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Modelling of oil substances migration in river Danube

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Abstract. Migration of contaminants in the river Danube was in the focus of study aimed at the risk assessment of industrial plant, which manipulates with hazardous substances. Modelling techniques were applied for the evaluation of impacts of possible serious industrial accidents at the Danube water quality.
Two basic concepts of contaminant migration in the surface water were considered:
1. Migration of contaminant at the water surface in the form of film, due to difference in densities and depending on the flow velocity.
2. Partial dissolution of contaminant in the water and migration at the water surface in the form of phase.
In the cases *of "major" oil spills* (from mobile tanks – vessels, assumed quantities 80-199 t) harmful effects of contamination with regard to *assumed toxic impacts at water organisms* (concentrations of petroleum hydrocarbons in the range 2-3 $mg.l^{-1}$ and higher) can be expected:

- in 11 km long river section from oil spill site (profile Patince) at the discharge of 1140 $m^3.s^{-1}$ (petroleum hydrocarbons concentrations in the range 2.0-7.8 $mg.l^{-1}$)
- in 3 km long river section from oil spill site (profile Szony) at the flood discharges 5350–9000 $m^3.s^{-1}$ (petroleum hydrocarbons concentrations in the range 2.0-4.6 $mg.l^{-1}$)
- in the close surrounding of oil spill site (around 500 m) even higher concentrations of petroleum hydrocarbons can be expected.

Total frequency of "major" oil spills in the estimated quantity 80–199 t as a consequence of mobile tanks (vessels) failure (collision with other vessel, or leakage) is substantially lower than in the case of "minor" spills. Analysis of "failure tree" (Kminiaková and Jelemenský, 2006) indicates that all possible sources of basic failures are of very low probability (frequency in the order $F=n.10^{-7}$ to $n.10^{-8}$ /year), comparable with meteor impact.

Keywords: modelling, surface water flow, surface water quality, oil pollution, serious industrial accidents

1. Introduction

Several research studies by Klúčovská and Topoľská (1994), Szolgay et al. (1994) and Szolgay et al. (1996), which were solved at the Water Research Institute in Bratislava, dealt with the modelling of the Danube river flow. These works focused at the calculation of surface water levels and discharges, based at the evaluation of roughness coefficients. Surface water quality of Danube was modelled in the frame of the project PHARE EC/ WAT/01 "Danubian Lowland – Groundwater Model" (MŽP, 1995). The focus was put at the oxygene regime, BOD, ammonia and nitrates. Modelling was based at the oxygene balance and connected parameters. The parameters of dispersion and advection for the river Danube were estimated.

Our study goal was to investigate migration of possible oil pollution in the Slovak-Hungarian border section of the Danube river. Study was performed in two basic steps. Firstly, water flow velocities and travel time were determined by previous modelling works, which are described in the reports (Szolgay et al., 1994, 1996). These data represented input information for further modelling of oil substances migration in the Danube river.

Theory of water quality modelling is described in Chapra (1997). Determination of transport parameters for substances dissolved in water was the key issue in our case. Detail study of oil pollution migration using the analytical models can be found in Hellweger (2005), together with practical examples of major oil spills in the rivers Missouri (1967), Rhine (1986), Sacramento (1991), as well as Tisza and Danube (2000). This study was based at real field data of pollution concentration and its variation along the investigated river sections. Based at these data, it was possible to determine advection-dispersion parameters in the conditions similar to our area of interest. Danube data from 2000 were taken into account after necessary adjustment, which was based at the actual flow area of river cross-sections in the model area.

2. Input data

Pollution migration in the surface waters was investigated in the frame of risk evaluation of industrial plant, which is involved in the operation of dangerous substances. It is located in Komárno, upstream from the confluence of the Danube and Vah rivers. Its services include

Slovak Geol. Mag., 12, 2 (2006), 103 – 116

transport, treatment, storage and distribution of fuels (propellants). Two kinds of dangerous substances according to the classification of the Act 261/2002 Dig. are stored and manipulated in this plant – petrol BA95 and fuel oil.

Evaluated division of plant deals with the storage of mentioned substances, as well as their permanent (24 hours a day) distribution between road, railway and waterway transport lines. Fuel entry and outgoing is realized via railway cisterns and cistern trucks. Upon entry fuel is distributed from cisterns through the pipelines to the river vessels – tankers, which are used as storage tanks. Outgoing fuel is pumped to railway cisterns or cistern trucks with pumping plant located at the anchored pontoon vessel. Individual products are pumped using self-priming pumps, hoses and rack (comb).

The layout of the Danube river in the investigated Slovak-Hungarian section is given in the Fig. 1a, b.

Fig. 1a. Layout of investigated Danube river section between the oil spill site and the end of Slovak-Hungarian section – part 1.

