

**Modelling the fate of priority organic pollutants in the River Váh,
Slovakia**
Annex to the Danube Case Study
WP 5
Final Report



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Abstract

The QWASI model of chemical fate and transport in the Váh river basin that simulates average annual conditions, was used to examine the behaviour of polycyclic aromatic hydrocarbons (PAHs), bis(2-ethylhexyl)phthalate (DEHP) and nonylphenol (NP) in the case study river basin of the Váh river, a major tributary to the river Danube in Slovakia. The model was used to predict the status of organic without knowing the actual loadings/emissions. Instead, the model was used to "back-calculate" total loadings to individual large water reservoirs/dams in the river basin. Chemical behaviour depended on the characteristics of the individual water reservoirs and physical-chemical properties of chemicals. Short water residence times of less than a week to several months result in chemicals being advected, unless subject to other, more rapid processes. In water reservoirs, rapid rates of sediment deposition and resuspension retard losses by advection of persistent chemicals such as PAHs and DEHP. Overall, behaviour in reservoirs is dominated by sediment-water exchange.

The effect of various factors on chemical status in the Váh river basin is analysed and remedial actions are recommended.

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1 Introduction

Quantifying discharges/emissions is often difficult because of inadequate emission data and the inability to verify the accounting of all emissions/loadings. It is also important to identify critical factors that may affect the response of the system to changes in chemical loading. In this situation, mass balance models are useful tools for quantifying and verifying major sources of chemicals, and identifying sources to control so that the desired effect may be achieved.²

The QWASI model quantitatively link chemical loadings to in-river concentrations, amounts, rates of movement and response times.⁵ Since there were incomplete loading and input data for most chemicals, the models were used to "back-calculate" approximate **loadings** from known, water or sediment concentrations measured in water reservoirs in the Váh river catchment.

In the presented case study, the fate of selected organic priority pollutants (PAHs, DEHP and NP) was modelled for large artificial dams constructed along the river. The modelled water reservoirs were Liptovská Mara, Bešeňová, Krpeľany, Žilina, Hričov, Nosice, Sĺňava and Kráľová that are distributed along the main stream on river kilometers 336, 333, 294, 257, 247, 209, 115 and 64, respectively. They form the so called Váh cascades. For these reservoirs (excepting Žilina), sediment quality data and hydrological parameters were available that enabled, with some parameter estimates, the application of the QWASI model. The modelling did not include smaller reservoir located in the main stream (Čierny Váh, Madunice, Selice) and water reservoirs located in Váh tributaries. Reservoirs accumulate/store large proportions of the sediments that are transported down the river. Most of the modelled compounds are hydrophobic with a high affinity to sediments and suspended matter. Therefore, it is reasonable to concentrate the modelling to the river stretches that accumulate most sediment. The distances between individual reservoirs under investigation are not very long, thus, with some simplification, the fate of priority pollutants in stretches between the individual „levels“ in the Váh cascade should be possible.

The modelling does not include metallic priority pollutants (e.g. mercury or cadmium) because of lack of required metal speciation data and information on partitioning of these species between environmental compartments (water, suspended solids and sediment) in the Váh river basin.

As a necessary simplification imposed by data constraints, the model considers average annual conditions and neglects seasonal variations. Also, the model does not take into account various ongoing water management activities, including dredging, downstream sediment „flushing“ etc. that have been performed in recent years in several water reservoirs on the Váh river. Most of these activities have been conducted in order to improve the hydroenergetic potential of the dams. Investigations of the impact of these activities on priority pollutant removal or mobilisation has started only recently.¹ The model provides an approximate, but not definitive, picture of chemical behaviour in the Váh river basin. However, it is often through the exercise of compiling quantitative data and parameterising the model that effective **remediation strategies become apparent**, or that major areas on which to focus attention are indicated. Furthermore, the process of developing the model becomes the means through which we improve our understanding of the system and chemicals within it. Additionally, the models are surprisingly robust (perhaps because of their simplicity), and major chemical sources and factors affecting chemical behaviour become evident.²

We describe a mass balance study of the fate of polycyclic aromatic hydrocarbons, DEHP and nonylphenols in the water and sediments of large artificial dams constructed along the river Váh. The major aims were to assess the relative significance of industrial and background sources, estimate prevailing concentrations, and apportion them to various sources. Chemical sources are analyzed^{9, 18, 19, 20} in order to suggest effective remedial measures, and the sensitivity of model results to changes in parameters and major factors affecting the individual water reservoirs are discussed. Further, the mass balance QWASI model can provide a clear picture of the key environmental processes, show which environmental and chemical properties are the most important determinants of fate, and can be used to assess the extent and rate at which reductions in emissions will translate into reduced concentrations.

2 Materials and methods

2.1 Model

The QWASI fugacity model was developed by Mackay and co-workers (e.g.³). The basic concepts of the fugacity approach are fully described elsewhere⁴. The QWASI software was downloaded from Trent University website.⁵

2.2 Physicochemical properties

Physical–chemical properties of selected contaminants (polycyclic aromatic hydrocarbons, DEHP and nonylphenol) are listed in Table 2 and 3 and half lives of chemicals in water and sediment are taken from Mackay et al.⁶.

2.3 Model parameters

In the models, the Váh catchment was simulated in 8 segments, selected according to the locations of major water reservoirs/dams on the river Váh⁷ as shown in Figure 1.

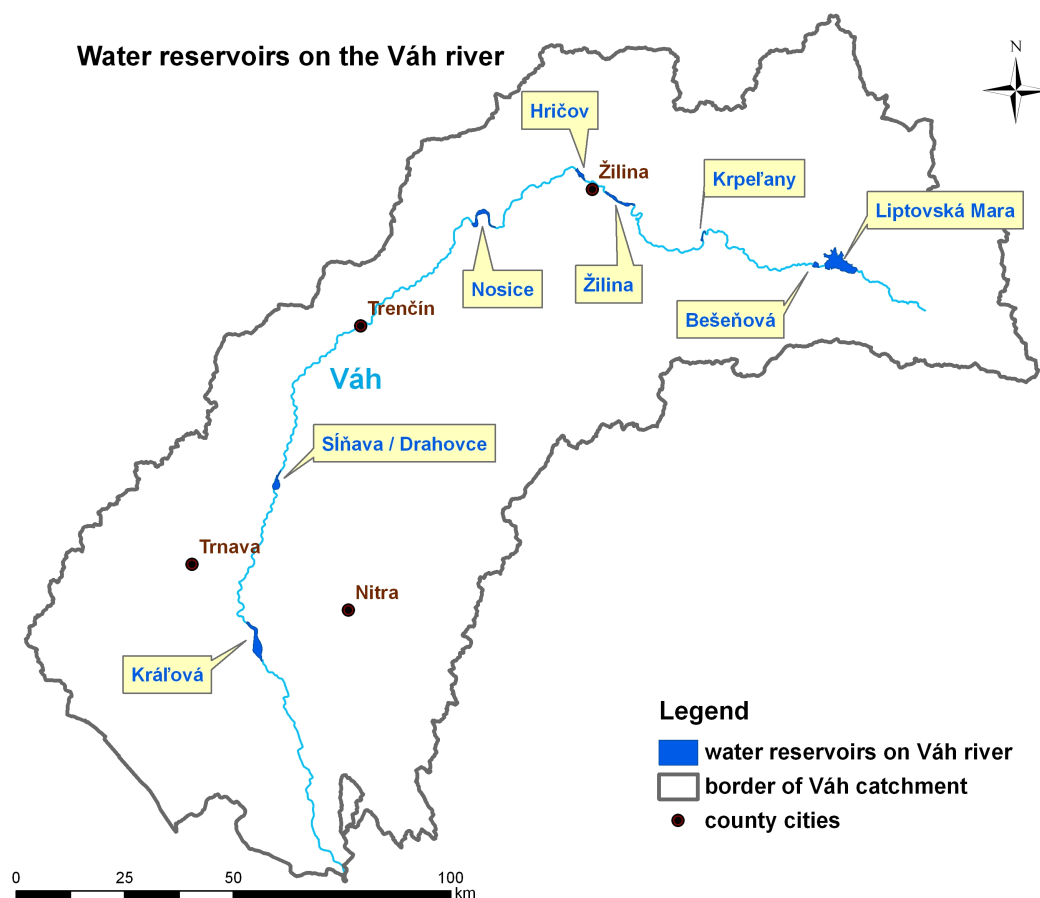


Figure 1. Location of large water reservoirs on the Váh river that were used in modelling of the fate of priority organic pollutants using QWASI model

2.4 Monitoring data

Hydrological and limnological parameters, such as dimensions, particle concentrations, inflows, and sediment deposition rate for the various water reservoirs located on the river Váh, have been obtained from the internal Large Water Reservoirs Database of the Water Research Institute^{8,9}. Unfortunately, few data were available on suspended particles, sediment solids and sediment-water interaction processes in the Váh catchment.

Sediment monitoring data was obtained from the Water Research Institute report „Evaluation of environmental impacts of water reservoir sediments and their management options“ (Hucko et al., 2007).¹

Water monitoring data was obtained from the joint report by the Slovak Hydrometeorological Institute and the Water Research Institute „Indicative evaluation of the chemical status of surface water bodies“¹⁰ and from the internal database of the Slovak National Water Reference Laboratory. Average background concentration of airborne priority pollutants were obtained from the Meteorological Synthesizing Centre-East.¹¹

2.5 Environmental Quality standards

The environmental quality standards of priority pollutants were used as a criterion of good chemical status of water bodies in the decision making process in the SOCOPSE case study. These were published recently in the Directive 2008/105/EC on environmental quality standards in the field of water policy.¹²

Table 1. Environmental quality standards (annual average values) of selected priority pollutants in inland surface waters

Compound	Abbreviations	EQS (ng/L)
Naphthalene	NAP	2400
Anthracene	ANT	100
Fluoranthene	FLT	100
Benzo[a]pyrene	BaP	50
Benzo(b)fluoranthene + Benzo(k)fluoranthene	BbF+BkF	30
Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene	BP+IP	2
Bis(2-ethylhexyl)phthalate	DEHP	1300
Nonylphenol	NP	300

Table 2. Physical properties of modelled chemicals at 25°C

Physical Properties		Naphtha-lene	Anthra-cene	Fluoran-thene	Benzo[a]-pyrene	Benzo(b+k)-fluoranthene	Benzo[g,h,i]- perylene + Indeno(2,3-cd)-pyrene	DEHP	Nonyl-phenol
Molar Mass	[g/mol]	128.19	178.2	202.26	252.3	252.3	276.3	390.57	220.36
Log Kow		3.37	4.57	5.16	6.04	6.04	6.5	7.5	5.76
Solubility	[g/m ³]	31	1.1	0.26	0.0038	0.0012	0.00026	0.003	6.35
Vapour Pressure	[Pa]	10.4	0.2	1.23E-03	7E-07	5E-07	1.25E-08	1.42E-07	9.42E-05
Melting Point	[°C]	80.5	101	107.8	175	168.3	273	-55	42
Fugacity Ratio		0.28	0.18	0.15	3.28E-02	3.83E-02	3.52E-03	1	0.678986
Sub-cooled Liquid V.P.	[Pa]	36.81	1.13	0.01	2.13E-05	1.31E-05	3.55E-06	1.42E-07	1.39E-04
Henry's Law Constant	[Pa m ³ /mol]	43.01	32.40	0.95	4.65E-02	0.105125	1.33E-02	1.85E-02	3.27E-03

