonice, and Olšava River – Uherský Brod. The basis of long-term monitoring for the evaluation of development of loading by the quoted substances has been thereby created, but also the delineation of problem risk sections of streams with the most serious pollution, and identification of possible pollution sources. The methods of sample collections and chemical analyses are based on the EU directives, international norms ISO, CSN and on recommendation by WMO, and are methods that have been accepted for CHMI monitoring (Rieder et al., 1999). The frequency of monitoring of the contents of heavy metals, metalloids and specific organic substances in sediments is 2-times a year in the spring and autumn months. In the case of suspended solids, point samples are collected once a month for the determination of the contents of heavy metals and metalloids, and 4-times a year samples are separated by flow-through centrifuge to determine both heavy metals and specific organic substances.

Besides the results of standard CHMI monitoring in the state network KJV, a significant advance in the research of the problem of dangerous substances in the water environment is the project VaV (Occurence and movement of dangerous substances in the CR hydrosphere). The CHMI was engaged in its solution during 2000-2002. Besides the research of the occurrence of wide spectrum of dangerous substances in the individual components of the hydrosphere (surface water, biota, suspended solids, sediments, groundweater) in the extent defined by European legislature, one of the main goals was the specification of dangerous substances relevant for the CR, and in the final phase also the adjustment of monitoring programs in the state networks of water quality monitoring both in the extent of the monitored parameters and in the localisation of the subjects of monitoring. On the basis of proven occurrence of substances in the hydrosphere, or the information of their manufacture or usage therefore about the potential occurrence, the design of a list of dangerous substances relevant for the hydrosphere of the CR has been prepared. For substances with so called relevance B (i.e. health-wise harmful substances quoted in European directives, whose occurrence in the CR has been partly proven or is possible with respect to existing sources), which have not so far been monitored within the framework of SSSJVT, reconnaissance monitoring was designed and then realized. With the exception of 5 substances (diurone, bromated diphenylethers, phtalates, chlorfenvinphos and tributylcene), all dangerous substances quoted in the Directive of the Council 76/464/EHS (including daughter directives) and in the Framework Directive were included in the monitoring. A part of the solution of the project was compilation of a list of priorities of individual dangerous substances using COMMPS procedure (Lepper, 2001). According to the measure of occurrence (exposition) of individual substances in the monitored matrices on the territory of the CR (from CHMI data) and their toxicity, a sequence of substances in individual matrices was compiled, which does justice to the weight of their occurrence and dangerousness, and to the necessity to monitor these substances in the CR. With respect to the harmful properties of dangerous substances, it is necessary besides monitoring to also to state limit values of their presence in the individual components of the environment. Within the project was therefore elaborated for the CR also a preliminary design of qualitative standards of dangerous substances, namely according to the method recommended by the Framework Directive.

3. Evaluation of occurrence and loading

Evaluation of sediments includes the results of chemical analyses of heavy metals and metalloids in fraction of 20 μm and analyses of organic substances from the overall sample of non-cohesive fresh sediment. In the case of suspended solids, heavy metals and metalloids contents are evaluated in overall samples of suspended solids gained by filtration and since 2001 also by centrifuge separation. Organic substances in suspended solids are evaluated solely from samples gained by centrifuge separation.

So far, qualitative standards valid in the EU or for the CR have not been accepted for solid matrices. In the requirements of directives 76/464/EHS and 2000/60/ES it is merely stated, that the contents of dangerous substances in solid matrices must not show a growing trend in the time series. The measure of loading of suspended solids and sediments by dangerous substances is here therefore evaluated on the basis of comparison of the contents, or of their characteristic yearly values with limits of the Methodical instruction of the department for ecological damages of the Ministry of Environment (ME) of the CR – Criteria of Soil and Groundwater Pollution, from 1996. The exceedance of the limiting value of category B of this normative is regarded as pollution, which can have negative influence on the health of man and on the individual components of the environment (see Table 1).

Table 1. Delineation of categories according to Criteria of soil and groundwater pollution of the ME for the evaluation of contents of dangerous substances in suspended solids and sediments

ME criteria	Categorisation
A	corresponds to natural contents of monitored substance, the exceeding of limit A is judged as a slight increase of the loading
B	corresponds to increased contents, the exceeding of limit B is judged as tion, which can have negative influence on the health of man and on the individual components of the environment
C	the exceeding of limit C represents pollution, which can mean significant risk of the endangering of human health and other components of the environment

Complete overview of dangerous substances monitored in suspended solids and sediments on installations of the CHMI state network in the Morava catchment is shown in Table 2. On the basis of results of reconnaissance monitoring, operation and situation monitoring programs have been designed for individual dangerous substances.

Substances of group A (demonstrably relevant)

For the calculation of characteristic values of group A in the matrix suspended solids and sediment, data from monitoring during 1999-2002 were taken. The decisive criterion was the number of values under the determinability limit (DL). In case that at least 20 % of the values of the evaluated set were above the DL, this substance was designed in the given locality into the operational monitoring (red field). In case that at least one value was aboe the DL, this substance was designed in the given locality into the situation monitoring (yellow field). For sets of values of concentration of dangerous substance on a profile, which contained more than 100 % values under the DL, they were not designed into any monitoring program (empty field).

Substances of group B (potentionally relevant)

For the calculation of the characteristic values of group B in the matrix suspended solids and sediments, data from reconnaissance monitoring during 2001-2002 were taken. Sets of a size 2 – 6 values for each profile were then at disposal. The deciding criterion was the number of values under the DL. In case that at least one value of the evaluated set was above the DL, the substance was designed in the given locality to the oparetional monitoring (red field). For sets of values of cocentrations of dangerous substance on a profile, which contained 100 % values under the DL, they were not designed into any monitoring program (empty field).

Table 2. Overview of dangerous substances monitored in suspended solids and sediments on installations of CHMI state network in the Morava catchment

	Suspended solids							Sediments						
	Raškov	**Olomouc**	**Kroměříž**	**Spytihněv**	**Lanžhot**	**Dluhonice**	**Uh.Brod**	**Raškov**	**Olomouc**	**Kroměříž**	**Spytihněv**	**Lanžhot**	**Dluhonice**	**Uh.Brod**
	Morava	**Morava**	**Morava**	**Morava**	**Morava**	**Bečva**	**Olšava**	**Morava**	**Morava**	**Morava**	**Morava**	**Morava**	**Bečva**	**Olšava**
Hg	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Cu	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Zn	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Mn total	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Al	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Cd	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Ni	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Pb	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Cr total	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Co	x	x	x	x	x	x	x	x	x	x	x	x	x	x
As	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Se	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Sb	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Be	x	x	x	x	x	x	x	x	x	x	x	x	x	x
B	x	x	x	x	x	x	x	x	x	x	x	x	x	x

Legend		
		non-relevant substance
	x	Relevant substance, operational monitoring
	x	Relevant substance, situation onitoring

Sequel of Tabel 2.

	Suspended solids	Sediments

Sequel of Tabel 2.