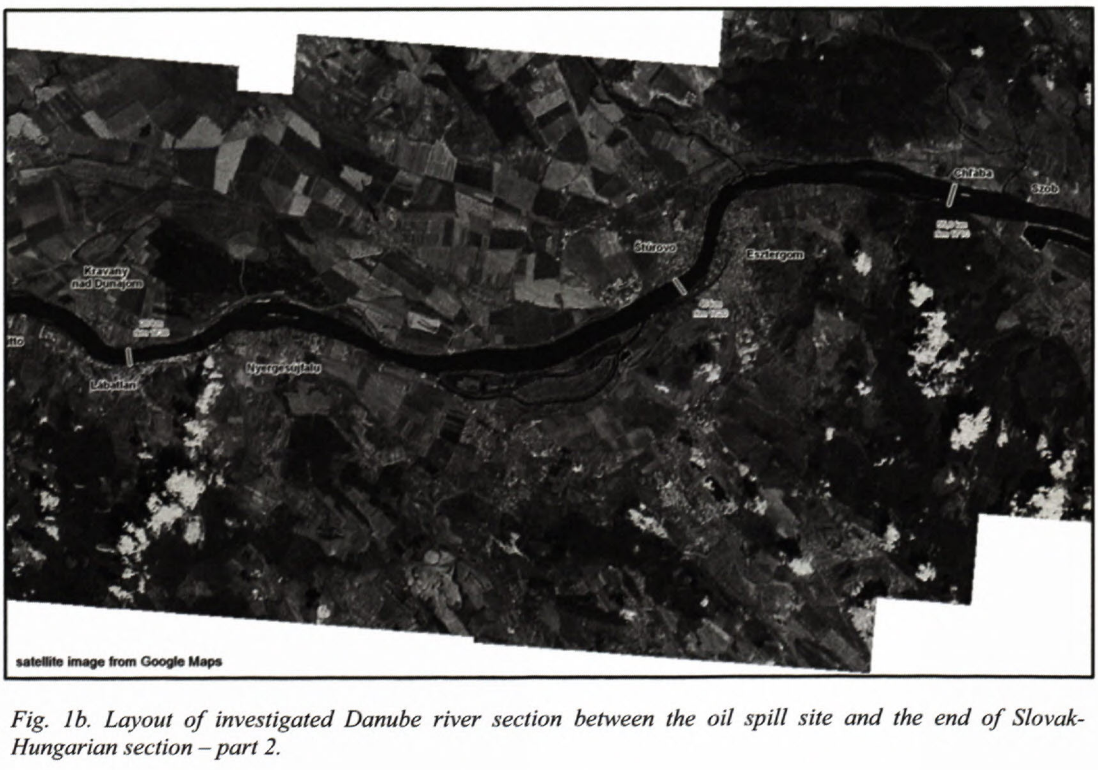

Fig. 1b. Layout of investigated Danube river section between the oil spill site and the end of Slovak-Hungarian section – part 2.

Oil spill scenarios

In general, spills of oil substances, which can potentially cause contamination of the Danube river water, can be divided into following two groups.

A) minor spills of petrol and fuel oil – from the connecting hose and delivery piping during the tanker filling, or from the suction piping when cisterns are not being filled. In such cases, spill quantities are as follows:

- 98-587 kg of fuel oil, with a total frequency of spill $F = 1.27 . 10^{-3}$ /year – $6.1 . 10^{-4}$ /year
- 35-530 kg of petrol, with a total frequency of spill $F = 1.2 . 10^{-3}$ /year – $3 . 10^{-3}$ /year

B) major spills of petrol and fuel oil – from the mobile tank (vessel)

In these cases, spill quantities are as follows:

- 80-199 t of fuel oil, with a total frequency of spill $F = 4.1 . 10^{-7}$ /year
- 188 t of petrol, with a total frequency of spill $F = 4.1 . 10^{-7}$ /year

3. Evaluation methodology

The impacts of oil spills at the Danube surface water quality in the cases of serious industrial accidents in the given plant were evaluated based on the modelling results.

Two basic concepts of contaminant migration in the surface water were assumed:

1. Film of spilling contaminant will originate at the water surface, as a result of difference in the density of water and contaminant (830/1000 for fuel oil or 750/1000 for petrol). This film will migrate downstream on the Danube water surface. The expected film thickness is less than 1 mm (in the case of minor spills from hoses and pipes) with respect to large surface area of Danube and relatively small spill quantity (approximately 100-600 kg), as well as low viscosity of oil substances and significantly turbulent water flow in the Danube river. Larger thickness of oil substances phase (several mm to several cm) can be expected in the case of spills (approximately 80–200 t).

Resulting effects are influenced with several uncertainties. Seasonal changes of climatic conditions can be considered as the most important. The influence of these conditions was omitted in the model.

2. Partial dissolution of contaminant in the surface water was assumed after the spill, with the rest migrating in the form of phase on the Danube water surface.

Both forms of pollution are transported downstream (advection) and dispersed due to varying flow velocity and diffusion (dispersion).

The estimate of Danube water travel time along the Slovak-Hungarian section represented basic input data for the evaluation of oil substances migration. The end of this section is situated in the river km 1708.5. Travel times were estimated for three selected hydrological situations, which were taken into account in the studies (Szolgay et al., 1994, 1996; Mišík et al., 1994):

- discharge **1140 $m^3.s^{-1}$**, which corresponds to so-called low regulation and navigation water level,
- discharge **5350 $m^3.s^{-1}$**, which approximately corresponds to so-called high navigation water level and
- flood discharge Q100 = 9000 $m^3.s^{-1}$, which corresponds to discharge with a return period of 100 years.