Table 3. Partition coefficients of modelled chemicals

Partition Coefficients	Naphtha-lene		Anthra-cene		Fluoran-thene		Benzo[a]-pyrene		Benzo(b+k)-fluoranthene		Benzo[g,h,i]-perylene + Indeno(2,3-cd)- pyrene		DEHP		Nonyl-phenol	
	L/kg	L/kg	L/kg	L/kg	L/kg	L/kg	L/kg	L/kg	L/kg	L/kg	L/kg	L/kg	L/kg	L/kg	L/kg	
Air-Water (log Kaw)	-1.76	-1.88	-3.41	-4.73	-4.37	-5.27	-5.13	-5.88								
Susp. Particles-Water (log)	2.84	2.46	4.04	3.66	4.63	4.25	5.51	5.13	5.51	5.13	5.97	5.59	6.97	6.59	5.23	4.85
Sediment-Water (log)	1.84	1.46	3.04	2.66	3.63	3.25	4.51	4.13	4.51	4.13	4.97	4.59	5.97	5.59	4.23	3.85
Resusp. Particles-Water (log)	1.84	1.46	3.04	2.66	3.63	3.25	4.51	4.13	4.51	4.13	4.97	4.59	5.97	5.59	4.23	3.85
Aerosol-Air (log)	5.21	6.73	8.87	11.45	11.66	12.23	13.63	10.64								
Org. Carbon-Water (log Koc)	2.98	4.18	4.77	5.65	5.65	6.11	7.11	5.37								

Table 4. Half lives of modelled chemicals

Half-lives	Naphtha-lene	Anthra-cene	Fluoran-thene	Benzo[a]-pyrene	Benzo(b+k)-fluoranthene	Benzo[g,h,i]-perylene + Indeno(2,3-cd)-pyrene	DEHP	Nonylphenol
Water [h]	170	550	1000	1700	1000	1700	360	360
Sediment [h]	5500	17000	30000	55000	30000	55000	3240	3240

Table 5. Hydrological and limnological parameters of modelled water reservoirs

Reservoir Data	Liptovská Mara			Bešeňová			Krpelany			Žilina		
River kilometre	336			333			294			257		
	Area	Depth	Volume	Area	Depth	Volume	Area	Depth	Volume	Area	Depth	Volume
	m ²	m	m ³	m ²	m	m ³	m ²	m	m ³	m ²	m	m ³
Water	2.17E+07	16.70	3.62E+08	1930000	5.56	1.07E+07	1260000	6.61	8329999	2550000	7.05	1.80E+07
Sediment	2.17E+07	0.05	1084000	1930000	0.05	96500	1260000	0.05	63000	2550000	0.05	127500
	Inflow	Outflow		Inflow	Outflow		Inflow	Outflow		Inflow	Outflow	
	m ³ /h	m ³ /h"		m ³ /h	m ³ /h"		m ³ /h	m ³ /h"		m ³ /h	m ³ /h"	
Water	100080	100080		100476	100476		280152	280152		344160	344160	
Suspended Particles	0.6255	0.2085		0.627975	0.209325		2.3346	0.58365		2.868	0.717	
Sediment	m ³			m ³			m ³			m ³		
Subcompartment												
Volumes												
Solids	162600			14475			9450			19125		
Pore-Water	921400			82025			53550			108375		
	m ³ /h			m ³ /h			m ³ /h			m ³ /h		
Rain Rate	3098	1.252	m / year	274	1.245	m / year	162	1.127	m / year	323	1.11	m / year
Sediment Deposition Rate	0.90	2.4	g/m ² .day	0.90	27	g/m ² .day	2.69	123	g/m ² .day	2.70	61	g/m ² .day
Sediment Resuspension Rate	0.45	1.2	g/m ² .day	0.43	13	g/m ² .day	1.31	60	g/m ² .day	1.33	30	g/m ² .day
Sediment Burial Rate	0.45	1.2	g/m ² .day	0.43	13	g/m ² .day	1.31	60	g/m ² .day	1.33	30	g/m ² .day

Table 5. continued. Hydrological and limnological parameters of modelled water reservoirs

Reservoir Data	Hričov			Nosice			Sĺňava			Kráľová		
River kilometer	247			209			115			64		
	Area	Depth	Volume	Area	Depth	Volume	Area	Depth	Volume	Area	Depth	Volume
	m ²	m	m ³	m ²	m	m ³	m ²	m	m ³	m ²	m	m ³
Water	2500000	3.38	8460000	5700000	6.32	3.60E+07	4300000	2.84	1.22E+07	1.09E+07	6.01	6.55E+07
Sediment	2500000	0.05	125000	5700000	0.05	285000	4300000	0.05	215000	1.09E+07	0.05	544500
	Inflow	Outflow		Inflow	Outflow		Inflow	Outflow		Inflow	Outflow	
	m ³ /h	m ³ /h"		m ³ /h	m ³ /h"		m ³ /h	m ³ /h"		m ³ /h	m ³ /h"	
Water	436320	436320		474480	474480		537480	537480		547200	547200	
Suspended Particles	6.363	0.909		3.954	0.9885		4.479	1.11975		4.56	1.14	
Sediment	m ³			m ³			m ³			m ³		
Subcompartment												
Volumes												
Solids	18750			42750			32250			81675		
Pore-Water	106250			242250			182750			462825		
	m ³ /h											
Rain Rate	316	1.108	m / year	707.9453	1.088	m / year	519.3379	1.058	m / year	1290.39	1.038	m / year
Sediment Deposition Rate	7.2	166	g/m ² .day	3.958333	40	g/m ² .day	4.479167	60	g/m ² .day	4.5375	24	g/m ² .day
Sediment Resuspension Rate	3.47	80	g/m ² .day	1.979167	20	g/m ² .day	2.239583	30	g/m ² .day	2.26875	12	g/m ² .day
Sediment Burial Rate	3.47	80	g/m ² .day	1.979167	20	g/m ² .day	2.239583	30	g/m ² .day	2.26875	12	g/m ² .day

3 Results and discussion

When comparing the results of the models with monitoring data it is important to appreciate that both quantities are subject to variability and error. The models are necessarily simplifications of a complex system and there may be errors and variability in quantities such as degradation half-lives and deposition rates. The monitoring data are subject to analytical error and can vary spatially and temporally over a fairly wide range. Given these considerations, differences between model and monitoring results less than a factor of 2 or 3¹³ are regarded as good agreement. It is important to note that the selected system parameter values are arbitrary and have been selected for illustrative purposes.

Despite the gaps in required datasets, modelling of the fate of priority pollutants these large water reservoirs of the main stream enable to identify the main processes affecting their distribution and mobility in the river and also to estimate the magnitude of priority pollutant emissions in a particular river stretch.

3.1 Factors affecting chemical behaviour

Sediment deposition and resuspension have a significant effect on chemical dynamics, especially those chemicals that sorb strongly to particles such as PAHs and DEHP. It is important to note this sensitivity because empirical estimates of these rates are uncertain, and indeed, the processes are difficult to quantify¹⁴. The suspended particulate matter (SPM) loads were reported on several profiles in the river Váh and its tributaries by the Slovak Hydrometeorological Institute.¹⁵ Unfortunately, the number of monitoring sites in the river basin is very limited (just several sites). No known data is available on real sediment resuspension and burial rates.

For the purpose of the model, the total sediment deposition rate in each water reservoir was estimated from the total load of suspended particulate matter (SPM) to the reservoir, divided by the water reservoir area. The SPM load was calculated from measured load of SPM from the inflow (or several inflows, when a tributary to the main river was located close upstream to the reservoir).¹⁵ Several scenarios were modelled for hydrophobic compounds with a high affinity to sediments (benzo[a]pyrene), keeping the sediment deposition rate constant at and varying the sediment resuspension or burial rate (data not shown). As a compromise, modelling was performed with burial and resuspension rates both equal 50 % of the sediment deposition rate. This parameter setting was chosen considering the dynamic character of most dams on the Váh river, with often sediment resuspension events caused by often rapid changes in flows due to dam operation. The deposition, resuspension and burial rates are shown in Table 5.

3.2 Estimate of maximum acceptable emissions

In the first step of the modelling process, maximum acceptable loadings/emissions [kg/year] to individual water reservoirs were estimated using QWASI model. For this purpose, total concentrations of individual priority pollutants in the water column were set equal to the respective EQS values. The resulting estimated maximum acceptable emissions are shown in Table 6. These maximum acceptable emission estimates represent total emissions and cumulate all possible sources and input pathways, i.e. both point sources and diffuse sources from both water and atmosphere. Exceedance of these emissions would likely cause a situation with the concentrations of priority pollutants in the water column higher than the EQS limits. This would result in the ultimate consequence that the water body will not achieve a „good chemical status“ and indicate a need for emission reduction measures.

Table 6. Identification of maximum acceptable emissions [kg/year] to reservoirs

Reservoir name	River km	NAP	ANT	FLT	BaP	BbF+ BkF	BP +IP	DEHP	NP
Liptovská Mara	336	36000	600	340	170	130	8.5	13500	2400
Bešeňová	333	3300	115	115	90	56	4.7	5550	570
Krpeľany	294	6800	280	300	245	150	12.5	13500	1400
Žilina	257	9200	350	360	280	170	14	15500	1700
Hričov	247	10400	450	515	500	310	28	31000	2850
Nosice	209	14000	500	510	400	250	20	24000	2500
Sĺňava	115	9200	530	560	440	270	23	25000	2650
Kráľová	64	18600	630	610	480	300	25	29000	3100

These maximum acceptable emission values vary widely from a few kg/year (BP+IP) to several tonnes/year (NAP or DEHP), depending on the physicochemical properties of modelled compounds, characteristics of the modelled system as well as on the EQS values set for each compound (Table 1).

The above described modelling scenario not only estimates the maximum acceptable emissions to the modelled system, but also calculates the approximate distribution and process rates (transport and degradation) of modelled compounds in the system. One of the outputs of the model scenario are maximum permissible concentrations of modelled compounds in sediment that correspond with the concentration equal to EQS in the water column (Table 7).

Table 7. Maximum acceptable concentrations in sediments [ng/g d.w.]

Reservoir name	River km	NAP	ANT	FLT	BaP	BbF+ BkF	BP +IP	DEHP	NP
Liptovská Mara	336	62	49	272	1165	447	79	6166	413
Bešeňová	333	100	203	1108	3391	1744	222	56223	3478
Krpeľany	294	212	361	1496	3970	2300	253	144161	8959
Žilina	257	145	289	1323	3763	2070	241	98408	6213
Hričov	247	253	389	1549	3974	2357	261	164012	10432
Nosice	209	238	238	1186	3502	1907	222	75769	4650
Sĺňava	115	145	283	1307	3648	2036	242	96999	6127
Kráľová	64	95	187	1015	3253	1664	215	51295	3210

These „threshold“ values can be compared with real monitoring data. Concentrations of modelled compounds in sediment higher than values in Table 1 identify water bodies at risk of not reaching a „good chemical status“.

3.3 Residence times

The general behaviour of chemicals in the Váh river basin is controlled by advective flows, sediment-water exchange, sediment characteristics and chemical transformation rates. The relative importance of each factor varies with the water reservoir/dam and chemical considered. Because of relatively large river flows, water residence times are fairly short, ranging from an estimated 1 day in Krpeľany reservoir to 5 days in Kráľová reservoir. Liptovská Mara reservoir is an exception, because it is a very large water reservoir located in the upper stretch of the river with a smaller inflow and outflow in comparison to other reservoirs downstream. Water residence times in Liptovská Mara reservoir are up to 96 days. The water column is replaced fairly rapidly, thus contaminant in the water will be substantially removed within less than a month (with the exception of Liptovská Mara reservoir).