	Suspended solids	Sediments

	Raškov	Olomouc	Kroměříž	Spytihněv	Lanžhot	Dluhonice	Uh.Brod	Raškov	Olomouc	Kroměříž	Spytihněv	Lanžhot	Dluhonice	Uh.Brod
	Morava	Morava	Morava	Morava	Morava	Bečva	Olšava	Morava	Morava	Morava	Morava	Morava	Bečva	Olšava
fenol	x	x	x	x	x	x	x	x	x	x	x	x	x	x
2-monochlorfenol	x	x	x	x	x	x	x	x	x	x	x	x	x	x
3 monochlorfenol	x	x	x	x	x	x	x	x	x	x	x	x	x	x
4 monochlorfenol	x	x	x	x	x	x	x	x			x	x	x	x
2,3-dichlorfenol	x	x	x	x	x	x	x	x	x	x	x	x	x	x
2,4-dichlorfenol	x	x	x	x	x	x	x	x	x	x	x	x	x	x
2,5-dichlorfenol	x	x	x	x	x	x	x	x	x	x	x	x	x	x
3,4-dichlorfenol	x	x	x	x	x	x		x	x	x	x	x	x	x
2,4,5-trichlorfenol	x	x	x	x	x	x		x	x	x	x	x	x	x
2,4,6-trichlorfenol	x	x	x	x	x	x	x	x	x	x	x	x	x	x
2,3,4,5-tetrachlorfenol	x	x	x	x	x	x		x	x	x	x	x	x	x
2,3,4,6-tetrachlorfenol	x	x	x	x	x	x		x	x	x	x	x	x	x
2,3,5,6-tetrachlorfenol	x	x	x	x	x	x		x	x	x	x	x	x	x
pentachlorfenol	x	x	x	x	x	x	x	x	x	x	x	x	x	x
o-kresol				x	x	x	x					x	x	
m-kresol	x	x	x	x	x	x			x			x	x	x
p-kresol	x	x	x	x	x	x			x			x	x	x
a-naftol	x	x	x	x	x	x						x		
b-naftol	x	x	x	x	x	x						x		
fluoranthen	x	x	x	x	x	x	x	x	x	x	x	x	x	x
benzo(a)pyren	x	x	x	x	x	x	x	x	x	x	x	x	x	x
benzo(b)fluoranthen	x	x	x	x	x	x	x	x	x	x	x	x	x	x
benzo(k)fluoranthen	x	x	x	x	x	x	x	x	x	x	x	x	x	x
benzo(g,h,i)perylen	x	x	x	x	x	x	x	x	x	x	x	x	x	x
indeno(1,2,3-c,d)pyren	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Benzo(a)antracen	x	x	x	x	x	x	x	x	x	x	x	x	x	x
dibenzo(a,h)antracen	x	x	x	x	x	x	x	x	x	x	x	x	x	x
naftalen	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Antracen	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Fenantren	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Pyren	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Chrysen	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Fluoren	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Aldrin	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Endrin	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Dieldrin				x	x		x					x	x	
Isodrin	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Alachlor	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Chlorpyrifos	x	x	x	x	x	x	x	x	x	x	x	x	x	x
a-endosulfan	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Trifluralin	x	x	x	x	x	x	x	x	x	x	x	x	x	x
PCB 153	x	x	x	x	x	x	x	x	x	x	x	x	x	x
PCB 180	x	x	x	x	x	x	x	x	x	x	x	x	x	x

With respect to the comparatively extensive spectrum of monitored dangerous substances, for further processing we made the selection of substances according to the following criteria:

- priority dangerous substance according to appendix X of the EU directive (WFD)
- relevant substance for the territory of the CR according to the procedure COMMPS (Hypr, Halířová, Beránková, 2003).
- relevance of substance for solid matrix according to Log_{Kow}, $K_{susp.sed-water}$ and according to values under the determinability limit (DL)

Their overview, including the quoting of order of priorities (Rank. cz) for the CR according to COMMPS, is shown in Table 3.

Table 3. Selection of substances relevant for evaluation of suspended solids and sediments (Hypr, Halířová, Beránková, 2003)

substance	RANK.cz suspended solids (SUSP)	RANK.cz sediments (SED)	SUSP %<MS	SED %<MS	Ksusp.sed-w	Ksusp.sed-w(med)	relevance according Kws and logKow	priority dangerous substances (WFD)	RANK.cz surface water	Water %<MS
As	6	7	0,0	0,0	4 486	13 800	solid		6	23,4
Cd	1	1	0,0	0,0	114 000	33 000	solid	yes	3	46,4
Cu	4	4	0,0	0,0	207 000	24 000	solid		4	6,1
Ni	2	3	0,0	0,0	11 400	25 600	solid		2	4,5
Pb	3	2	0,0	0,0	157	46 800	solid	yes	5	45,0
Hg	5	5	0,0	0,0	73 605	15 000	solid	yes	7	80,6
ZN	9	9	0,0	0,0	11 400	35 150	solid		9	15,5
benzo(a)antracen	4	4	0,0	9,9	5 508	221 000	solid		4	21,2
benzo(a)pyren	2	1	0,0	8,7	12 283	184 000	solid	yes	6	17,3
benzo(b)fluoranthen	3	3	0,0	0,0	14 366	213 500	solid	yes	5	9,9
benzo(g,h,i)perylen	1	2	0,0	13,0	33 628	148 500	solid	yes	3	16,5
benzo(k)fluoranthen	-	5	1,0	15,9	54 614	176 700	solid	yes	10	29,7
dibenzo(a,h)antracen	6	7	41,7	84,6	46 175	226 000	solid			81,8
fluoranthen	16	12	0,0	1,9	1 465	123 000	solid		21	6,2
fluoren	15	15	34,8	34,1	382	43 400	solid			23,6
chrysen	9	9	1,1	13,2	7 988	296 700	solid			16,8
indeno(1,2,3-c,d)pyren	7	6	0,5	15,4	42 063	161 212	solid	yes	8	52,6
pyren	8	8	1,1	5,0	451	169 000	solid		11	75,0
aldrin	24	18	33,9	28,6	28 900		solid		2	58,5

For the detailed evaluation, the selection of substances was further narrowed according to the signal value of exceedance of the referential limit (limit of category B of the ME). Selected were substances whose 90 percentile concentration or maximum value of concentration during 1999 – 2003 exceeded on one of the monitored profiles in the Morava catchment at least limit B (increased, or risk concentration). Out of heavy metals and metalloids it is arsenic, nickel, mercury and cadmium, out of specific organic substances polyaromatic hydrocarbons (PAH) – benzo(a)pyrene, benzo(b)fluoranthene and further chlorphenols (2,3,4,5 tetrachlorphenol, 2,3,4,6 tetrachlorphenol, 2,4,5 trichlorphenol, 2,4 dichlorphenol, 2,5 dichlorphenol and 2 monochlorphenol, pentachlorphenol).