According to the assessment of period 1931-1980, done by the Slovak Hydrometeorological Institute, discharge of 1140 m3.s-1 was exceeded by about 330 days in the average year and discharge of 5350 $m^3.s^{-1}$ by about 3-5 days. Discharge regime of Danube in the Komárno gauging station can be further characterized with the following parameters:

- mean annual discharge in the period 1931-1980: 2290 $m^3.s^{-1}$,
- maximum observed discharge in the period 1931-1980: 8290 $m^3.s^{-1}$ * (17. 6. 1965),
- minimum observed discharge in the period 1931-1980: 660 $m^3.s^{-1}$

Fig. 2 provides information about the occurrence of different discharges in the period 1931-1980 in the average year, up to the value of around 4600 $m^3.s^{-1}$. Site of possible oil spill is located in Komárno, around 200 m upstream from the Váh and Danube rivers confluence (river km 1766.2). Above mentioned studies provided necessary output data in the whole modelled section between Komárno and Szob (river km 1766.2-1708.5). Travel time of water and migrating contaminant (in seconds) in the sub-sections bordered with neighbouring cross-sections of the river, was determined based on the values of average cross-sectional flow velocity for different discharges, according to relation:

$$T = \frac{\Delta L}{0.5(v_1 + v_2)}$$

where:

ΔL – length of partial sub-section, based on the distance of neighbouring cross-sections (m),

v_1, v_2 – average cross-sectional flow velocities in the neighbouring cross-sections ($m.s^{-1}$).

Resulting travel time between the oil spill site (Komárno) and any site situated downstream, on the Slovak-Hungarian section of Danube river, was determined by summarizing of partial travel times.

Travel times between Komárno and any site (determined with river chainage) for three basic discharge conditions (discharge Q in $m^3.s^{-1}$) are given in the Fig. 3. Numerical values of travel time for selected sites at the Slovak side of Danube river are given in Tab. 1. Fig. 4 provides more details on the estimated travel times for selected sites. Using presented graphs, it is possible to estimate travel time between oil spill site (Komárno) and given site also for different discharges than analysed.

The second concept of pollution transport, i.e. migration of dissolved oil substances in surface water, was simulated by means of 1-dimensional model of advection-dispersion transport (Nordin and Troutman, 1980; Hellweger, 2005). The following assumptions were taken into account:

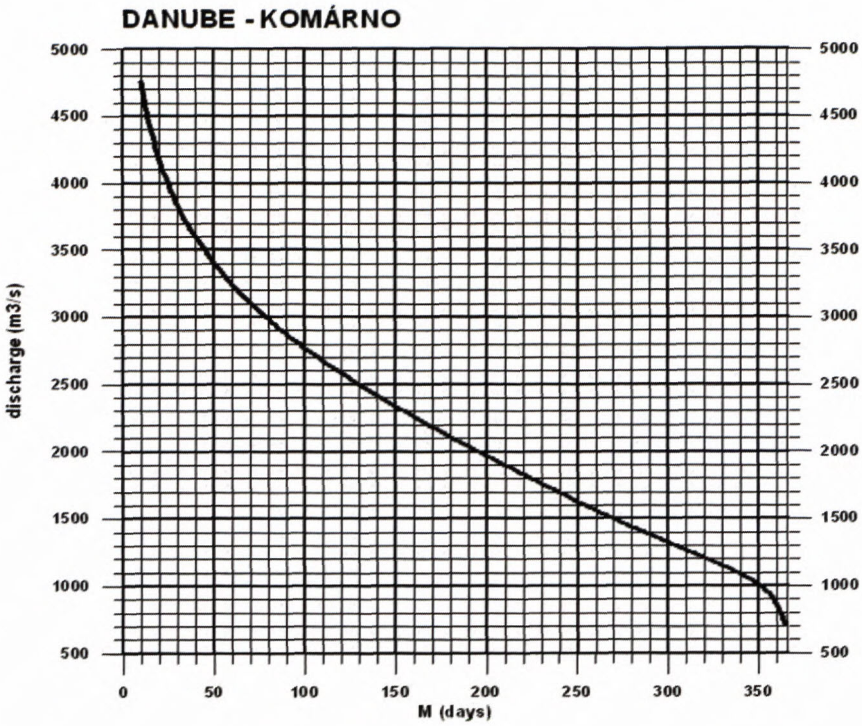

Fig. 2. Occurrence of discharges in the average year – M-days discharges.