Table 8. Residence times of priority pollutants in the reservoir [days]

Reservoir name	River km	Compartment	NAP	ANT	FLT	BaP	BbF+ BkF	BP +IP	DEHP	NP
Liptovská Mara	336	Water	10	32	58	96	58	96	21	21
		Sediment	324	957	1610	2710	1610	2710	192	192
		Overall	10	33	74	308	144	438	31	24
Bešeňová	333	Water	3	4	4	4	4	4	4	4
		Sediment	271	589	784	976	783	976	171	171
		Overall	3	26	126	480	397	601	129	79
Krpeľany	294	Water	1	1	1	1	1	1	1	1
		Sediment	164	233	258	275	257	275	118	118
		Overall	1	12	42	135	128	168	89	54
Žilina	257	Water	2	2	2	2	2	2	2	2
		Sediment	219	379	451	508	450	508	147	147
		Overall	2	16	63	226	205	289	107	62
Hričov	247	Water	1	1	1	1	1	1	1	1
		Sediment	140	185	200	211	200	211	104	104
		Overall	1	15	50	131	125	154	87	60
Nosice	209	Water	2	3	3	3	3	3	3	3
		Sediment	247	480	601	708	600	707	160	160
		Overall	3	21	90	330	287	418	119	71
Sĺňava	115	Water	2	1	1	1	1	1	1	1
		Sediment	219	379	451	508	450	508	147	147
		Overall	2	16	67	235	214	298	110	66
Kráľová	64	Water	3	4	5	5	5	5	4	4
		Sediment	275	609	820	1032	819	1032	172	172
		Overall	3	25	123	488	399	617	128	76

Nonylphenol is a short-lived chemical that establishes concentrations in water that respond closely to the current discharge rate. Thus, a reduction in loading is predicted to yield an immediate reduction in water concentrations. However, the rest of the investigated chemicals are hydrophobic, with a high affinity to sediments. Thus, most of the compounds become associated with sediment and tend to remain there for some years. They will slowly "bleed" back into the water column as a result of significant sediment-water exchange. Sediment "residence times" (Table 8) are in the range of

0.4 - 7.4 yr, assuming a 5 cm depth of active sediments. The overall residence times will also be significantly affected by this fact and are in the range of days (less hydrophobic compounds, e.g. naphthalene or nonylphenol) to years (extremely hydrophobic chemicals, e.g. BaP, BP, IP).

The sediments act as a "buffer" to the system, slowing their response to changes in loading. The implication is that the sediments act as the primary repository of most of the modelled compounds and will respond in a characteristic time of up to 7 years (extreme case, Liptovská Mara reservoir) to changes in loadings.

3.4 Estimate of real emissions from the monitoring data

For the purpose semi-quantitative assessment of the real situation in the river Váh, pollutant loadings/emissions to individual water reservoirs were obtained by „back-calculating“ from measured concentrations of priority pollutants in sediment. For DEHP and NP, data on concentrations in sediment were not available. For these compounds, emissions were calculated from average (12 measurements/year in 2007) concentrations in the water column at profiles inside or close to the modelled water reservoirs.

Results of this modelling scenario is shown here in detail only for cases (compounds and reservoirs) where a risk of failing the objective of a good chemical status was identified. Practically, the identification was performed by comparing the sediment monitoring data (Table 9) with the „threshold“ values (Table 7).

This modelling scenario identified ten cases at risk of failing environmental quality objectives. In several cases the identification of bodies at risk was not possible because of insufficient monitoring data for some substances (NAP, ANT, DEHP and NP). The results of this analysis are shown in Table 10. The fate of priority pollutants in systems with an identified risk is discussed in detail below.

Table 9. Monitoring data - concentrations of priority compounds in sediments^{1, 10}

Reservoir name	River km	NAP	ANT	FLT	BaP	BbF+ BkF	BP +IP	DEHP	NP
Liptovská Mara	336	n.d. ^a	n.d.	95	43	128	58	n.d.	n.d.
Bešeňová	333	n.d.	n.d.	187	78	165	156	n.d.	n.d.
Krpeľany	294	30	33	368	133	198	195	171000 ^b	n.d.
Žilina	257	n.d.	n.d.	n.d.	n.d.	n.d.	344 ^f	65394 ^c	n.d.
Hričov	247	70	660	3363	1047	1657	907	86239 ^d	n.d.
Nosice	209	n.d.	n.d.	1325	507	897	733	n.d.	n.d.
Síňava	115	n.d.	n.d.	592	255	439	469	n.d.	n.d.
Kráľová	64	n.d.	n.d.	332	166	297	298	69867 ^e	n.d.

n.d. – no monitoring data for sediment available

Concentrations of DEHP in sediment were estimated with QWASI model using annual average concentrations (2007) in water column in the river profile closest to the water reservoir (Váh – Hubová, 1.55 µg/L)

Steady state concentrations of DEHP in sediment were estimated with QWASI model using annual average concentrations (2007) in water column in the river profile closest to the water reservoir (Váh – Dubná skala, 0.86 µg/L)

Steady state concentrations of DEHP in sediment were estimated with QWASI model using annual average concentrations (2007) in water column in the river profile closest to the water reservoir (Váh – downstream of Hričov, 0.69 µg/L)

Steady state concentrations of DEHP in sediment were estimated with QWASI model using annual average concentrations (2007) in water column in the river profile closest to the water reservoir (Váh – Komárno, 1.77 µg/L)

Steady state concentrations of BP+IP in sediment were estimated with QWASI model using annual average concentrations (2007) in water column in the river profile closest to the water reservoir (Váh – Dubná skala, 2.8 ng/L)

Table 10. Identification of water reservoir where the priority compound concentrations are at risk of EQS exceedance

Reservoir name	River km	NAP	ANT	FLT	BaP	BbF+ BkF	BP +IP	DEHP	NP
Liptovská Mara	336	n.d. ^a	n.d.	OK ^b	OK	OK	OK	n.d.	n.d.
Bešeňová	333	n.d.	n.d.	OK	OK	OK	OK	n.d.	n.d.
Krpeľany	294	OK	OK	OK	OK	OK	OK	RISK	n.d.
Žilina	257	n.d.	n.d.	n.d.	n.d.	n.d.	RISK	OK	n.d.
Hričov	247	n.d.	RISK	RISK	n.d.	n.d.	RISK	OK	n.d.
Nosice	209	n.d.	n.d.	RISK	OK	OK	RISK	n.d.	n.d.
Síňava	115	n.d.	n.d.	OK	OK	OK	RISK	n.d.	n.d.
Kráľová	64	n.d.	n.d.	OK	OK	OK	RISK	RISK	n.d.

n.d. – no monitoring data for sediment available

OK – concentration in sediment in the system at steady state corresponds with concentrations in the water column that likely does not exceed the EQS value

RISK – concentration in sediment in the system at steady state corresponds with concentrations in the water column that likely exceeds the EQS value

3.4.1 Anthracene in the Hričov reservoir

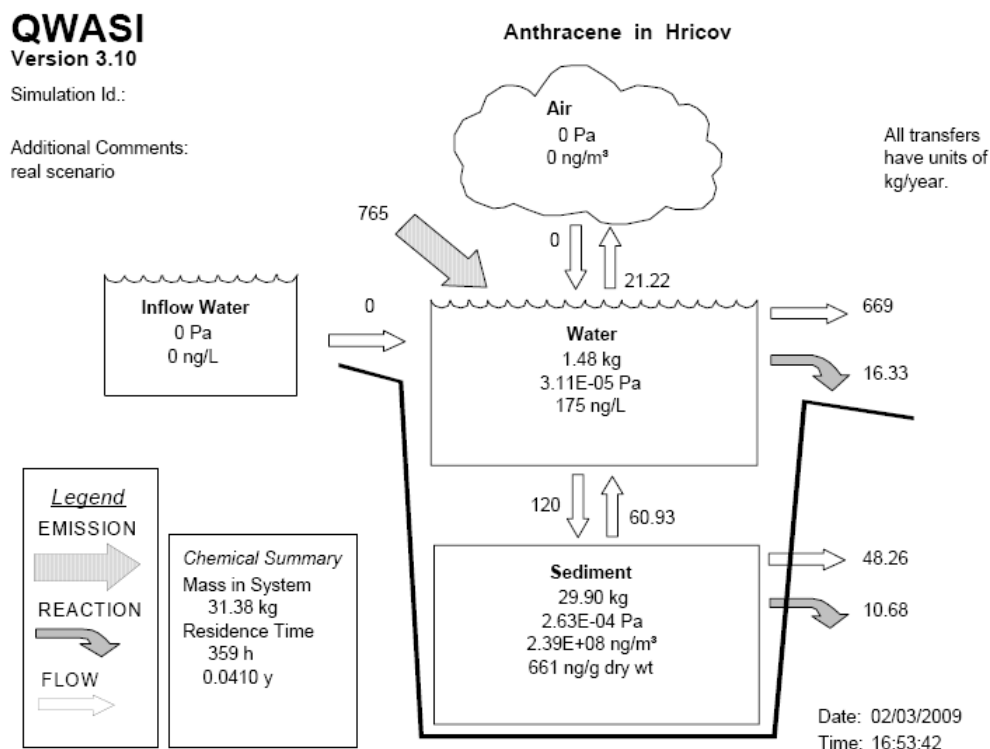


Figure 2. Mass balance diagram of anthracene in the Hričov reservoir

In the sediment the average measured concentration is 661 ng/g. The corresponding estimated concentration in water is 175 ng/L, exceeding the EQS value of 100 ng/L by a factor of 1.75. The estimated input rate of anthracene to the reservoir, based on the sediment concentration, is **765** kg/year. The quantity of anthracene in the water column at steady state is 1.48 kg and in the

sediment it is 29.9 kg, totaling 31.38 kg. This yields an overall residence time of approximately 359 h or 15 days. The water and sediment fugacities are, respectively, $3.11\text{E-}05$ and $2.63\text{E-}04$ Pa and are thus a factor of 8.5 from equilibrium.

The transport and transformation processes in order of decreasing importance are as follows:

Water/particle outflow	669 kg/year
Water to sediment transport	120 kg/year
Sediment to water transport	60.93 kg/year
Burial in the sediment	48.26 kg/year
Evaporation	21.22 kg/year
Degradation in water	16.33 kg/year
Degradation in sediment	10.68 kg/year

In summary the key processes are the water/particle outflow and water to sediment transport with most of the chemical residing in the sediment. Cca 90% of the annual emission is transported downstream by the water/particle outflow from the reservoir.

3.4.2 Fluoranthene in the Hričov reservoir

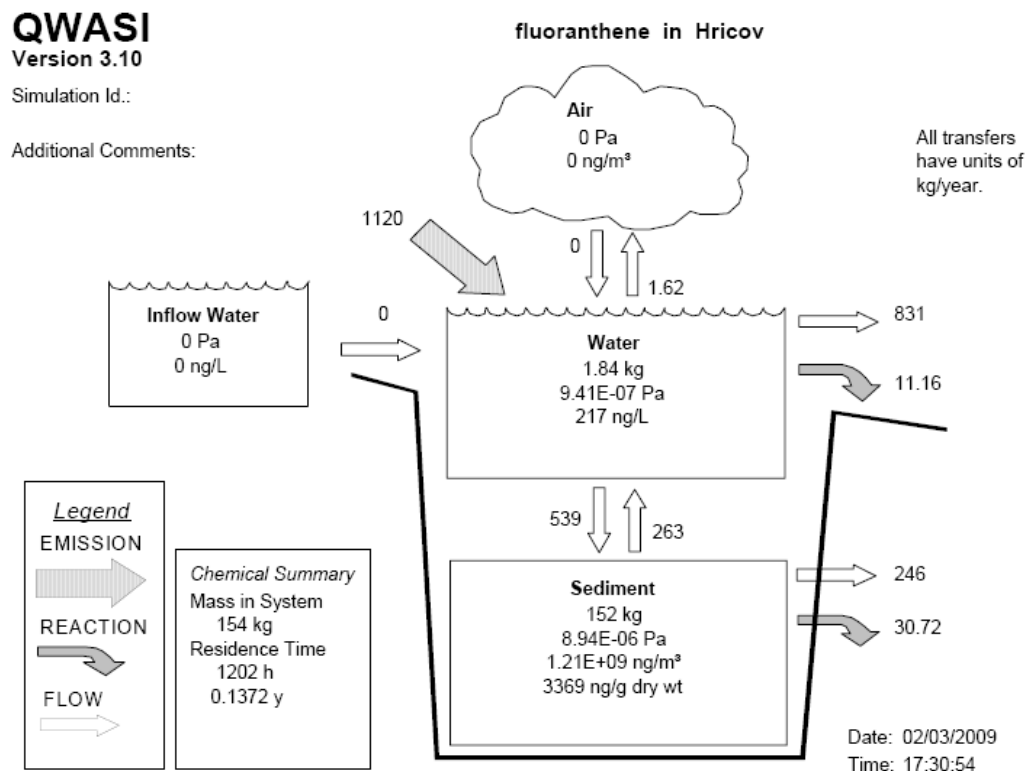


Figure 3. Mass balance diagram of fluoranthene in the Hričov reservoir

In the sediment the average measured concentration is 3369 ng/g. The corresponding estimated concentration in water is 217 ng/L, exceeding the EQS value of 100 ng/L by a factor of 2.17. The estimated input rate of fluoranthene to the reservoir, based on the sediment concentration, is **1120 kg/year**. The quantity of fluoranthene in the water column at steady state is 1.84 kg and in the sediment it is 152 kg, totaling 154 kg. This yields an overall residence time of approximately 1202 h or 50 days. The water and sediment fugacities are, respectively, $9.41\text{E-}07$ and $8.94\text{E-}06$ Pa and are thus a factor of 9.5 from equilibrium.