Tabular overview of a narrower selection of substances for sediments and for suspended solids is quoted by Tables 4 and 5.

Table 4. Selection of substances, which during 1999 – 2003 had P90 or MAX at least in category B (sediments)

Raškov	Olomouc	Dluhonice	Kroměříž	Spytihněv	Uherský Brod	Lanžhot
	2,3,4,6-tetrachlorfenol					
				2,3,4,5-tetrachlorfenol		
						2,4,5-trichlorfenol
benzo(a)pyren	benzo(a)pyren	benzo(a)pyren		benzo(a)pyren	benzo(a)pyren	
				benzo(k)fluoranthen		

Table 5. Selection of substances, which during 1999 – 2003 had P90 or MAX at least in category B (suspended solids)

Raškov	Olomouc	Dluhonice	Kroměříž	Spytihněv	Uherský Brod	Lanžhot
	arsen	arsen	arsen	arsen	arsen	arsen
		beryllium				
chrom veškerý		chrom veškerý	chrom veškerý	chrom veškerý	chrom veškerý	chrom veškerý
kadmium		kadmium	kadmium	kadmium	kadmium	kadmium
		měď		měď		
nikl	nikl	nikl	nikl	nikl	nikl	nikl
		olovo	olovo			
rtuť	rtuť	rtuť	rtuť	rtuť	rtuť	rtuť
zinek	zinek	zinek	zinek	zinek		zinek
	2,3,4,6-tetrachlorfenol			2,3,4,5-tetrachlorfenol		
			2,4-dichlorfenol	2,4-dichlorfenol		
						2,4,6-trichlorfenol
2,5-dichlorfenol						
2-monochlorfenol						
benzo(a)antracen		benzo(a)antracen				
benzo(a)pyren	benzo(a)pyren	benzo(a)pyren	benzo(a)pyren	benzo(a)pyren	benzo(a)pyren	benzo(a)pyren
benzo(b)fluoranthen		benzo(b)fluoranthen	benzo(b)fluoranthen	benzo(b)fluoranthen		
		indeno(1,2,3-c,d)pyren				
	pentachlorfenol		pentachlorfenol			

In suspended solids, out of the quoted substances, 2,4,5 trichlorphenol is not signalized. In sediments, the number of substances whose 90 percentile concentration or maximum value of concentration during 1999-2003 exceeded on one of the monitored profiles of the Morava catchment at least qualitative limit B, lower and from the quoted it is only benzo(a)pyrene, 2,3,4,5-tetrachlorphenol, 2,3,4,6-tetrachlorphenol and 2,4,5-trichlorphenol.

3.1. Evaluation of contamination of suspended solids

In suspended solids, the maximum (signal) values of data sets exceede the limits of categories of increased and risk loading by the contents of arsenic, nickel and mercury, benzo (a)pyrene, benzo(a)antracene, benzo(b)fluoranthene, indeno(1,2,3-c,d)pyrene and most of the substances from the chlorphenol group. The same limits of the ME are exceeded also by 90 percentile nickel, mercury, benzo(a)pyrene and benzo(b)fluoranthene. Approximately 85 – 94 % of data falls into categories corresponding to natural background or to slightly increased loading. Only in the case of benzo(a)pyrene is the loading of the ecosystem considerable and

30.6 % of measured data exceeds the limit of of increased loading and 26.4 % the limit of risk loading. The overview of statistical and qualitative parameters of selected substances in the suspended solids of the Morava River is shown in Table 6.

Table 6. Overview of statistical and qualitative parameters of selected substances in suspended solids

Morava catchment(1999-2003)	statistics and evaluation according to limits of ME							%< MS	% of exceedance of ME limits			
substance	**MIN**	**MED**	**AVG**	**P75**	**P90**	**MAX**	**Count**		**A1**	**A2**	**B**	**C**
As	2	26,10	31,26	42,075	59,63	123,9	354	0,0	57,6	36,4	1,1	4,8
Be	0,22	1,73	1,98	2,39	3,049	36,73	308	0,0	97,4	2,3	0,0	0,3
Cr total	11,8	95,6	127,70	148	237,8	758	429	0,0	69,2	28,7	0,7	1,4
Cd	0,11	2,10	3,20	4,05	6,6	24,9	351	0,0	3,4	93,2	2,8	0,6
Cu	13,4	73,00	92,87	99,9	152,98	728	429	0,0	45,2	54,3	0,2	0,2
Ni	11,1	84,20	104,96	118,4	181,34	736,4	427	0,0	22,2	67,2	6,6	4,0
Pb	12	48,45	56,86	63,9	86,15	473,1	426	0,0	88,3	11,0	0,5	0,2
Hg	0,05	0,80	1,60	1,8	3,4	30,2	346	0,3	31,5	51,7	15,6	1,2
Zn	41,5	419,50	584,87	602,6	937,2	9604	429	0,0	0,7	96,7	1,2	1,4
benzo(a)antracen	128	1226,00	1738,47	1826,25	3538,6	6144	30	0,0	0,0	93,3	0,0	6,7
benzo(a)pyren	0	1578,00	1900,06	2112	3220,2	7270	72	1,4	1,4	41,7	26,4	30,6
benzo(b)fluoranthen	276	1552,50	2116,58	2239,75	4062,6	10119	72	0,0	0,0	88,9	5,6	5,6
benzo(g,h,i)perylen	0	1075,00	1140,07	1522,5	2195,8	4409	72	13,9	15,3	84,7	0,0	0,0
benzo(k)fluoranthen	60	759,50	910,21	1065,25	1520,4	3448	72	0,0	0,0	100,0	0,0	0,0
dibenzo(a,h)antracen	0,5	138	208,13	305,5	545,8	948	30	33,3	40,0	60,0	0,0	0,0
fluoranthen	0	3389,00	4126,57	5056,25	7404,7	16508	72	1,4	2,8	97,2	0,0	0,0
fluoren	0	78,50	135,95	205,25	372,7	688	74	37,8	66,2	33,8	0,0	0,0
chrysen	194	1651,00	2050,23	2221,25	3809,3	8527	74	0,0	0,0	100,0	0,0	0,0
indeno(1,2,3-c,d)pyren	0	979,50	1072,11	1355,75	1957,5	4183	72	1,4	1,4	97,2	1,4	0,0
pyren	28	2715,00	3361,66	3721,75	6321,5	14825	74	0,0	1,4	98,6	0,0	0,0
aldrin	0,5	2,00	3,28	5	7,9	17	72	37,5	100,0	0,0	0,0	0,0
2,3,4,5-tetrachlorfenol	5	100,00	330,89	200	860	2600	28	46,4	46,4	46,4	0,0	7,1
2,3,4,6-tetrachlorfenol	5	5,00	143,39	5	420	2100	28	82,1	82,1	14,3	0,0	3,6
2,4,5-trichlorfenol	5	52,00	126,23	188,5	300	900	71	40,8	46,5	53,5	0,0	0,0
2,4,6-trichlorfenol	5	135,00	231,06	300	620	1600	69	29,0	34,8	63,8	1,4	0,0
2,4-dichlorfenol	5	5	214,28	200	620	3625	69	58,0	63,8	33,3	1,4	1,4
2,5-dichlorfenol	5	5	228,75	28,75	430	2800	28	75,0	75,0	17,9	3,6	3,6
2-monochlorfenol	5	5	191,39	100	476	3800	69	53,6	66,7	29,0	2,9	1,4
pentachlorfenol	5	5	256,65	100	320	8300	69	71,0	71,0	26,1	0,0	2,9