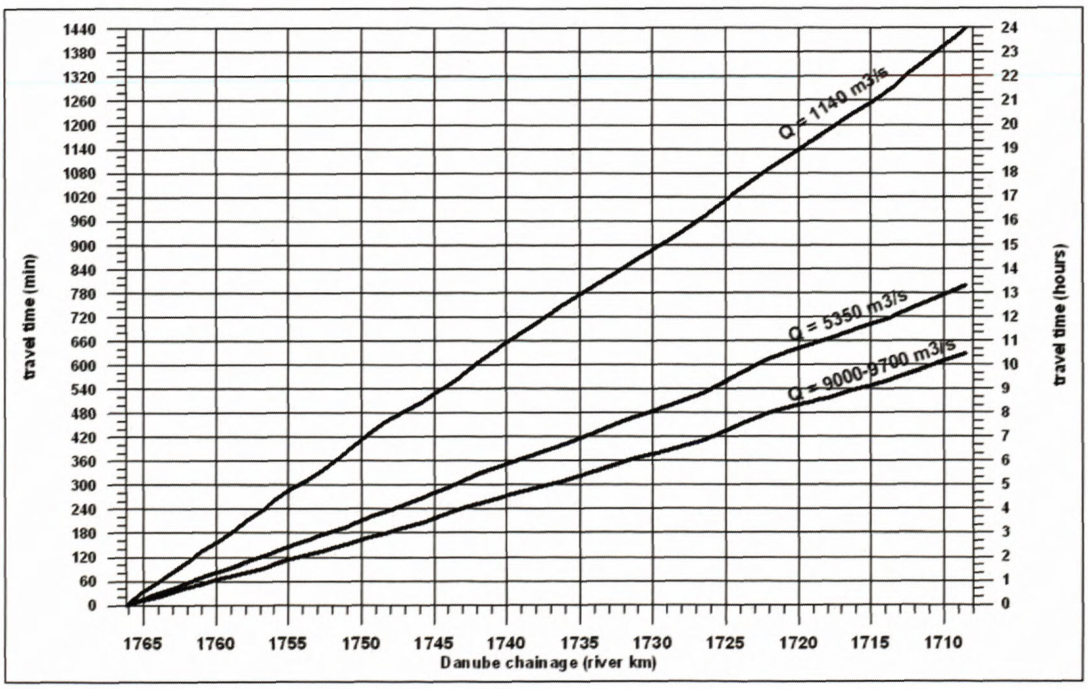

Fig. 3. Travel times of Danube river for different discharges.

- Oil spill site is situated in the active part of river cross-section, not in the so-called dead zone, which does not contribute to flow conveyance (bay, for instance).
- After the spill, petrol or fuel oil will be partially dissolved in the Danube water. Oil pollution will be transported in the form of petroleum hydrocarbons (non-polar extractable substances).
- Pollution will be dispersed gradually in the Danube water as a result of diffusion and flow velocity variability.

No data are available at the Slovak-Hungarian section of the Danube on the experiments to investigate coefficients of both longitudinal and lateral dispersion. Data from real cases of industrial oil spills, which could enable to estimate the coefficients, are not available as well.

In our study, we used published results from the reconstruction of pollution migration at the Somes-Tisza-Danube rivers (Sorentino, 2000; UNEP, 2000; Hellweger, 2005). This accident happened on January 30th, 2000.

Tab. 1. Travel times – sites on the Slovak side of Danube

Site / km from oil spill site	River km	Travel time T (min), Slovak side of Danube		
		Q = 1140	Q = 5350	Q = 9000
Iža, beginning /5.7 km/	1760.5	145	75	60
Iža, end /7.7 km/	1758.5	195	100	75
Patince, beginning /10.2 km/	1756	260	130	100
Patince, end /12.2 km/	1754	310	160	120
Stara Žitava /15.2 km/	1751	385	195	150
Radvaň, beginning /16.2 km/	1750	415	210	160
Radvaň, end /18.7 km/	1747.5	475	245	190
Moča, beginning /20.2 km/	1746	505	265	205
Moča, end /21.7 km/	1744.5	540	290	225
Kravany nad Dunajom, beginning /25.7 km/	1740.5	645	345	270
Kravany nad Dunajom, end /27.2 km/	1739	680	365	285
Štúrovo, beginning /43.7 km/	1722.5	1080	605	470
Štúrovo, end /48.7 km/	1717.5	1200	670	525
Chľaba, beginning /55.2 km/	1711	1365	760	595
Chľaba, end /56.2 km/	1710	1400 23.3 hours	775 12.9 hours	610 10.2 hours

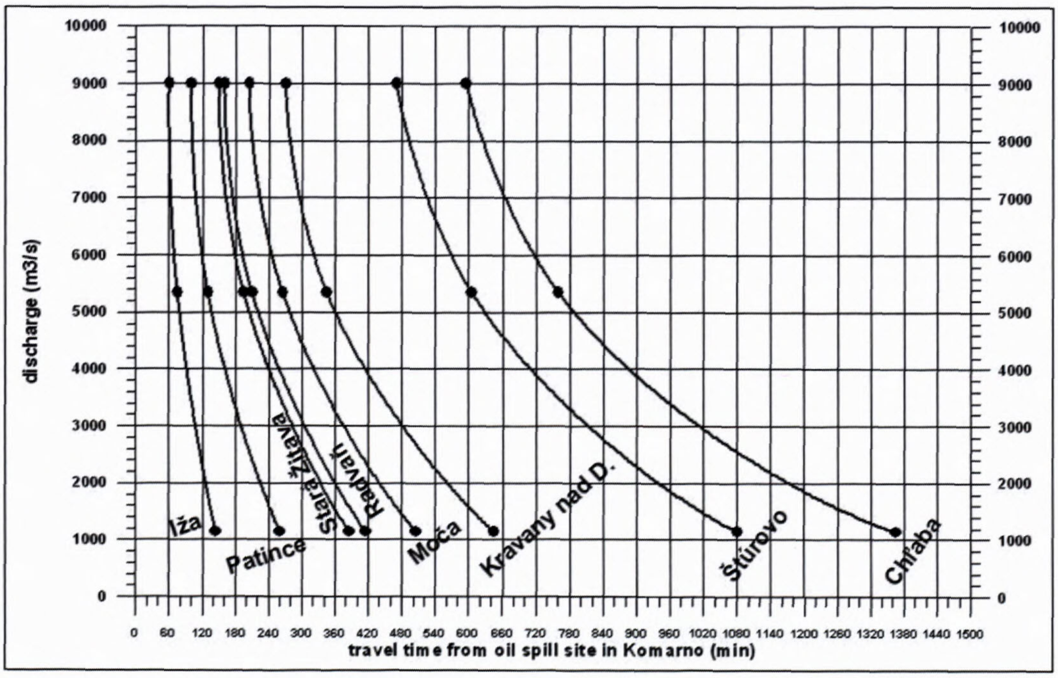

Fig. 4. Travel times for individual sites – Slovak side of Danube river.