The transport and transformation processes in order of decreasing importance are as follows:

Water/particle outflow	831 kg/year
Water to sediment transport	539 kg/year
Sediment to water transport	263 kg/year
Burial in the sediment	246 kg/year
Degradation in sediment	30.72 kg/year
Degradation in water	11.16 kg/year
Evaporation	1.62 kg/year

In summary the key processes are the water/particle outflow and water to sediment transport with most of the chemical residing in the sediment. Cca 87% of the annual emission is transported downstream by the water/particle outflow from the reservoir

3.4.3 Fluoranthene in the Nosice reservoir

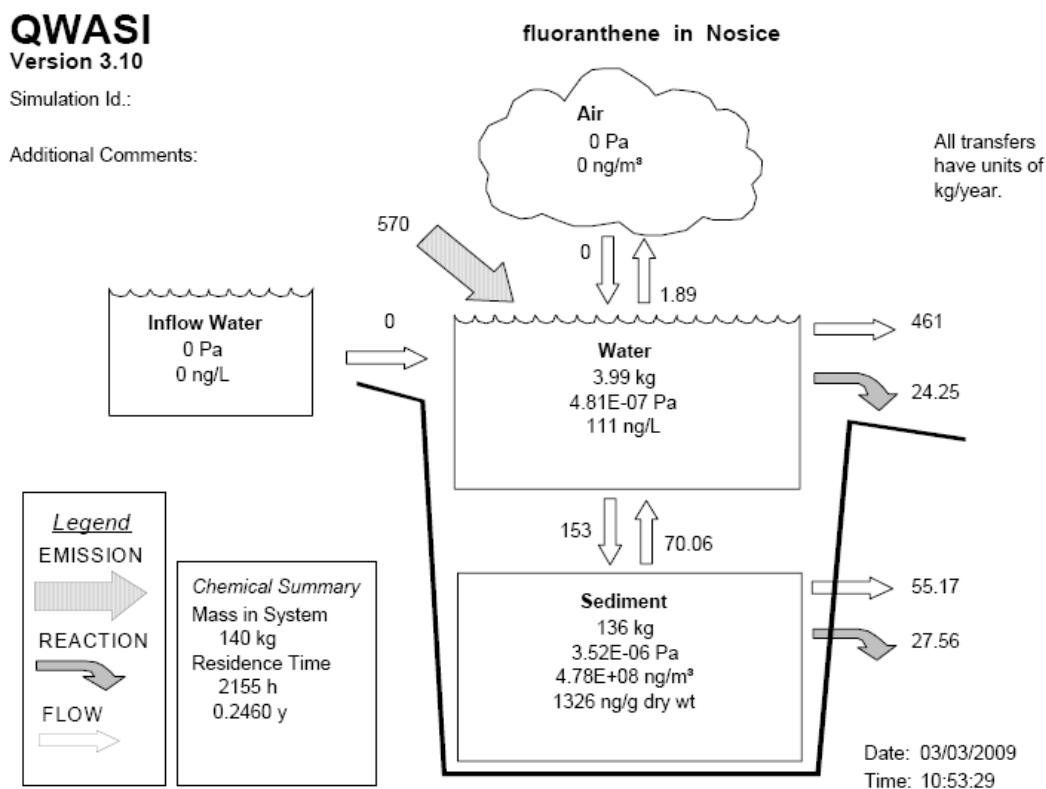


Figure 4. Mass balance diagram of fluoranthene in the Nosice reservoir

In the sediment the average measured concentration is 1326 ng/g. The corresponding estimated concentration in water is 111 ng/L, slightly exceeding the EQS value of 100 ng/L by a factor of 1.11. The estimated input rate of fluoranthene to the reservoir, based on the sediment concentration, is **570** kg/year. The quantity of fluoranthene in the water column at steady state is 3.99 kg and in the sediment it is 136 kg, totaling 140 kg. This yields an overall residence time of approximately 2155 h or 90 days. The water and sediment fugacities are, respectively, 4.81 E-07 and 3.52E-06 Pa and are thus a factor of 7.3 from equilibrium.

The transport and transformation processes in order of decreasing importance are, similar to the case of fluoranthene in Hričov, as follows:

Water/particle outflow	461 kg/year
------------------------	-------------

Water to sediment transport	153 kg/year
Sediment to water transport	70 kg/year
Burial in the sediment	55 kg/year
Degradation in sediment	27.6 kg/year
Degradation in water	24.3 kg/year
Evaporation	1.89 kg/year

In summary the key processes are the water/particle outflow and water to sediment transport with most of the chemical residing in the sediment. Cca 74% of the annual emission is transported downstream by the water/particle outflow from the reservoir.

3.4.4 Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene in the Žilina reservoir

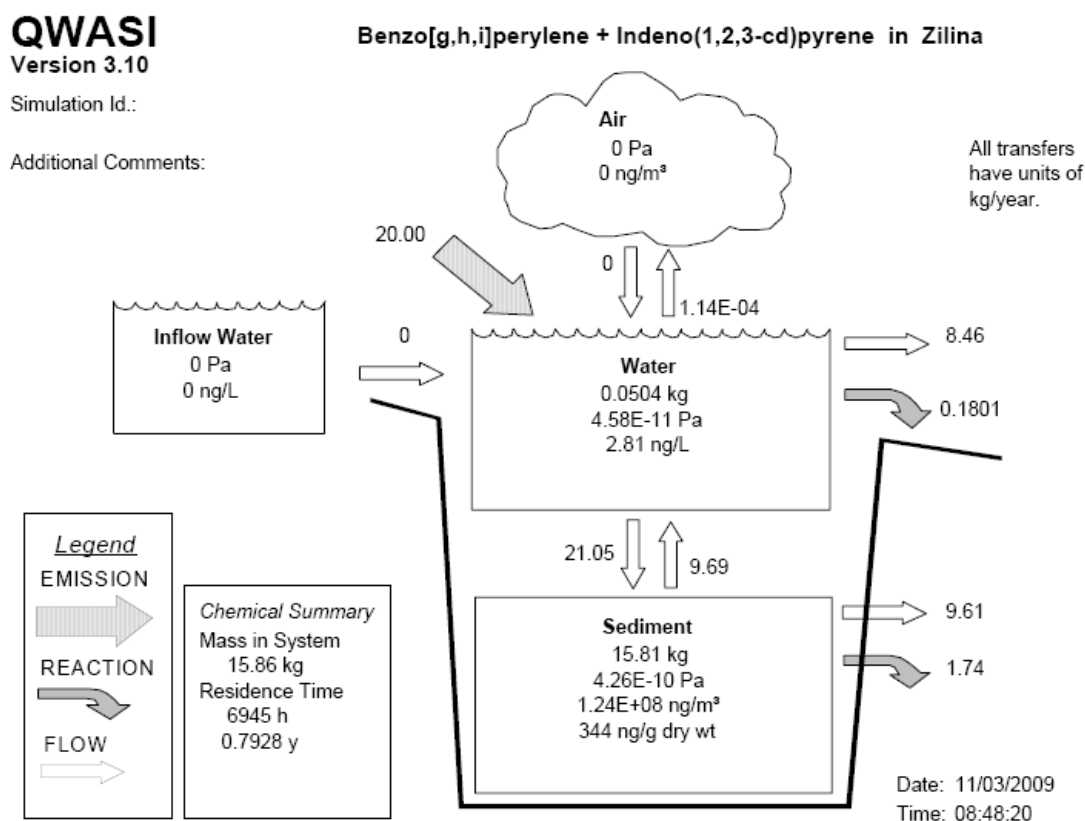


Figure 5. Mass balance diagram of Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene in the Žilina reservoir

No sediment monitoring data Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene was available in the water dam of Žilina. For the purpose of modelling, steady state concentrations of BP+IP in sediment were estimated with QWASI model using annual average concentrations (2007) in water column in the river profile closest to the water reservoir (Váh –Dubná skala, 2.8 ng/L). This concentration in water column, exceeds the EQS value of 2 ng/L by a 40%. The estimated input rate of Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene to the reservoir, based on the sediment concentration, is **20** kg/year. The quantity of Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene in the water column at steady state is 0.05 kg and in the sediment it is 15.81 kg, totaling 15.86 kg. This yields an overall residence time of approximately 6945 h or 0.79 years. The water and

sediment fugacities are, respectively, $4.58 \text{ E-}11$ and $4.26\text{E-}10$ Pa and are thus a factor of 9.30 from equilibrium.

The transport and transformation processes in order of decreasing importance are as follows:

Sediment to water transport	21.05 kg/year
Water to sediment transport	9.69 kg/year
Burial in the sediment	9.61 kg/year
Water/particle outflow	8.46 kg/year
Degradation in sediment	1.74 kg/year
Degradation in water	0.18 kg/year
Evaporation	negligible

In summary the key processes are the water to sediment transport and sediment to water transport with most of the chemical residing in the sediment. The high proportion of chemical resuspended (9.69 kg/year) suggests that the sediments could be cleared of chemical fairly rapidly. Of the 9.69 kg of resuspended sediment, 8.46 kg will be removed by advective flow. This means also that cca 40% of the annual emission is transported downstream by the water/particle outflow from the reservoir.

3.4.5 Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene in the Hričov reservoir

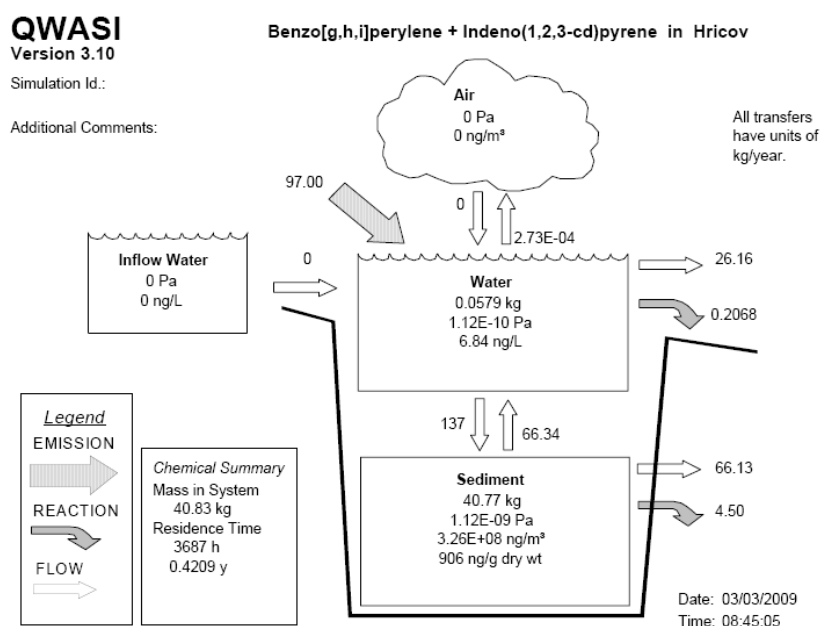


Figure 6. Mass balance diagram of Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene in the Hričov reservoir

In the sediment the average measured concentration is 906 ng/g. The corresponding estimated concentration in water is 6.84 ng/L, exceeding the EQS value of 2 ng/L by a factor of 3.42. The estimated input rate of Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene to the reservoir, based on the sediment concentration, is **97** kg/year. The quantity of Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene in the water column at steady state is 0.0579 kg and in the sediment it is 40.77 kg, totaling 40.83 kg. This yields an overall residence time of approximately 3687 h or 153 days. The water and sediment fugacities are, respectively, $1.12 \text{ E-}10$ and $1.124\text{E-}09$ Pa and are thus a factor of 10 from equilibrium.