<u>Arsenic</u>

The average value of the contents of arsenic is 31.3 $mgkg^{-1}$. 90 percentile of data still falls only to the category of slight loading. Most data corresponds to the level of natural background (57.6 %) or slight loading (36.4 %). Maximum values on most profiles except of Raškov point to the existence of pollution, which corresponds to increased contents (1.1 %) with a possible negative influence on aquatic communities or to contents which can represent a risk of exposure to danger of the aquatic system, or even the health of man (4.8 % of data). The most frequent exceedance of limit B and C was found on profile Uherský Brod (Olšava River). Remote and extreme values of maxima on individual profiles usually occurred in November to February.

<u>Nickel</u>

The average value of nickel content is 105 $mgkg^{-1}$. 75 percentile still falls into the category of slight loading, but 90 percentile is already on the level of increased contents of category B. Most of the data corresponds to the level of geogennous background (22.2 %) and slight loading (67.2 %). Maximum values on profiles point to the existence of pollution, which corresponds to increased contents (6.6 % of the data) or to risk contents (4.0 % of the data). Remote and extreme values of the maxima on individual profiles usually occurred in October to February, and out of this half in 2003. This can signalize worsening of the state of loading by nickel with a possible negative influence on aquatic communities and also health of man.

Mercury

Average value of the contents of mercury is 1.6 $mgkg^{-1}$. 75 percentile still falls into the category of slight pollution, but 90 percentile is already at the level of increased content of category B. Most of the data corresponds to the level of geogennous background (31 %) and to slight loading (51.7 %). The values on profiles point to the existence of loading, which corresponds to increased contents (15.6 % of the data), or even risk contents (1.2 % of the data). Remote values and extreme values of maxima on individual profiles usually occur in November to February. Out of 22 extremely high values above 5 $mgkg^{-1}$, one to five values were found at profiles Kroměříž, Dluhonice, Olomouc, Spytihněv and Uherský Brod. Mostly the limit of at least category B was exceeded on the upper stream of Morava in profile Raškov. Most frequent exceedance of limit of category B was recorded within the framework of the whole catchment in 2001 and 2003. This can signalize worsening of state by mercury loading, but it more likely just illustrates the accidentality in the data set, given by the sampling system.

Cadmium

The average value of the contents of cadmium is 3.6 $mgkg^{-1}$. 90 percentile still falls into the category of slight loading. Maximum value of the data set is already at the level of risk contents of category C. Only 3.4 % of the data is on the level of geogennous background. Most of the data corresponds to slight loading (93.2 %). Values on profiles point to the existence of pollution, which corresponds to increased contents (2.8 % of data) and exceptionally also to risk contents (0.6 % of data). Remote or increased values of maxima on individual profiles usually occur in November to February. Out of 12 high values (category B and C) they are maximum values on profiles Kroměříž, Dluhonice, Spytihněv, Uherský Brod and Lanžhot. Most often the limit of at least category B was exceeded on profile Raškov. The greatest number of exceedancies in the whole catchment was recorded in 2000, 2001 and 2003 on profile Raškov.

Benzo(a)pyrene

The average value of the contents of benzo(a)pyrene is 1900 μgkg^{-1}. Already the median (1578 μgkg^{-1}) falls into the category of increased loading (B) and 75 percentile is at the level of risk contents of category C. Only 1.4 % of the data is at the level of insignificant contents of natural background. 41.7 % of the data corresponds to slight pollution. Most values on the profiles show the existence of considerable loading, which corresponds to increased contents (26.4 % of data) and risk contents (30.6 % of data, Figure 1). Remote or extreme values on individual profiles occur irregularly throughout the year (Figure 2). Out of 22 extreme values (category C), they are values on profiles Kroměříž, Dluhonice, Spytihněv, Olomouc and Lanžhot. Most often the limit of at least category B was exceeded on profile Raškov. Most of the high values were recorded in 2003.

Benzo(b)fluoranthene

The average value of the contents of benzo(b)fluoranthene is 2116.6 μgkg^{-1}. 75 percentile (remote value) still lies at the level of slight loading, but 90 percentile is already at the level of increased contents of category B and the maximum exceedes the limit of risk pollution category C. Most of the data corresponds to slight loading (88.9 % of data). Only a few values on profiles show the existence of loading, which corresponds to increased contents (5.6 % of data) and risk contents (5.6 %, Figure 1). Remote or extreme values in individual profiles occur irregularly throughout the whole year. Out of 8 extreme values (category B and C) they are values on profiles Kroměříž, Dluhonice and Spytihněv. Most often the limit of at least category B was exceeded in profile Raškov. Most of the high contents were measured in 2003 (Figure 2).

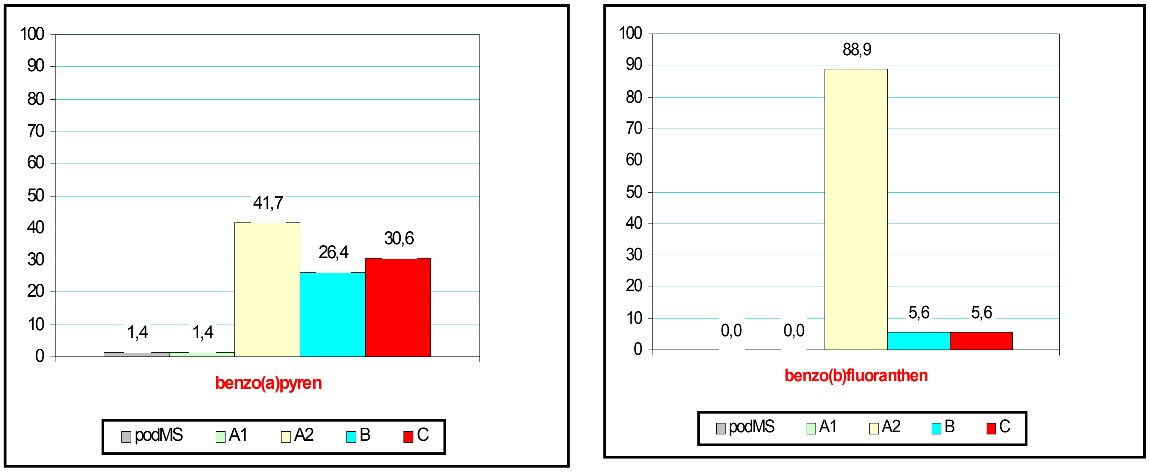

Figure 1. Qualitative classification of substance contents of PAH group in suspended solids of Morava catchment into categories according to the ME