The numerical scheme according to Nordin and Troutman (1980) was applied in the calculations, which takes into account influence of river dead zones. Such zones are characteristic with stagnant (or almost stagnant) water and no contribution to flow conveyance – bays, old river branches, meanders, areas behind groynes, etc.:

$$\frac{\partial c_m}{\partial t} = -U\frac{\partial c_m}{\partial x} + E\frac{\partial^2 c_m}{\partial x^2} - K c_m + \frac{\varepsilon}{T}(c_d - c_m)$$

$$\frac{\partial c_d}{\partial t} = -K c_d + \frac{1}{T}(c_m - c_d)$$

c = pollutant concentration [g m^{-3}]
c_m = concentration in the main river channel [g m^{-3}]
c_d = concentration in the dead zone [g m^{-3}]
A_t = area of cross-section which contributes to flow conveyance [m^2] (reach specific)
E = coefficient of longitudinal dispersion [m^2 s^{-1}] (reach specific)
K = pollution decay constant (1st order) [s^{-1}]
T = retention time in dead zone [s]
$\varepsilon = A_d / A_m$ = ratio between dead zones area and cross-section area
$Q = A_t U$ = discharge [m^3 s^{-1}]
M = quantity of spilling pollutant [g]
A_m = cross-section area [m^2]
A_d = dead zones area [m^2]
U = flow velocity [m s^{-1}]

Model HUSKY1, which accounts the influence of dead zones was applied for the numerical solution. Governing equations were solved using the method of finite differences, as published by Hellweger (2005).

Cross-section areas and flow velocities for individual discharges were based at above mentioned hydraulic studies. Dispersion parameters based on river Tisza real case were used in the model of longitudinal migration of pollution - $E=30\ m^2/s$ and $\varepsilon = 0.05$. These values are equal to minimum values recommended by the MIKE 11 software manual (MIKE 11 1-Dimensional Surface water modeling software - Reference manual) for the Danube-type rivers. This model of DHI Water & Environment (Denmark) was applied for the water quality modelling at the Slovak section of Danube in the frame of project Phare EC/WAT/01.

Solubility ratio of oil substances (petroleum, fuel oil) is not known for the Danube river. Available publications indicate only inconsiderable solubility of oil substances in the water. As a consequence, persistence of oil substances in water organisms is not assumed.

Therefore, the following simplified considerations were used in our model:

– *for alternatives of minor oil spills (from suction pipings and connecting hoses in the amount of approximately 35-600 kg of oil substances)* there was assumed dissolution of 5 % of contaminants in 10 % of surface water volume in the given cross-section,

– *for alternatives of major oil spills (from the mobile tankers in the amount of approximately 80-200 t of oil substances)* there was assumed dissolution of 5 % of spilling contaminants in the whole water volume (100 %) in the given cross-section.

Tables 8–10 provide overview of the highest assumed concentration for individual alternatives of oil spills (both minor and major) taking into account average concentration of petroleum hydrocarbons 0.05 mg/l in the profile Danube – Komárno as a background value of concentration (determined from the period 2002-2005).

From the viewpoint of environmental impacts (water and biota), the effects of industrial accidents can be divided according two evaluation criteria:

1) Legislation viewpoint – Appendix Nr. 1 of the governmental Decree Nr. 296/2005, which appoints requirements for quality and qualitative goals of surface waters and limit values of pollution parameters for waste waters and special waters. For oil substances (indicator – petroleum hydrocarbons) it is a concentration of 0.1 $mg.l^{-1}$.

We do not recommend applying this criterion in the given case, as the implementation of the Water Framework Directive 2000/60/ES is currently on the way in the Slovak Republic. Directive will settle new reference limits for physical, chemical and biological quality indicators, separately for individual water bodies (including Danube). The finishing of implementation process is assumed in 2015.

In the frame of WFD implementation in the Slovak Republic the benthic fauna, namely benthic macrovertebrates, benthic diatoms and macrophytes, was used as one of evaluation criterion.

Reference conditions for fishes and phytoplankton had not been settled yet. Until now, ichtyofauna was not a part of the surface waters status evaluation. Comparable data are not available. Therefore, the impact at the water organisms can not be designated clearly.