The transport and transformation processes in order of decreasing importance are as follows:

Water to sediment transport	137 kg/year
Sediment to water transport	66.3 kg/year
Burial in the sediment	66.13 kg/year
Water/particle outflow	26.16 kg/year
Degradation in sediment	4.50 kg/year
Degradation in water	0.21 kg/year
Evaporation	negligible

The key processes are the water to sediment transport and sediment to water transport with most of the chemical residing in the sediment. Cca 27% of the annual emission is transported downstream by the water/particle outflow from the reservoir.

3.4.6 Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene in the Nosice reservoir

In the sediment the average measured concentration is 734 ng/g. The corresponding estimated concentration in water is 6.34 ng/L, exceeding the EQS value of 2 ng/L by a factor of 3.17. The estimated input rate of Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene to the reservoir, based on the sediment concentration, is **66** kg/year. The quantity of Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene in the water column at steady state is 0.2282 kg and in the sediment it is 75.27 kg, totaling 75.50 kg. This yields an overall residence time of approximately 10021 h or 1.14 years. The water and sediment fugacities are, respectively, 1.04 E-10 and 9.07E-10 Pa and are thus a factor of 8.72 from equilibrium.

The transport and transformation processes in order of decreasing importance are as follows:

Water to sediment transport	69.7 kg/year
Sediment to water transport	30.90 kg/year
Burial in the sediment	30.52 kg/year
Water/particle outflow	26.35 kg/year
Degradation in sediment	8.31 kg/year
Degradation in water	0.81 kg/year
Evaporation	negligible

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Simulation Id.:

Additional Comments:

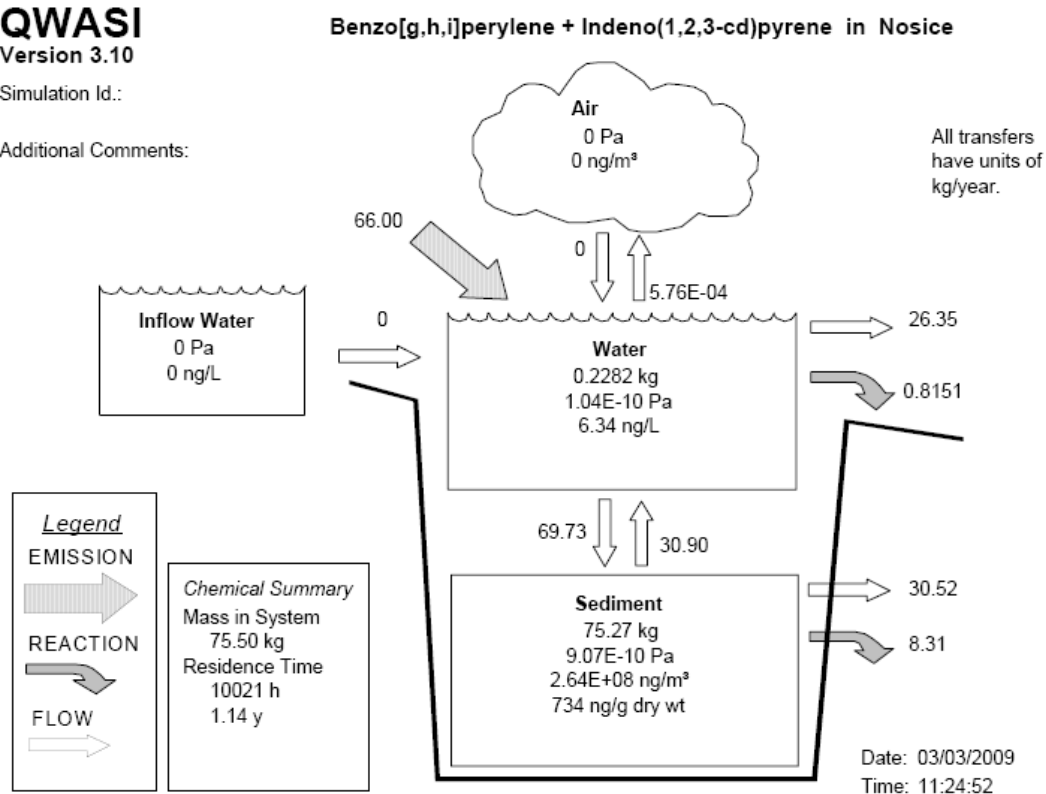


Figure 7. Mass balance diagram of Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene in the Nosice reservoir

The key processes are the water to sediment transport and sediment to water transport with most of the chemical residing in the sediment.

The high proportion of chemical resuspended (30.90 kg/year) suggests that the sediments could be cleared of chemical fairly rapidly. Of the 30.90 kg of resuspended sediment, 26.35 kg will be removed by advective flow. This means that cca 40% of the annual emission is transported downstream by the water/particle outflow from the reservoir.

3.4.7 Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene in the Sĺnava reservoir

QWASI

Version 3.10

Simulation Id.:

Additional Comments:

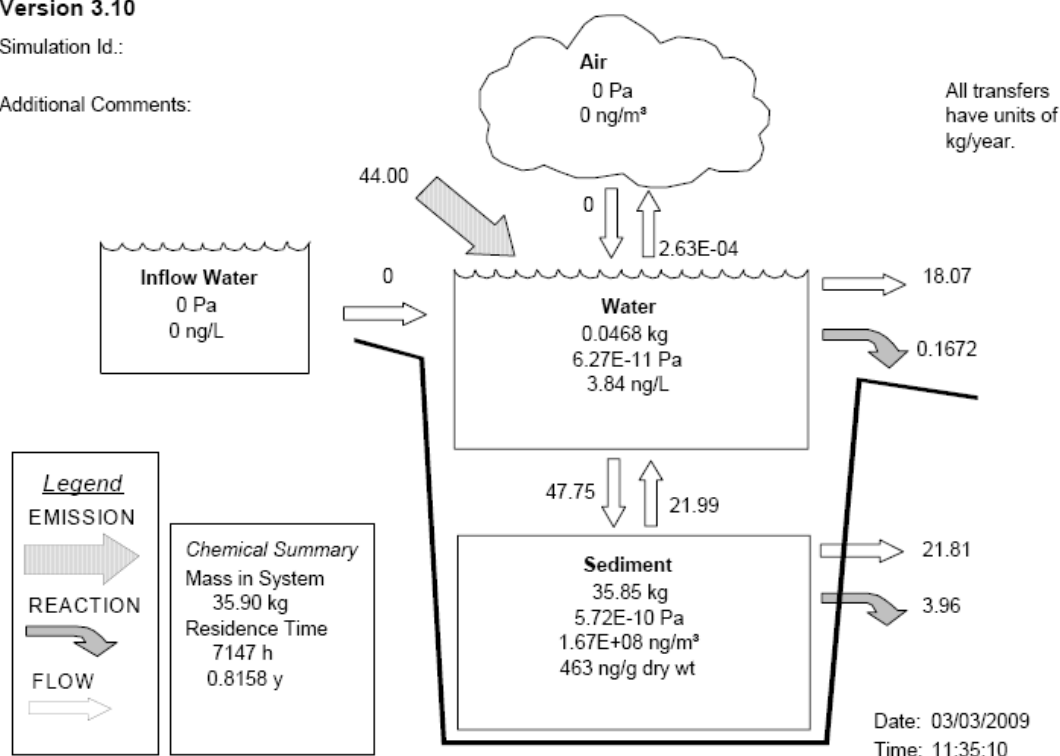


Figure 8. Mass balance diagram of Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene in the Sĺnava reservoir

In the sediment the average measured concentration is 463 ng/g. The corresponding estimated concentration in water is 3.84 ng/L, exceeding the EQS value of 2 ng/L by a factor of 1.92. The estimated input rate of Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene to the reservoir, based on the sediment concentration, is **44** kg/year. The quantity of Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene in the water column at steady state is 0.0468 kg and in the sediment it is 35.85 kg, totaling 35.90 kg. This yields an overall residence time of approximately 7147 h or 0.82 years. The water and sediment fugacities are, respectively, 6.27 E-11 and 5.72 E-10 Pa and are thus a factor of 9.12 from equilibrium.

The transport and transformation processes in order of decreasing importance are as follows:

Water to sediment transport	47.75 kg/year
Sediment to water transport	21.99 kg/year
Burial in the sediment	21.81 kg/year
Water/particle outflow	18.07 kg/year
Degradation in sediment	3.96 kg/year
Degradation in water	0.17 kg/year
Evaporation	negligible

In summary the key processes are the water to sediment transport and sediment to water transport with most of the chemical residing in the sediment. The high proportion of chemical resuspended (21.99 kg/year) suggests that the sediments could be cleared of chemical fairly rapidly. Of the 21.99 kg of resuspended sediment, 18.07 kg will be removed by advective flow.

This means that cca 40% of the annual emission is transported downstream by the water/particle outflow from the reservoir.

3.4.8 Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene in the Kráľová reservoir

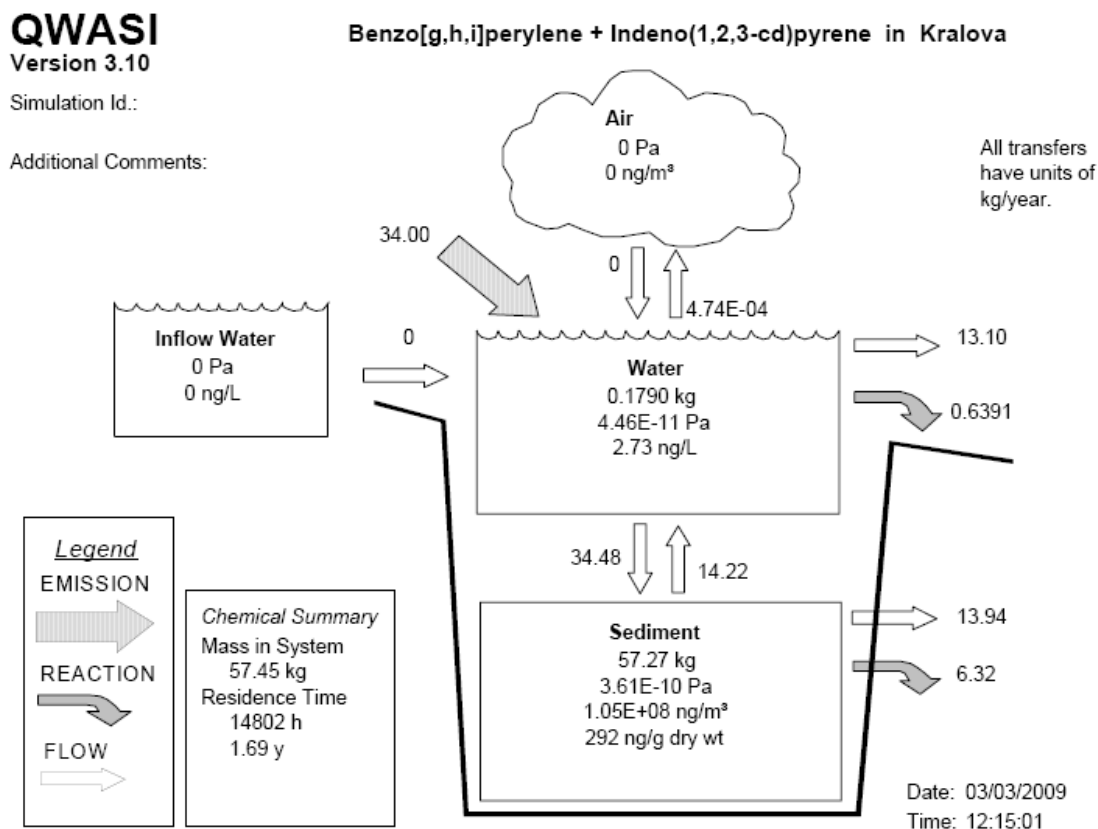


Figure 9. Mass balance diagram of Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene in the Kráľová reservoir

In the sediment the average measured concentration is 292 ng/g. The corresponding estimated concentration in water is 2.73 ng/L, slightly exceeding the EQS value of 2 ng/L by a factor of 1.37. The estimated input rate of Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene to the reservoir, based on the sediment concentration, is **34** kg/year. The quantity of Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene in the water column at steady state is 0.1790 kg and in the sediment it is 57.27 kg, totaling 57.45 kg. This yields an overall residence time of approximately 14802 h or 1.69 years. The water and sediment fugacities are, respectively, 4.46 E-11 and 3.61 E-10 Pa and are thus a factor of 8.09 from equilibrium.