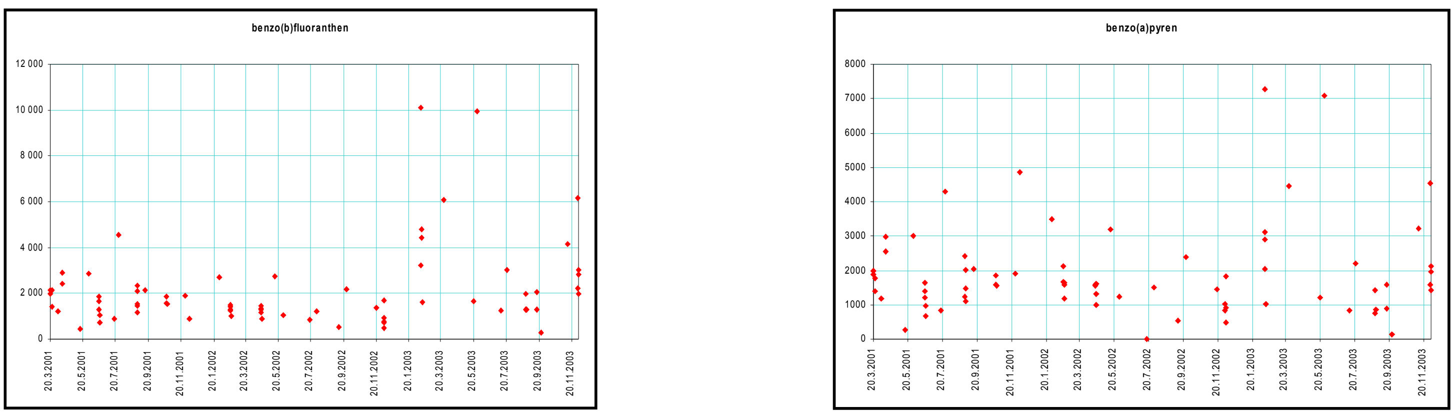

Figure 2. Contents of substances of PAH group in suspended solids of Morava catchment [μgkg^{-1}]

<u>Chlorphenols</u>

2,3,4,5-tetrachlorphenol

Values are mostly low (average is 330.9 μgkg^{-1}). Almost 50 % of the values are under the DL. Out of the rest, 92.9 % is at the level of non-significant to slight loading. Only two values from the profile Spytihněv from the break of years 2001-2002 exceede the limit and fall only to the risk category C.

2,3,4,6-tetrachlorphenol

Values are mostly low (average is 143.4 μgkg^{-1}). Most of the samples contained non-determinable amounts (82 % of the values are under the DL). Out of the remaining, 82 % are at the level of non-significant loading and 14.3 % of data are at the category of slight loading. Only one value in profile Olomouc from April 2002 (2100 μgkg^{-1}) exceedes the limit and falls only to the risk category C.

2,4,5-trichlorphenol

Values are mostly low (average is 126.2 μgkg^{-1}). Alltogether 41 % of the values are under the DL. Out of the remaining, 46.5 % of data are at the level of non-significant loading and 53.5 % of data are in the category of slight loading. No measured value, as opposed to sediments, exceeded limits of category B or C.

2,4-dichlorphenol

Values are mostly low (average is 214.3 μgkg^{-1}). Most of the samples contained non-determinable amounts (52 % of the values are under the DL). Out of the remaining, 63.8 % of data are at the level of non-significant loading and 33.3 % of data are in the category of slight loading. Only two values on profiles Kroměříž and Spytihněv from April 2002 (1622 and 3625 μgkg^{-1}) exceede the limits and fall into the category of increased contents and into the risk category C.

2,5-dichlorphenol

Values are mostly low (average is 228.8 μgkg^{-1}). Most of the samples contained non-determinable amounts (75 % of values are under the DL). Out of the remaining, 75 % of data are at the level of non-significant loading and 17.9 % of data are in the category of slight loading. Only two values in profile Raškov (2100 μgkg^{-1} from 27.5.2003 and 2800 μgkg^{-1} from 1.11.2003) exceede the limits and fall into the category of increased contents and into risk category C.

2-monochlorphenol

Values are mostly low (average is 191.4 μgkg^{-1}). Most of the samples contained non-determinable amounts (53.6 % of values are under the DL). Out of the remaining, 66.7 % of data are at the level of non-significant loading and 29 % of data are in the category of slight loading. Only on profile Raškov, three values exceede limits and fall into the category of increased contents and into the risk category C.

Pentachlorphenol

Values are mostly low (average is 256.7 μgkg^{-1}). Most of the samples contained non-determinable amounts (71 % of the values are under the DL). Out of the remaining measured values, 71 % of the data are at the level of non-significant loading and 26.1 % of the data are in the category of slight loading. Only two values in profiles Olomouc and Kroměříž (4000 and 8000 μgkg^{-1} in 2001) exceede the limits and fall into the risk category C.

In the case of chlorphenols, 2,5-dichlorphenol and 2-monochlorphenol show worsening of pollution in the suspended solids matrix in 2003 in profile Raškov.

3.2. Evaluation of the contamination of sediments

Loading of sediments is in comparison with suspended solids lower, contents of selected substances are in sediments approximately half. In sediments, maximum (signal) values of data sets exceede the limits of the ME categories of increased and risk loading only contents of specific organic substances, namely 2,3,4,5-tetrachlorphenol, 2,3,4,6-tetrachlorphenol and 2,4,5-trichlorphenol. The value of 90 percentile data sets of the contents of dangerous substances exceedes the limit of the increased contents only in the case of benzo(a)pyrene. The overview of qualitative parameters of selected substances in sediments of the Morava catchment is shown in Table 7.

Table 7. The overview of statistical and qualitative parameters of selected substances in sediments