Tab. 2. Evaluation of surface water quality (Danube) according to petroleum hydrocarbons-UV concentration in 2005 (governmental Decree Nr. 296/2005 and Slovak technical standard STN 75 7221; Mucha et al., 2006)

Micropollutants	**OH** Decree Nr. 296/2005	**STN 75 7221**			
		II.	**III.**	**IV.**	**V.**
petroleum hydrocarbons [mg/l]	*< 0.1*	*< 0.05*	*> 0.05 and < 0.1*	*>0.1 and < 0.3*	*> 0.3*
petroleum hydrocarbons-UV [mg/l]	1x (3530, 1205, 4016, 111, 311, 3739) 2x (109, 112, 308, 309, 2560) 3x (307)	measured values usually ranged from values below detection limit (corresponding with class II) to values representing class III		1x (1205, 4016, 111, 311, 3739) 2x (109, 112, 308, 309, 2560) 3x (307)	1x (3530)

Explanation: (3530) – ID codes of sampling profiles, where limit values were exceeded

Tab. 3. Maximum values of petroleum hydrocarbons$_{UV}$ at the Danube in mg/l (Mucha et al., 2003-2006)

ID	site	1996-2001	2002	2003	2004	2005
109	Bratislava (New bridge, C)	0.10	0.09	0.10	0.13	**0.17**
112	Medveďov (road bridge, C)	**0.37**	0.11	0.17	0.17	0.14
1205	**Komárno (road bridge, C)**		0.13	0.14	0.12	**0.17**
3376	Dobrohošť (intake structure)	**0.63**	0.13	0.11	0.15	0.09
3530	Sap (tailrace canal, LB)	0.35	0.07	0.09	0.13	**0.56**
4016	Dobrohošť (upstream from weir Dunakiliti, LB)	0.05	0.10	0.10	**0.15**	0.11

Note: C - central part of cross-section, LB – left bank

The qualitative data from the summary report of Danube surface waters monitoring from 2005 (Mucha et al., 2006) are summarized in the Tabs. 2-5 for illustration.

The layout of sampling profiles in the frame of Danube water quality monitoring is shown in Fig. 5.

It is evident, that petroleum hydrocarbons concentrations in the range 0.1-0.3 mg.l^{-1} occur 1-3 times a year (from 12 measurements in some profiles). It can be concluded from given facts, that risk of Danube water pollution due to oil spills has to be evaluated keeping in mind existing background values, which are given in Tabs. 3-5.

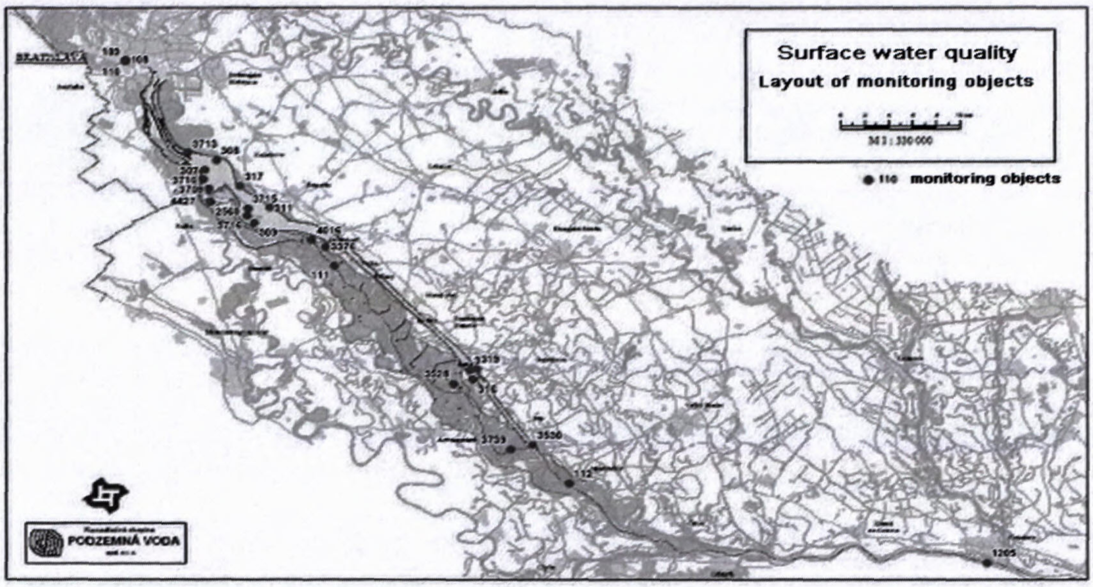

Fig. 5. Layout of monitoring objects.

Tab. 4. Average values of petroleum hydrocarbons$_{UV}$ for Danube in mg.l^{-1} (Mucha et al., 2003-2006)

ID	Site	1996-2001	2002	2003	2004	2005	1996-2005
109	Bratislava (New bridge, C)	0.060	0.040	0.053	0.053	0.075	**0.056**
112	Medveďov (road bridge, C)	0.055	0.040	0.055	0.062	0.043	**0.051**
1205	**Komárno (road bridge, C)**		0.042	0.061	0.048	0.050	**0.050**
3376	Dobrohošť (intake structure)	0.044	0.039	0.042	0.054	0.033	**0.043**
3530	Sap (tailrace canal, LB)	0.043	0.029	0.039	0.053	0.072	**0.045**
4016	Dobrohošť (upstream from weir Dunakiliti, LB)	0.032	0.037	0.031	0.048	0.032	**0.035**

Tab. 5. Occurrence frequency of petroleum hydrocarbons values in the period 1996-2005 (Mucha et al., 2003-2006)

ID	Site	N total	N <0.05 mg/l	N >0.1 mg/l	N >0.3 mg/l
109	Bratislava (New bridge, C)	59	29	8	0
112	Medveďov (road bridge, C)	71	43	10	1
1205	**Komárno (road bridge, C)**	48	28 / 58.3 %	6 / 12.5 %	0
3376	Dobrohošť (intake structure)	120	82	6	1
3530	Sap (tailrace canal, LB)	119	78	5	2
4016	Dobrohošť (upstream from weir Dunakiliti, LB)	77	63	5	0
	Total:	*494*	*323 / 65.4 %*	*40 / 8.1 %*	*4 / 0.8 %*