The transport and transformation processes in order of decreasing importance are as follows:

Water to sediment transport	34.48 kg/year
Sediment to water transport	14.22 kg/year
Burial in the sediment	13.94 kg/year
Water/particle outflow	13.10 kg/year
Degradation in sediment	6.32 kg/year
Degradation in water	0.64 kg/year
Evaporation	negligible

In summary the key processes are the water to sediment transport and sediment to water transport with most of the chemical residing in the sediment.

The high proportion of chemical resuspended (14.22 kg/year) suggests that the sediments could be cleared of chemical fairly rapidly. Of the 14.22 kg of resuspended sediment, 13.10 kg will be removed by advective flow. This means that cca 39% of the annual emission is transported downstream by the water/particle outflow from the reservoir.

3.4.9 DEHP in the Krpeľany reservoir

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Version 3.10

Simulation Id.:

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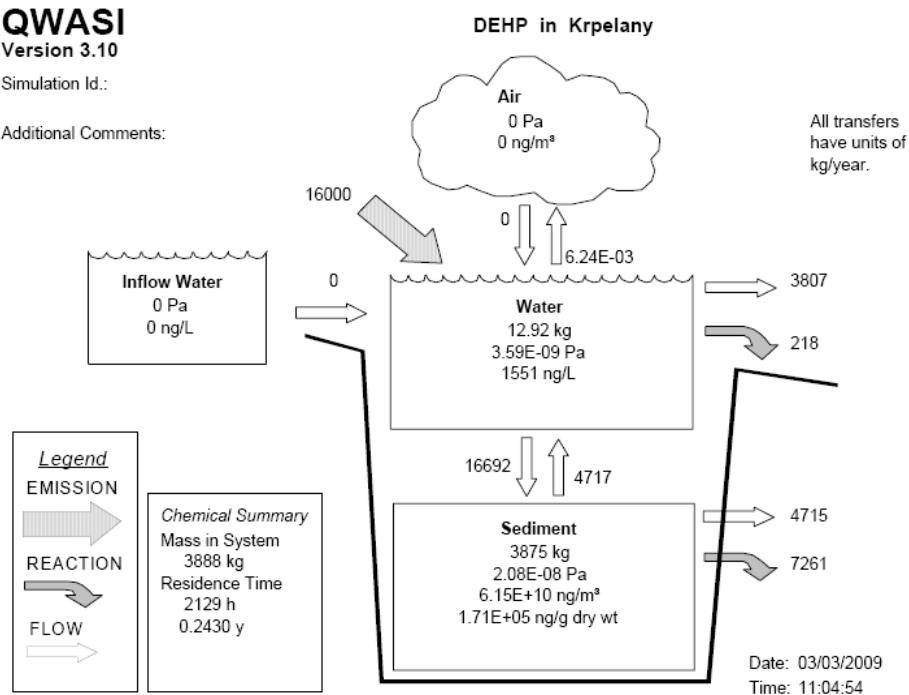


Figure 10. Mass balance diagram of DEHP in the Krpeľany reservoir

The measured concentration in water is 1551 ng/L, slightly exceeding the EQS value of 1300 ng/L. In the sediment the corresponding model-estimated concentration is 171 µg/g.

The estimated input rate of DEHP to the reservoir, based on the measured water concentration, is **16000** kg/year. The quantity of DEHP in the water column at steady state is 12.92 kg and in the sediment it is 3875 kg, totaling 3888 kg. This yields an overall residence time of approximately 2129 h or 89 days. The water and sediment fugacities are, respectively, 3.59 E-09 and 2.08 E-08 Pa and are thus a factor of 5.8 from equilibrium.

The transport and transformation processes in order of decreasing importance are as follows:

Water to sediment transport	16692 kg/year
Degradation in sediment	7261 kg/year
Sediment to water transport	4717 kg/year
Burial in the sediment	4715 kg/year
Water/particle outflow	3807 kg/year
Degradation in water	218 kg/year
Evaporation	negligible

In summary the key processes are the water to sediment transport and degradation in sediment with most of the chemical residing in the sediment. Of the 4717 kg of resuspended sediment, 3807

kg will be removed by advective flow. This means that only cca 24% of the annual emission is transported downstream by the water/particle outflow from the reservoir.

3.4.10 DEHP in the Kráľová reservoir

The measured concentration in water is 1782 ng/L, exceeding the EQS value of 1300 ng/L. In the sediment the corresponding model-estimated concentration is 69.9 µg/g.

The estimated input rate of DEHP to the reservoir, based on the measured water concentration, is **39500** kg/year. The quantity of DEHP in the water column at steady state is 117 kg and in the sediment it is 13695 kg, totaling 13812 kg. This yields an overall residence time of approximately 3063 h or 128 days. The water and sediment fugacities are, respectively, 4.12 E-09 and 8.50 E-09 Pa and are thus a factor of 2.1 from equilibrium.

The transport and transformation processes in order of decreasing importance are as follows:

Water to sediment transport	32332 kg/year
Degradation in sediment	25661 kg/year
Water/particle outflow	8540 kg/year
Sediment to water transport	3339 kg/year
Burial in the sediment	3333 kg/year
Degradation in water	1967 kg/year
Evaporation	negligible

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Version 3.10

Simulation Id.:

Additional Comments:

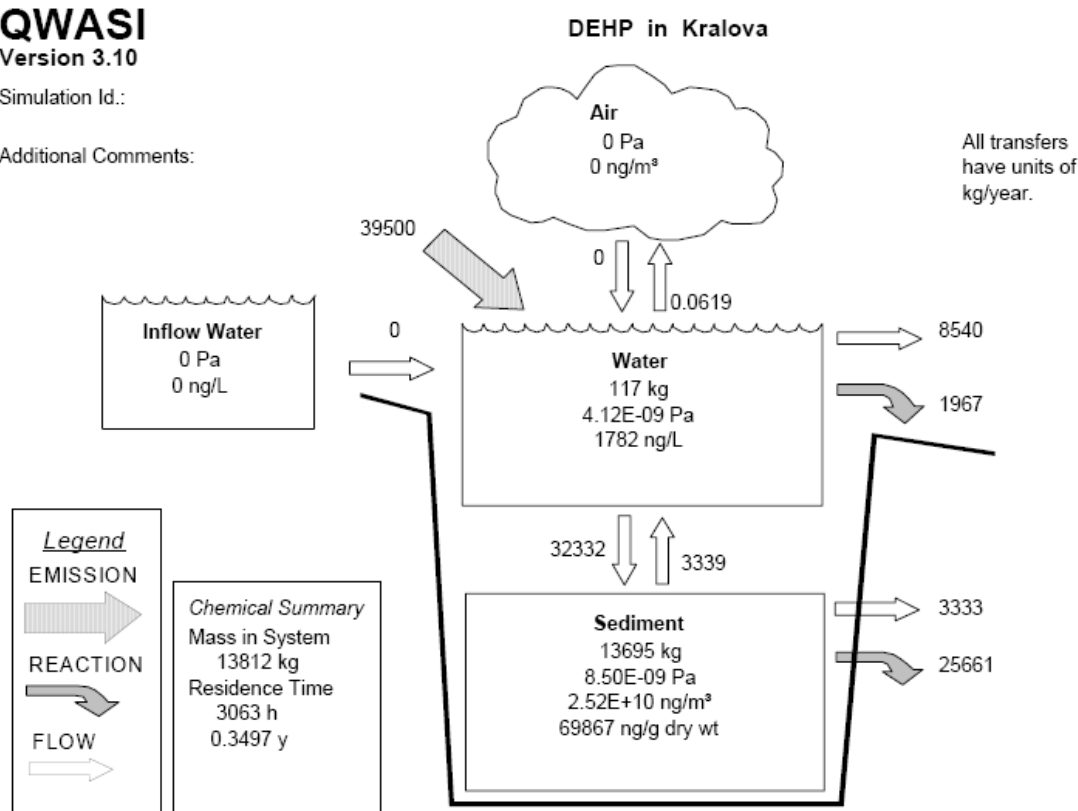


Figure 11. Mass balance diagram of DEHP in the Kráľová reservoir

In summary the key processes are the water to sediment transport and degradation with most of the chemical residing in the sediment. Cca 26% of the annual emission is transported downstream by the water/particle outflow from the reservoir.

3.5 Estimates of necessary emission reductions

Results of modelling scenario are for cases (compounds and reservoirs) with identified risk enabled to estimate the total emissions of compounds to the reservoirs. These estimates are shown in Table 11. These estimates represent total emissions and cumulate all possible sources and input pathways, i.e. both point sources and diffuse sources from both water and atmosphere. Substraction of these emissions from the estimated maximum acceptable emissions for a particular compound and reservoirs results in estimates of required emission reductions [kg/year] of a compounds to a particular water reservoir (Table 12). This information is useful when management options are considered.

Table 11. Estimate of emissions [kg/year] to reservoirs where the water bodies are at risk of EQS exceedance

Reservoir name	River km	NAP	ANT	FLT	BaP	BbF+ BkF	BP +IP	DEHP	NP
Liptovská Mara	336								
Bešeňová	333								
Krpeľany	294							16000	
Žilina	257						20		
Hričov	247		765	1120			97		
Nosice	209			570			66		
Sĺňava	115						44		
Kráľová	64						34	39500	

Table 12. Identification of required emission reductions [kg/year] to reservoirs where the water bodies are at risk of EQS exceedance

Reservoir name	River km	NAP	ANT	FLT	BaP	BbF+ BkF	BP +IP	DEHP	NP
Liptovská Mara	336								
Bešeňová	333								
Krpeľany	294							2500	
Žilina	257						6		
Hričov	247		315	605			69		
Nosice	209			60			46		
Sĺňava	115						21		
Kráľová	64						9	10500	

3.6 Recovery time period

The residence times can be applied to calculate the time series of recovery of that compartment when emissions cease using the first order decay equation:

$$M = M_0 \exp(-t/t_{res})$$

,where t is time (years) for calculating the mass M based on the initial mass M_0 and t_{res} is the residence time. Table 13 summarises the minimum time of the system to recover so that pollutant

concentrations would fall below EQS concentrations in the water column. This calculations are based on a scenario that assumes immediate cease of all emissions, which is not realistic. Even this over-optimistic scenario indicates that in some cases it would take more than two years (e.g. BP+IP in Nosice) to achieve water quality status that would comply with EQS. To be more realistic, the minimum time of the system to recover could be calculated for a scenario that assumes adjustment of emissions to maximum acceptable values in order to meet the EQS objective (data not shown). In such case the recovery times would be significantly longer.

Table 13. Estimation of required **minimum time of the system to recover** [years] for cases where the priority compound concentrations are at risk of EQS exceedance

Reservoir name	River km	NAP	ANT	FLT	BaP	BbF+ BkF	BP +IP	DEHP	NP
Liptovská Mara	336								
Bešeňová	333								
Krpeľany	294							0.1	
Žilina	257						0.2		
Hričov	247		0.3	0.4			0.7		
Nosice	209			0.1			2.3		
Sĺňava	115						0.9		
Kráľová	64						1.9	0.9	

Note: The minimum time is calculated for a scenario **if all emissions stopped immediately**. The calculated time period to achieve concentration of priority pollutants in the water column equal to EQS is calculated.