Morava catchment(1999-2003)	statistics and evaluation according to limits of ME							%< MS	% of exceedance of ME limits			
substance	MIN	MED	AVG	P75	P90	MAX	Count		A1	A2	B	C
As	2,5	14,00	16,65	22,1	31,9	43,7	61	0,0	85,2	14,8	0,0	0,0
Be	0,6	1,80	1,86	2,3	2,7	4,9	61	0,0	100,0	0,0	0,0	0,0
Cr total	27,8	73,90	85,78	98	141	319,4	61	0,0	86,9	13,1	0,0	0,0
Cd	0,2	1,20	1,53	2	2,8	5,9	61	0,0	14,8	85,2	0,0	0,0
Cu	20,4	40,50	45,19	57	73	107	61	0,0	88,5	11,5	0,0	0,0
Ni	28,8	60,30	61,10	70,4	81,1	130,6	61	0,0	49,2	50,8	0,0	0,0
Pb	21,1	43,10	47,97	49	71,2	171	61	0,0	95,1	4,9	0,0	0,0
Hg	0,1	0,30	0,42	0,5	0,8	1,9	61	0,0	73,8	26,2	0,0	0,0
Zn	94	211,00	235,23	296	334	459	61	0,0	8,2	91,8	0,0	0,0
benzo(a)antracen	68	547	680,89	971,5	1445	1639	36	0,0	2,8	97,2	0,0	0,0
benzo(a)pyren	61	721	889,13	1087	1633	4863	61	0,0	1,6	85,2	8,2	4,9
benzo(b)fluoranthen	0	824,00	954,07	1300,5	1635,2	2571	43	2,3	2,3	97,7	0,0	0,0
benzo(g,h,i)perylen	0	286,00	385,72	540	686	3396	61	21,3	23,0	77,0	0,0	0,0
benzo(k)fluoranthen	12,5	304,00	371,61	500	753	1068	61	1,6	1,6	98,4	0,0	0,0
dibenzo(a,h)antracen	0,25	88,5	106,79	109,5	212,8	499	18	27,8	61,1	38,9	0,0	0,0
fluoranthen	0	1456	1866,34	2353	3468	11170	61	3,3	4,9	95,1	0,0	0,0
fluoren	0	0,00	68,75	100,5	206,1	393	44	52,3	84,1	15,9	0,0	0,0
chrysen	0	808,00	936,37	1320,25	1607,6	5022	62	1,6	1,6	98,4	0,0	0,0
indeno(1,2,3-c,d)pyren	0	336,00	469,57	535	1026	2700	61	3,3	6,6	93,4	0,0	0,0
pyren	0	1227,50	1553,23	1918,5	2704	9195	62	1,6	1,6	98,4	0,0	0,0
aldrin	0,25	5,00	5,47	10	14,8	20	43	48,8	100,0	0,0	0,0	0,0
2,3,4,5-tetrachlorfenol	2,5	2,50	217,50	100	360	2600	19	68,4	68,4	26,3	0,0	5,3
2,3,4,6-tetrachlorfenol	0	0,00	157,89	0	200	2500	19	78,9	78,9	15,8	0,0	5,3
2,4,5-trichlorfenol	2,5	2,50	135,16	21	100	2800	45	71,1	77,8	17,8	0,0	4,4
2,4,6-trichlorfenol	2,5	2,50	39,22	64	134,4	200	43	67,4	74,4	25,6	0,0	0,0
2,4-dichlorfenol	2,5	2,5	13,33	2,5	18,4	140	43	83,7	90,7	9,3	0,0	0,0
2,5-dichlorfenol	2,5	2,5	49,47	2,5	100	700	19	84,2	84,2	15,8	0,0	0,0
2-monochlorfenol	2,5	2,50	98,28	93,5	280	1300	43	60,5	72,1	27,9	0,0	0,0
pentachlorfenol	2,5	2,5	73,23	8,25	180	912	43	74,4	81,4	18,6	0,0	0,0

Heavy metals and metalloids

The matrix of sediments is not increasingly loaded by the contents of heavy metals and metalloids. Their contents are overwhelmingly corresponding to geogennous background or to slight pollution. The exceedance of limits of category B or C in sampling did not occur.

Benzo(a)pyrene

Average value of the contents of benzo(a)pyrene is 889.1 μgkg^{-1}. Only the 90 percentile falls into the category of increased loading (category B) and the maximum is at the level of risk contents of category C. Only 1.6 % of the data are at the level of non-significant background contents and most of the data (86.7 %) correspond to slight loading. Approximately one eighth of the values on profiles show the existence of pollution, which corresponds to increased contents (8.2 % of data) and risk contents (4.9 % of data, Fig. 3). Remote or extreme values in individual profiles occur irregularly throughout the whole year (Fig. 4). Extreme values (categories B and C) were measured in profiles Dluhonice, Spytihněv and Raškov. Most often the limit of at least the category B was exceeded in profile Olomouc. The loading of the sediments is significantly lower compared to suspended solids.

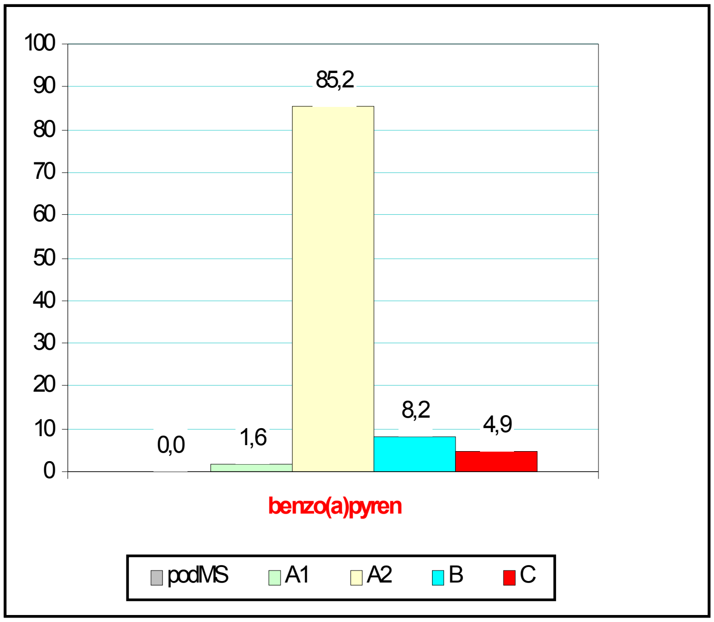

Figure 3. Qualitative classification of the contents of benzo(a)pyrene in sediments of the Moravacatchment into categories according to the ME

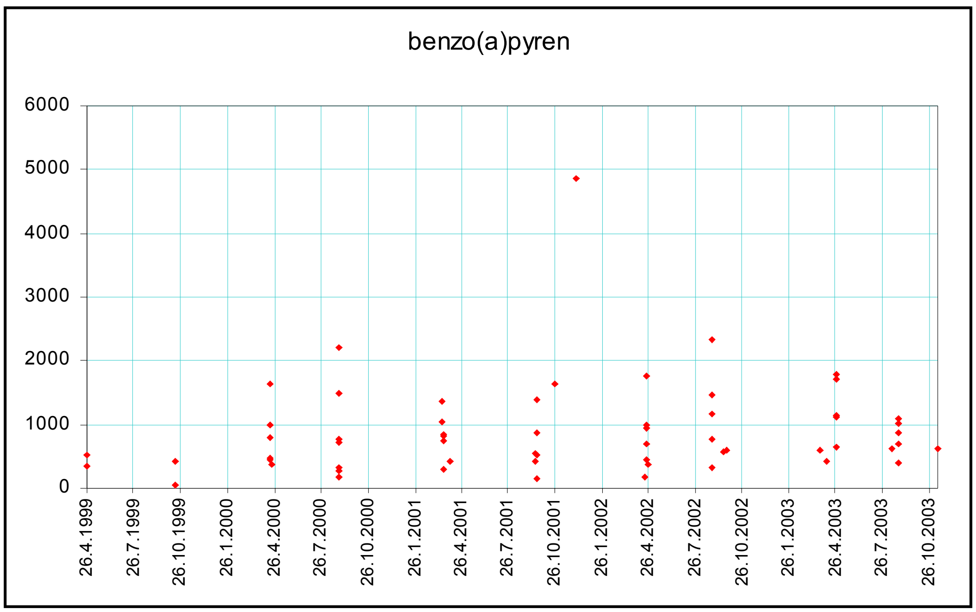

Figure 4. Contents of benzo(a)pyrene in sediments of the Morava catchment [μgkg^{-1}]

Benzo(b)fluoranthene

Average value of the contents of benzo(b)fluoranthene is 954.1 μgkg^{-1}. The remote value of the maximum lies at the level of slight loading. Most of the data corresponds to slight loading (97.7 % of data). Other data are at the level of very slight loading and exceptionally even under the DL. Not one value, as opposed to suspended solids, exceedes the limit of category B or C.