Tab. 6. (based on the data of Danube river waterboard)

Control profile	*petroleum hydrocarbons UV characteristic value (c_{90}) year 2005 mg.l^{-1}*	*petroleum hydrocarbons UV maximum value (c_{90}) year 2005 mg.l^{-1}*	*petroleum hydrocarbons UV maximum value 01.- 06/2006 mg.l^{-1}*
Danube **Komárno – bridge C, r. km 1767**	0.11	0.17	0.19
Danube **Radvaň LB, r. km 1748**	0.12	0.21	0.15

Monitoring reports provide overview of maximum concentrations of petroleum hydrocarbons$_{UV}$, which are given in Tab. 3 for individual monitoring profiles.

Besides maximum values of petroleum hydrocarbons concentrations, average values for individual profiles (Tab. 4), as well as frequency of significant values occurrence (Tab. 5) are given for the illustration. These data were derived from values published in monitoring reports, taking into account also the values below the detection limit. Detection limit value for petroleum hydrocarbons$_{UV}$ is 0.05 mg.l^{-1}. The concentration values below this limit were considered in the calculation of average as a value of 0.025 mg.l^{-1}

Based on the data given in Tab. 5 and keeping in mind, that sampling is performed once a month, it can be stated that value of petroleum hydrocarbons$_{UV}$>0.3 mg.l^{-1} use to occur once in 10.3 years at the Danube and the values of petroleum hydrocarbons$_{UV}$>0.1 mg.l^{-1} once in 1.03 years. The concentration value of petroleum hydrocarbons$_{UV}$>0.5 mg.l^{-1} occurred once in 20.3 years in the evaluated period of years 1996-2005 (see Tab. 6).

Due to intensive shipment, increased values of petroleum hydrocarbons$_{UV}$ were observed in the period 2005–June 2006 in the monitoring profiles, being situated in our area of interest (Komárno – bridge C, river km 1767 and Radvan LB, river km 1748). Concentration c_{90} (with probability of non-exceedance 90 %) was higher than qualitative limit (0.11 and 0.12 mg/l – see Tab. 6) in both profiles.

Based on above mentioned facts, the concentration values of petroleum hydrocarbons in the range 0.1-0.2 mg.l^{-1} were considered as background values in the given section of the Danube river. It is evident from Tab. 4, that average value (period 2003-2006) of petroleum hydrocarbons concentration 0.05 mg/l can be treated as a background value. This value was also considered in the modelling of accident scenarios.

2) *Eco-toxicological viewpoint* – harmful effects on the water organisms. Published works were used in the evaluation (database of ESIS system - European Chemical Substances Information System and cards of safety data KBU), based on which toxic conditions can be defined with following harmful parameters (indicators):

– concentration of dissolved components in the range from 2–3 mg.l^{-1} up to 8 mg.l^{-1} and higher values,

– occurrence of oil substances phase or oil substances film of larger extent.

4. Discussion

Travel times computed in the first scenario of pollution migration (Tab. 1) represent average values, which were determined, based on simulated average cross-sectional flow velocities. They have to be treated with care, as approximate values. Real distribution of flow velocity in the cross-section is uneven. Maximum flow velocities in the river streamline may differ substantially from the average value. The maximum average cross-sectional velocity simulated at the given section of Danube river in the mentioned studies of Water Research Institute is around 2 m.s^{-1} (river km 1736). Field measurements at the Danube during real floods indicate, that flow velocities higher than 2.5-3 m.s^{-1} were measured locally. On the other hand, flow velocities in shallow parts (usually near the river bank) are much lower than the average value.

More reliable estimate of travel times would require simulations with detailed 2-dimensional numerical model, which provides better information on the flow velocity distribution and flow direction.

Results indicate, that under simplified assumptions (scenario 1) when contaminants (phase or film of oil substance) migrate at the water surface with velocity equal to flow velocity, transport of oil spill pollution into the end profile of investigated river section (river km 1708.5, end of Slovak-Hungarian section, approximately 55.6 km away from the oil spill site) can be expected in the time range from about 23 hours at a discharge 1140 m^3.s^{-1} to about 10 hours at a flood discharge 9000 m^3.s^{-1}. Occurrence of oil spill at a lower discharge can be expected with higher probability. Discharge of 1140 m^3.s^{-1} was exceeded in the given section of Danube river for about 330 days in the average year (evaluated period 1931-1980).

Fast migration of oil substances film in the case of oil spill in the investigated industrial plant, as well as its relatively large impact can be documented with further facts. Pollution – film of oil substances, could reach distance of 6 km in 2.4 hours at lower discharges or in 1 hour during 100-years flood (Q = 9000 m^3.s^{-1}). Details are summarized in Tabs. 1, 2 and 7.

It has to be emphasized, that in this concept contaminant behaves as water molecule. Several characteristics of contaminant are not taken into account, like solubility of solid phase, evaporation of volatile components, contaminant sorption at the suspended load, film fragmentation as a consequence of turbulent flow, as well as emulsion creation. For instance, Pitter (1990) reports fuel oil solubility value of around 6 mg.l^{-1}.