3.7 Analysis of emissions

In order to evaluate remedial actions it is essential to determine the major sources of pollutants to the system. This can be accomplished by running the model with specific sources deleted sequentially. It is perhaps easier, however, to interpret these results by applying the Linear Additivity Principle (LAP) of Stiver and Mackay (1990)¹⁶. The LAP asserts that, provided the model is linear with respect to concentrations and amounts, the net behaviour of a chemical in a system is the sum of behaviours attributable to individual chemical sources. These sources may vary spatially, e.g. river inflows and atmospheric deposition, or temporally, e.g. present inputs and in-place pollution. Practically, this implies that estimated concentrations, amounts and rates obtained from running the model with each chemical source individually, can be summed to obtain the total estimated behaviour. In this way, the contribution of each source can be estimated effectively¹⁷.

Compounds enter the modelled systems by several routes:

3.7.1 Effluent discharges

As a main source of priority substances were industrial sources identified. Their selection was based on the results of the research activity Analyses of pollution sources^{9, 18}, done in cooperation of Water Research Institute, Slovak Hydrometeorological Institute and Slovak Water Management Enterprise. The period for which the data used for analyses are valid is 2006-2007.

The identification of significant industrial sources of pollution was based on following criteria:

- source discharging waste waters with content of priority substances or substances relevant for Slovak republic;
- source with IPPC permission;

- ratio of amount of waste water to minimum amount of water discharge into the river is equal 1.1 or more;
- industrial source with more than 10 000 m³/year or 1 000 m³/month of discharged waste water volume;
- source is located in any kind of protected area;

According these criteria were identified 84 significant industrial pollution sources, there of 28 with IPPC permission (Figure 13). All of them are listed in the Table 14 and shown on the Figure 12. Sources are categorised according their production activity, based on the data available we have used the classification valid until 31.12.2007.

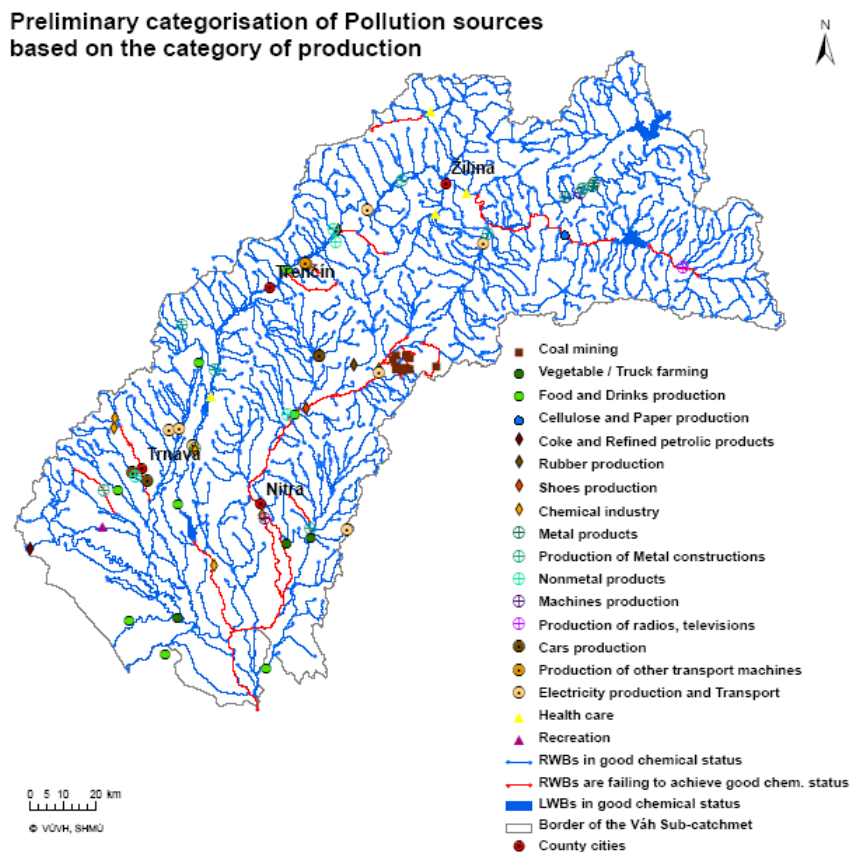


Figure 12. Identification of significant industrial pollution sources divided according the category of their production

Preliminary categorisation of Pollution sources emitting / not emitting Priority Substances

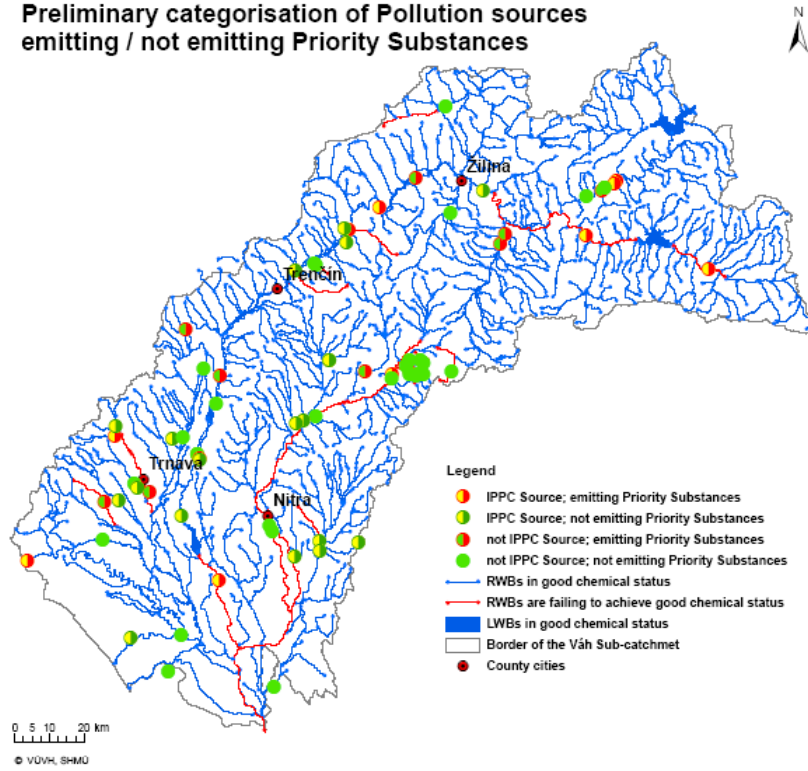


Figure 13. Categorisation of industrial pollution sources based on identification of IPPC sources discharging priority substances

Table 14. Significant industrial sources of pollution divided according the classification of economic activity (status 2006-2007)

No.	Subcatchment Name	Industrial enterprise	Specific location	Classification of Economic activity				
				No.	general		specific	
1	Váh	Mondi Business Paper SCP a.s.	Mondi Business Paper SCP a.s.	21.1	21000	Production of celulosis, paper and paper products	21100	Production of celulosis, paper and cardboard
4	Nitra	Novácke Chemické Závody a.s.	Novácke Chemické Závody	24.1	24000	Production of chemicals and chemical products	24100	Production of basic chemicals
21	Váh	Chemolak a.s. Smolenice		24.3			24300	Production of paints, lacquers and similar cover materials, print colours and sealants
33	Váh	Chemolak a.s. Smolenice		24.3				
5	Váh	OFZ a.s. Istebné	Prevádzka Široká	27.10	27000	Production of metals	27100	Production of pig iron, steel and ferroalloys
36	Váh	OFZ a.s. Istebné	OFZ a.s. Prevádzka Istebné	27.10				
37	Váh	OFZ a.s. Istebné	Prevádzka Široká	27.10				
46	Váh	OFZ a.s. Istebné	Prevádzka Široká	27.10				
8	Váh	Matador a.s. Púchov	Matador a.s. Púchov	25.11	25000	Production of rubber and plastic products	25110	Production of rubber tires and bladders
28	Váh	Kinex a.s. Bytča	Kinex a.s. Bytča	28.11	28000	Production of metal constructions, metal products and except production of machines and equipments	28110	Production of metal constructions and their parts
1	Malý Dunaj	Agrotop Topolníky	Agrotop Topolníky	01.12	01000	Agriculture, hunting and related services	01120	Cultivation of vegetable, garden specialties and products garden nurseries
28	Nitra	Hybrav a.s.-hydínárska farma	Hybrav a.s.	01.23			01230	Pig farm
29	Nitra	Hybrav a.s.-hydínárska farma	Hybrav a.s.	01.23				
1	Nitra	HPB a.s., Hornonitrianske Bane	HPB a.s. Baňa Nováky	10.20	10000	Extraction of black coal, brown coal, lignite and extraction of peat soil	10200	Extraction of brown coal and lignite, production of brown coal briquettes
3	Nitra	HPB a.s., Hornonitrianske Bane	HPB a.s. Baňa Handlová	10.20				
5	Nitra	HPB a.s., Hornonitrianske Bane	HPB a.s. Baňa Nováky	10.20				

No.	Subcatchment Name	Industrial enterprise	Specific location	Classification of Economic activity				
				No.	general		specific	
6	Nitra	HPB a.s., Hornonitrianske Bane	HPB a.s. Baňa Nováky	10.20				
8	Nitra	HPB a.s., Hornonitrianske Bane	HPB a.s. Baňa Nováky	10.20				
10	Nitra	HPB a.s., Hornonitrianske Bane	HPB a.s. Baňa Handlová	10.20				
11	Nitra	HPB a.s., Hornonitrianske Bane	HPB a.s. Baňa Nováky	10.20				
13	Nitra	HPB a.s., Hornonitrianske Bane	HPB a.s. Baňa Nováky	10.20				
14	Nitra	HPB a.s., Hornonitrianske Bane	HPB a.s. Baňa Nováky	10.20				
17	Nitra	HPB a.s., Hornonitrianske Bane	HPB a.s. Baňa Nováky	10.20				
18	Nitra	HPB a.s., Hornonitrianske Bane	HPB a.s. Baňa Nováky	10.20				
23	Nitra	HPB a.s., Hornonitrianske Bane	HPB a.s. Baňa Handlová	10.20				
25	Nitra	HPB a.s., Hornonitrianske Bane	HPB a.s. Baňa Nováky	10.20				
27	Nitra	HPB a.s., Hornonitrianske Bane	HPB a.s. Baňa Nováky	10.20				
30	Nitra	HPB a.s., Hornonitrianske Bane	Banská mechanizácia a elektrifikácia a.s.	10.20				
32	Nitra	HPB a.s., Hornonitrianske Bane	Banská mechanizácia a elektrifikácia a.s.	10.20				
20	Váh	HYZA a.s. Topoľčany		15.13	15000	Production of food and beverages	15130	Production of meat and poultry products
5	Malý Dunaj	Euromilk a.s.	Euromilk a.s.	15.51			15510	Diary, production of butter and cheeses
3	Malý Dunaj	Eastern Sugar Slovensko a.s.	Eastern Sugar Slovensko a.s.	15.83			15830	Sugar production
15	Váh	Považský cukor a.s.	Považský cukor a.s.	15.83				

No.	Subcatchment Name	Industrial enterprise	Specific location	Classification of Economic activity				
				No.	general		specific	
34	Váh	Slovenské cukrovary a.s. Rimavská Sobota	Slovenské cukrovary a.s. Rimavská Sobota prevádzka Sereď	15.83				
40	Váh	Slovenské cukrovary a.s. Rimavská Sobota	Slovenské cukrovary a.s. Rimavská Sobota prevádzka Sereď	15.83				
29	Váh	Slovenské liehovary a likérky a.s.	Slovenské liehovary a likérky a.s.	15.91			15910	Production of distilled alcoholic beverages
12	Nitra	Topvar a.s.	Topvar a.s.	15.96			15960	Beer production
11	Váh	Heineken Slovensko a.s., Pivovar Hurbanovo		15.96				
16	Nitra	ZDA HOLDING SLOVAKIA a.s.	ZDA HOLDING SLOVAKIA a.s.	19.30	19000	Treatment o leather, production of bags, saddler products and shoes	19300	Shoe production
21	Nitra	Vulkan a.s.	ZDA HOLDING SLOVAKIA a.s.	19.30				
6	Malý Dunaj	Slovnaft a.s.	Slovnaft a.s. Bratislava, P-4.2 Technologické a energetické rozvody	23.20	23000	Production of coke, refined oil products and fuels	23200	Refinery
7	Malý Dunaj	Slovnaft a.s.	Slovnaft a.s. Bratislava, P-4.2 Technologické a energetické rozvody	23.20				
2	Váh	Duslo a.s.Šaľa	Duslo a.s. Šaľa	24.15			24150	Production of industrial fertilisers and nitrous compounds
41	Váh	Johns Manville Slovakia		24.16			24160	Production of plastics in primary form
24	Nitra	MEVAK a.s. Nitra	MEVAK a.s. Nitra	24.42			24420	Production of pharmaceutical products
24	Váh	Zentiva a.s.	Zentiva a.s.	24.42				
9	Nitra	Vegum a.s.	Vegum a.s.	25.13			25130	Production of other rubber products
20	Nitra	Vegum a.s.	Vegum a.s.	25.13				