Chlorphenols

Limits of at least increased loading (category B) insignificantly exceede from the group of phenols and chlorphenols the contents of 2,3,4,5-tetrachlorphenol, 2,3,4,6-tetrachlorphenol and 2,4,5-trichlorphenol. The contents of other substances identified in suspended solids even at the level of increased loading with the possible negative influence on aquatic communities (category B), or at the level of risk contents (category C) in sediments are low and even the maxima of the measured data sets of substances such as 2,4-dichlorphenol, 2,5-dichlorphenol, 2-monochlorphenol and pentachlorphenol are at the highest at the level of the category of slight loading.

2,3,4,5-tetrachlorphenol

Values are mostly low (average is 219.2 μgkg^{-1}). Almost 70 % of the values are under the DL. Out of the remaining, 68.4 % of data are at the level of non-significant loading and 26.3 % of data are at the level of slight loading. Only one value in profile Spytihněv from December 2001 falls only to the risk category C and shows that even such contents may exist (2600 μgkg^{-1}).

2,3,4,6-tetrachlorphenol

Values are mostly low (average is 161.8 μgkg^{-1}). Almost 80 % of the values are non-determinable amounts (78.9 % of the values are under the DL). Out of the remaining values, 78.9 % are at the level of non-significant loading and 15.8 % of data are in the category of slight loading. Only one value in profile Olomouc from 2002 (2500 μgkg^{-1}) exceedes the limit and falls only to the risk category C.

2,4,5-trichlorphenol

Values are mostly low (average is 136.9 μgkg^{-1}). Altogether 71.1 % of values are under the DL. Out of the others, 77.8 % of data are at the level of non-significant loading and 17.8 % of data are in the category of slight loading. Two measured values exceeded the limit of category C, namely in 2001 in profile Spytihněv (2100 μgkg^{-1}) and in profile Lanžhot (2800 μgkg^{-1}).

3.2. Development of loading

The evaluation of the long-term trend of loading of suspended solids and sediments is only orientation-wise, with respect to the comparatively short time series of monitoring (4 years). In the suspended solids matrix, which informs about the existing pollution, a more significant long-term trend for selected dangerous substances was not recorded. Only the average yearly contents of cadmium and arsenic show in the time series all-area-wise a certain hint of decrease. On the other hand in the contents of the PAH group – benzo(a)pyrene and benzo(b)fluoranthene a more significant increase has been recorded in the last year of monitoring on the upper and middle part of the Morava River, and especially on the Bečva River. The yearly average values of benzo(a)pyrene here indicate up to risk pollution.

In the sediment matrix, where the contents of dangerous substances are recorded for a longer time period, can be seen a lowering trend for all of the selected heavy metals. Especially in the contents of mercury, the average yearly values on all monitored profiles diminished in 2003 under the level of slight pollution. Similarly as in suspended solids, in sediments was recorded a slight increase in contents of substances of the PAH group, especially for benzo(b) fluoranthene. Their contents however still satisfy the limits for slight pollution. Generally for organic substances in sediments, stagnation may be seen.

Local differences in the contents of the evaluated dangerous substances, which we may despite a certain fluctuation of the values observe in the longitudinal profile of the Morava River, point to the increase of the contents of As, Hg and Cd in suspended solids especially in the section under the joining of Bečva, and on the middle stream of Morava in the Spytihněv section. At the same time the largest average yearly contents of cadmium in the catchment are surprisingly measured in both matrices on the upper section of Morava in Raškov. The contents of the substances from the PAH group in suspended solids gradually diminish from Raškov towards the lower section of the stream with a significant peak at where the Bečva joins, and a slight elevation in the section of Kroměříž – Spytihněv. Rather a different picture (mirror image) is shown by the contents of substances of the PAH group in sediments in the section of Raškov – Spytihněv. Here it is necessary to emphasise, that in the case of metals we evaluate the contents and loading only in part of the sediment (fraction 20 μm), and for organic substances the whole sample is concerned. In the case of profiles Raškov, Dluhonice and Kroměříž the collected sediment usually contains a higher ratio of rough fractions like sand, which are from the point of view of pollutant bond uninteresting and ballast. On the other hand on profiles of Olomouc and Spytihněv, the sediment is collected just above the weir in a section with an increased sedimentation as a consequence of slowed-down water flow, where a great part of fine material originally transported in suspension settles. The ratio of fine clay-dust fraction here is close to its ratio in suspended solids, and the contents of substances of the PAH group here are comparable with its contents in suspended solids.

4. Transport of dangerous substances in suspended solids

The calculation of transport of the amount of pollutants bonded to suspended solids represents an orientation view at the amount of dangerous substances carried by the river. It is based on the data of the daily monitoring of suspended solids concentrations. A series of factors exist, which can influence the difference and the disproportion in the amounts of transported suspended solids and dangerous substances that are bonded onto them. This fact is clearly shown on a number of profiles in the long section of the Morava River. We cannot satisfactorily explain the discrepancies in the yearly totals of transported dangerous substances bonded to suspended solids in individual profiles, and so far there is a lack of measured data to be able to use a solution of the problem by model. This also follows from the temporal accidentality and unsatisfactory frequency of sampling for chemical analyses (technical, financial and organisational limitations do not allow to sample with greater frequency at least during "suspended solids" waves).

As a demonstration, we show the graphs of the transport of selected dangerous substances in the long section of the Morava from profile Raškov on the upper stream to the border profile of Lanžhot (Figure 5, 6).

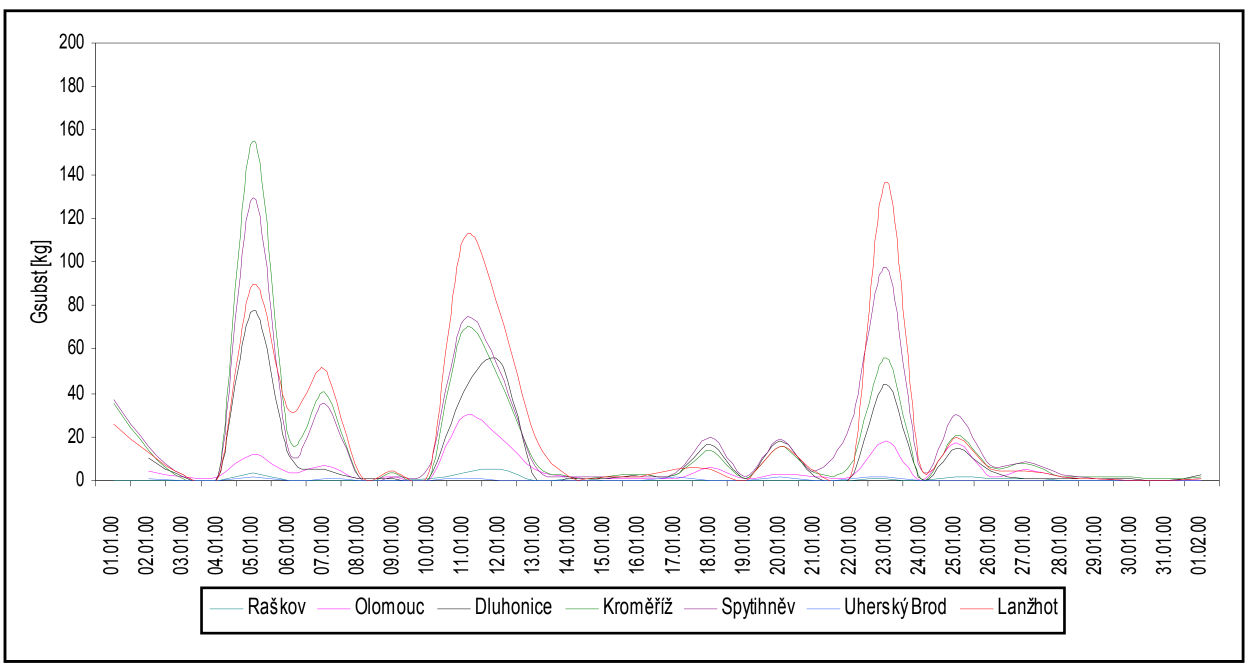

Figure 5. Transport of benzo(a)pyrene (Gsubst) in suspended solids

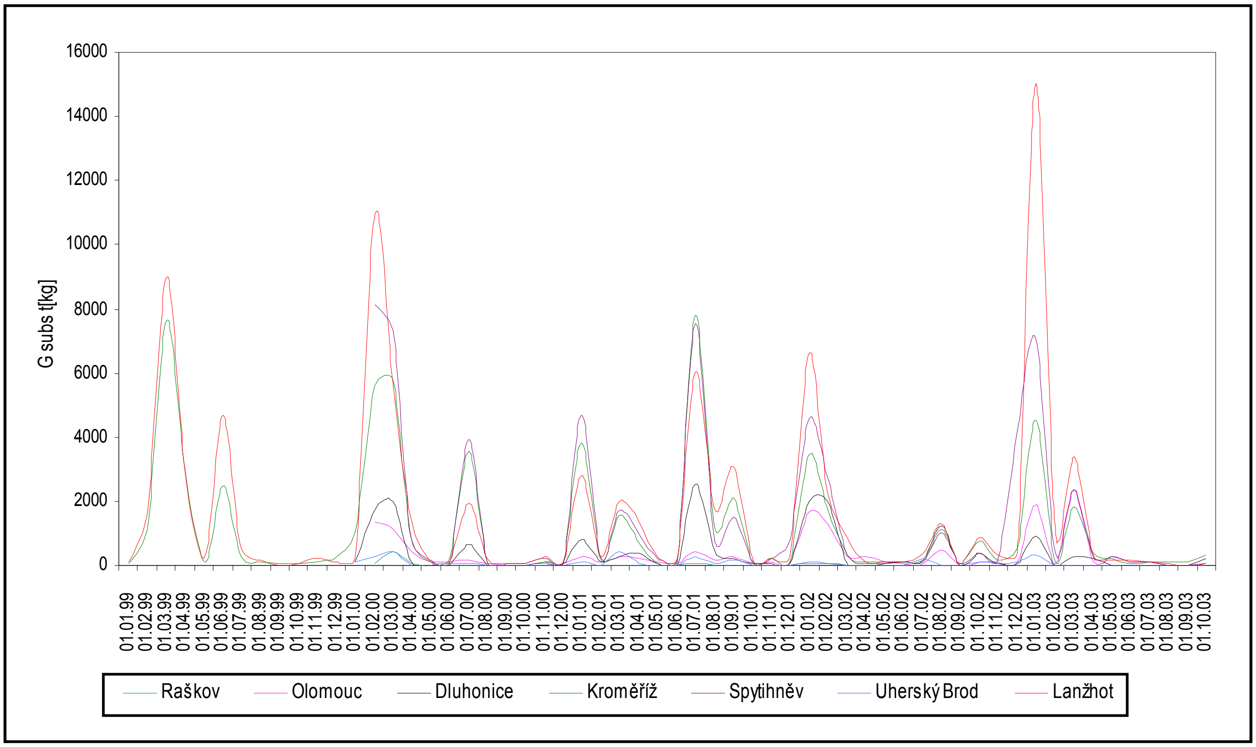

Figure 6. Transport of nickel (Gsubst) in suspended solids

5. Identification of possible sources of pollution

The highest values of dangerous substances were mostly identified in profiles Dluhonice (Bečva River), Raškov, Kroměříž and Spytihněv. They can be due to the influence of larger municipalities (Kroměříž, Olomouc) and industrial installations. The profile Dluhonice shows contamination caused by the operation of firms such as PSP Special Machine Works Přerov, chemical factory Deza, Meopta Přerov, TCT Rožnov or Metalplat in Lipník nad Bečvou. In the middle reaches of the Morava River in the profile Spytihněv, the influence of the industrial agglomeration of Zlín – Otrokovice is felt (e.g. Aliachem Fatra Napajedla). In the case of mercury, the sources cannot easily be identified, they can be both of point origin (from chemical and electrotechnical industry) and of areal origin (waste waters from agriculture – mercurious pesticides, treatment work muds). The pollution in the profile Raškov is probably connected with emissions and aerial pollution. A similar connection with emissions can be derived for the "omnipresent" benzo(a)pyrene and other substances of the PAH group.

6. Conclusion

The occurrence of dangerous substances in solid matrices of the Morava catchment is from a state-wide view on a comparatively low level. Of the most serious occurrences, one may mention significant loading by substances from the PAH group especially on the Bečva River, but also in relatively industry-free reaches (upper reaches of the Morava River). In the case of heavy metals we can see an overall slight pollution, but despite that, signal values of e.g. As, Hg and Ni are being recorded. Sediments show a decreasing trend. As opposed to other Czech catchments, we can detect here also pollution by substances of the chlorphenol group. Information on the amount of selected dangerous substances transported in suspended solids from the territory of the CR is shown in the paper titled "Complex Monitoring of Water Quality in the Border Part of the Morava River on the Territory of the Czech Republic".

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