No.	Subcatchment Name	Industrial enterprise	Specific location	Classification of Economic activity				
				No.	general		specific	
23	Váh	Rona a.s.	Rona a.s.	26.13	26000	Production of other non-metallic mineral products	26130	Production of hollow glass
42	Váh	Rona a.s.	Rona a.s.	26.13				
49	Váh	Rona a.s.	Rona a.s.	26.13				
27	Váh	Považská cementáreň a.s.	Považská cementáreň a.s.	26.51			26510	Cement production
19	Nitra	Elektrokarbon a.s.	Elektrokarbon a.s.	26.82			26820	Production of non-metallic mineral products i. n.
22	Váh	Bekaert Hlohovec a.s.	Bekaert Hlohovec a.s.	27.34	27000	Production of metals	27340	Wire towing
31	Nitra	Tesgal s r.o.	Tesgal s r.o.	28.40	28000	Production of metal constructions, metal products and except production of machines and equipments	28400	Forging, moulding, punching and milling of metals, powder metallurgy
4	Malý Dunaj	ETI ELB s.r.o. Báhoň	ETI ELB s.r.o. Báhoň	28.51			28510	Processing and surface treatment of metals
35	Váh	Glacier Tribometal Slovakia a.s.	Glacier Tribometal Slovakia a.s.	28.51				
43	Váh	Chirana-Prema Energetika a.s.	Chirana - Prema Energetika a.s.	28.51				
44	Váh	Vacuumschmelze s.r.o.	Vacuumschmelze s.r.o.	28.51				
10	Váh	MT- Energetika s.r.o.	MT - Energetika	28.52			28520	General engineering
47	Váh	ZŤS Strojárne a.s. Námestovo	ZŤS Strojárne a.s. Námestovo	28.52				
30	Váh	WWT s.r.o.	WWT s.r.o.	28.75			28750	Production of other metal products
26	Nitra		Výroba textilných strojov s.r.o. ČOV	29.24	29000	Production of machines and equipments.	29240	Production of machines for general purposes
45	Váh	SEZ a.s. Dolný Kubín	SEZ a.s. Dolný Kubín	29.56.9			29569	Production of other specific machines and equipments
19	Váh	Tesla Liptovský Hrádok a.s.	Tesla Liptovský Hrádok a.s.	32.20	32000	Production of radio, television and communication installations and appliances	32200	Production of television and radio broadcasters for phone and telegraph lines

No.	Subcatchment Name	Industrial enterprise	Specific location	Classification of Economic activity				
				No.	general		specific	
32	Váh	Peugeot Citroen Slovakia, s.r.o.- PCA		34.1	34000	Production of cars, trailers and semi-trailers	34100	Production of cars
9	Váh	Comax TT a.s. Trnava		34.3			34300	Production of spare parts and accessories for cars and their engines
7	Nitra	KORD Slovakia, a. s.	KORD Slovakia, a.s.	34.30				
22	Nitra	KORD Slovakia, a. s.	KORD Slovakia, a.s.	34.30				
6	Váh	DNV Energo a.s.	DNV Energo	35.50	35000	Production of other transport installations	35500	Production of other transport installations
48	Váh	DNV Energo a.s.	DNV Energo	35.50				
50	Váh	DNV Energo a.s.	DNV Energo	35.50				
7	Váh	Martinská Teplárenská a.s.	Martinská Teplárenská a.s.	40.1	40000	Production and distribution of electricity, gas, steam and hot water	40100	Production and distribution of electricity
15	Nitra	Slovenské elektrárne a.s.	Atómové elektrárne Mochovce	40.10				
3	Váh	Slovenské elektrárne a.s.	Atómové elektrárne Bohunice	40.10				
4	Váh	Jadrová vyradovacia spoločnosť, a.s.	Jadrová vyradovacia spoločnosť, a.s.	40.10				
13	Váh	Slovenské elektrárne a.s.	Atómové elektrárne Bohunice	40.10				
18	Váh	Slovenské elektrárne a.s.	Atómové elektrárne Bohunice	40.10				
31	Váh	Jadrová vyradovacia spoločnosť, a.s.	Jadrová vyradovacia spoločnosť, a.s.	40.10				
2	Nitra	Slovenské elektrárne a.s.	SE a.s. ENO Zemianske Kostolany	40.11			40110	Production of electricity
12	Váh	Tepláreň a.s. Považská Bystrica	Tepláreň a.s.	40.30			40300	Production and distribution of steam and hot water
14	Váh	Slovenské liečebné kúpele a.s. Trenčianske Teplice	Slovenské Liečebné kúpele a.s.	85.14	85000	Health services and social support	85140	Other activities in health service

No.	Subcatchment Name	Industrial enterprise	Specific location	Classification of Economic activity				
				No.	general		specific	
16	Váh	Slovenské liečebné kúpele	Slovenské Liečebné Kúpele	85.14				
17	Váh	Slovenské liečebné kúpele	Slovenské Liečené Kúpele Piešťany a.s.	85.14				
25	Váh	Slovenské liečebné kúpele	Slovenské Liečené Kúpele Piešťany a.s.	85.14				
26	Váh	Slovenské liečebné kúpele	Slovenské Liečené Kúpele Piešťany a.s.	85.14				
38	Váh	Slovenské liečebné kúpele	Slovenské Liečebné Kúpele	85.14				
39	Váh	VAS s r.o.	VAS s r.o.	85.20			85200	Veterinary activities
2	Malý Dunaj	AQUATHERMAL SENEK, a.s.	AQUATHERMAL SENEK, a.s.	92.72	92000	Recreation, cultural and sport activities	92720	Other recreation activities

Problems with measured data – priority substances are not measured at appropriate scale or at least and frequency.

The second source of information used for substances loads quantification are national reporting tools. One serves for reporting of IPPC polluters data emitting pollutants into the air and water, is called Integrated Register of Information System (IRIS, data availability 2006)¹⁹. The second one more comprehensive reporting system serves for reporting the data of all polluters emitting pollutants into the air, water, soil and as solid waste, this system is called National Register of polluters (NRZ, data availability 2007)²⁰. The biggest uncertainty in quantification of emissions is, that the data available in these reporting tools are reported by polluters itself and their relevance has very low confidence level. There are many of cases when the polluter is reporting data only for very few of expected emitted pollutants. It is obvious also by comparing the obtained data with back-calculated results.

3.7.2 Advective inputs in water

The models indicate that a significant portion (up to 87 % in the extreme case of anthracene in Hričov) of the local emissions of priority pollutants to the reservoirs is transported downstream by the water/particle outflow. Thus, a risk of contamination by water from upstream located polluted sites has to be considered. In a first approximation, a scenario was modelled that takes advective outputs from one reservoir as emission inputs to the next one downstream. Results of this simulation indicate that in several cases simply the outflow of priority pollutants from a reservoir upstream is sufficient to cause a risk of failing good chemical status objectives in the water reservoir located a few kilometres downstream and likely also in the river stretch between the two sites under investigation.

Pollutant outflow from the water reservoir Hričov has been identified to significantly contribute to the pollution by anthracene, fluoranthene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene in the Nosice reservoir. Moreover, outflow of benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene from the Nosice reservoir is sufficiently high to cause problems further downstream.

3.7.3 Background advective inputs in air

An important set of input data is the concentration of the PAHs in the background air flowing into the air compartment. Background air concentration monitoring data (available for BaP, BbF + BkF and BP+IP) was taken from¹¹.

Data indicates that contribution to the total emissions from the background air pollution deposition is negligible when compared to local sources. The background advective inputs in air contribute less than 6 % of the above mentioned PAH emissions to the reservoirs. This analysis could, unfortunately not be performed for more volatile PAHs (NAP, ANT and FLT) because of lack of air monitoring data in the studied area. Analysis was not performed for DEHP and NP, because of their low volatility. Considering the estimated magnitude of total emissions, contributions of NP and DEHP from the background atmospheric deposition to these emissions are negligible.

Table 15. Estimate of background advective contribution in air to the emissions [kg/year and (%) of total emissions] to reservoirs

Reservoir name	River km	NAP	ANT	FLT	BaP (0.42) ¹¹	BbF+BkF (0.89) ¹¹	BP+IP (0.51) ¹¹	DEHP	NP
Liptovská Mara	336								
Bešeňová	333								
Krpeľany	294							?	
Žilina	257				0.30	0.64	0.37 (1.9%)		
Hričov	247		?	?	0.30	0.63	0.36 (0.4%)		
Nosice	209			?	0.66	1.41	0.81 (1.2%)		
Sĺňava	115				0.49	1.04	0.60 (1.4%)		
Kráľová	64				1.22	2.60	1.49 (5.6%)	?	

Note: Cases where the priority compound concentrations are at risk of EQS exceedance are labelled bold. Available mean measured background air concentrations¹¹ [ng m⁻³] are given in parentheses the legend.

4 Conclusions

A mass balance model of chemical fate and transport in the Váh river was used to analyse the behaviour of several priority pollutants, including polycyclic aromatic hydrocarbons (PAHs), bis(2-ethylhexyl)phthalate (DEHP) and nonylphenol (NP) and factors affecting their behaviour in the system of artificial water reservoirs along the river. The model was used to predict the status of organic without knowing the actual loadings/emissions. Instead, the model was used to "back-calculate" total loadings to individual large water reservoirs/dams in the river basin. Following this analysis, attribution of emissions to individual chemical sources should be possible by applying the Linear Additivity Principle (LAP). Once the contribution of individual sources to total emissions is known, management options should become remediation or management strategies should become apparent.

The QWASI model, being relatively simple, has moderate data requirements. Once applied for one chemical in a system, it is relatively easy to examine the fate of others in that system. It is the absence of some important hydrological and limnological data (e.g. sediment deposition, resuspension and burial rates) or insufficient monitoring data that frustrates the effort, and hence the development of effective control measures.

Concentrations and amounts of persistent chemicals such as PAHs and DEHP, are controlled by rapid advection in the river system, however, depending on the modelled river segment, more rapid sediment deposition rates reduce and retard losses by advection and increase sediment concentrations. Sediment-water exchange, primarily through particle movement, maintains chemicals in the system longer than predicted by water residence times alone. An analysis of the model indicates that the importance of sediments as a chemical source depends on the rate of permanent removal from sediments (by burial and chemical transformation), the tendency of chemical to return to the water from sediments, and the proportion of released chemical that returns to the sediments following release. These results emphasize the importance of sediment-water exchange via particle movement, even for less hydrophobic chemicals such as naphthalene or nonylphenol.

For degrading chemicals such as naphthalene, DEHP and nonylphenol, the critical factors affecting fate and transport are transformation rates, which are seldom known under environmental conditions.

Model results indicate the need to control specific sources to reduce the priority compound inputs, i.e. to Hričov reservoir for anthracene, fluoranthene, benzo[g,h,i]-perylene and indeno(2,3-cd)-pyrene, DEHP in Krpeľany and Kráľová and some others. Required annual emission reductions were

estimated with the criterion of achievement a good chemical status in all water bodies (priority pollutant concentrations falling below EQS levels).

Residence time of the compounds in the sediment are up to several years in comparison to a much faster response (several days or weeks) in the water column. If loadings are reduced, the entire residence time of the system will respond substantially within several years. It can thus be argued that for these contaminants in this system there is little merit in considering dredging because natural remediation processes are would take effect in the time frame necessary for design and implementation of a remedial dredging program. The corollary to this is that if loadings are not reduced, and dredging is done, the system will recontaminate fairly rapidly to its pre-dredged condition.

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