Real migration of oil substances (in the form of film) in the river can differ to some extent from the assumptions. Our model concept does not take into account different characteristics of both evaluated media due to lack of information. It can be assumed, that petrol would evaporate intensively especially in the summer period.

Due to several uncertainties and simplifications, results on the migration of oil substances phase/film in the case of accidental oil spill should be considered as rough estimates.

In the second scenario, where migration of dissolved oil substances was simulated using 1-dimensional model of advection-dispersion transport (Nordin and Troutman, 1980) and (Hellweger, 2005), the results (concentration of petroleum hydrocarbons in mg.l^{-1}) summarized in Tabs. 8-10 were obtained.

River channel morphology was taken into account along the whole evaluated river section (from oil spill site in Komárno down to Chľaba/Szob) based on the results of water level regime modelling for different discharge

Tab. 7. Travel times of pollution along Danube at discharges 1140, 5530 and 9000 $m^3.s^{-1}$.

		Q = 1140 $m^3.s^{-1}$		**Q = 5530 $m^3.s^{-1}$**		**Q = 9000 $m^3.s^{-1}$**	
D (distance from oil spill site)	Site	Travel time					
		min	hours	min	hours	min	hours
cca 6 km	Iža	145	2.4	75	1.25	60	1
cca 10 km	Patince	260	4.3	130	2.2	100	1.7
cca 15 km	Stará Žitava	385	6.4	195	3.2	150	2.5
cca 20 km	Moča	505	8.4	265	4.4	205	3.4
cca 48 km	Štúrovo	1200	20	670	11.1	525	8.8
cca 56 km	Chľaba	1400	23.3	775	12.9	610	10.1

Tab. 8. Maximum values of petroleum hydrocarbons ($mg.l^{-1}$) in Danube, discharge 1140 $m^3.s^{-1}$

Km			**Var. 1a**	**Var. 1b**	**Var. 2a**	**Var. 2b**	**Var. 3a**	**Var. 3b**	**Var. 4a**
from oil spill site	**Site**	**Rkm**	**117 kg FO**	**460 kg FO**	**212 kg P**	**420 kg P**	**180 kg FO**	**587 kg FO**	**163 kg FO**
1.1	Szony	1765	0.096	**0.230**	**0.133**	**0.214**	**0.120**	**0.279**	**0.114**
3.2	Szony	1763	0.076	**0.151**	0.096	**0.142**	0.089	**0.179**	0.086
7.3	Iža - Almasfuzito	1758.8	0.066	**0.114**	0.080	**0.109**	0.075	**0.132**	0.073
11.6	Patince	1754.8	0.063	0.099	0.073	0.095	0.069	**0.113**	0.067
16.8	Radvaň - Neszmely	1749.5	0.060	0.088	0.068	0.085	0.065	0.099	0.063
26	Kravany - Labaztjan	1738	0.058	0.080	0.064	0.078	0.062	0.089	0.061
46	Štúrovo - Esztergom	1720	0.055	0.071	0.060	0.069	0.058	0.077	0.058
55.6	Chľaba - Szob	1710	0.055	0.068	0.058	0.067	0.057	0.073	0.056

Km			**Var. 4b**	**Var. 5**	**Var. 6**	**Var. 7a**	**Var. 7b**	**Var. 8**
from oil spill site	**Site**	**Rkm**	**530 kg FO**	**98 kg FO**	**35 kg P**	**199 t FO**	**79,7 t FO**	**180 t P**
1.1	Szony	1765	**0.257**	0.088	0.064	***7.831***	***3.163***	***7.081***
3.2	Szony	1763	**0.166**	0.071	0.058	***4.412***	**1.795**	***3.991***
7.3	Iža - Almasfuzito	1758.8	**0.124**	0.064	0.055	***2.825***	**1.160**	***2.558***
11.6	Patince	1754.8	**0.107**	0.060	0.054	***2.178***	**0.901**	***1.973***
16.8	Radvaň - Neszmely	1749.5	0.094	0.058	0.053	**1.697**	**0.709**	**1.538**
26	Kravany - Labaztjan	1738	0.085	0.056	0.052	**1.365**	**0.576**	**1.238**
46	Štúrovo - Esztergom	1720	0.074	0.055	0.052	**0.968**	**0.417**	**0.880**
55.6	Chľaba - Szob	1710	0.071	0.054	0.051	**0.835**	**0.364**	**0.759**

Explanations: **0.10** – exceedance of limit concentration 0.1 mg/l in accordance with Act Nr. 296/2005; 2.6 mg/l – toxic effects on water organisms can be assumed; FO – fuel oil, P - petrol

Tab. 9. Maximum values of petroleum hydrocarbons ($mg.l^{-1}$) in Danube, discharge 5350 $m^3.s^{-1}$

Km			**Var. 1a**	**Var. 1b**	**Var. 2a**	**Var. 2b**	**Var. 3a**	**Var. 3b**	**Var. 4a**
from oil spill site	**Site**	**Rkm**	**117 kg FO**	**460 kg FO**	**212 kg P**	**420 kg P**	**180 kg FO**	**587 kg FO**	**163 kg FO**
1.1	Szony	1765	0.077	**0.154**	0.098	**0.145**	0.091	**0.183**	0.087
3.2	Szony	1763	0.064	**0.105**	0.075	**0.100**	0.072	**0.121**	0.070
7.3	Iža - Almasfuzito	1758.8	0.060	0.088	0.067	0.084	0.065	0.098	0.063
11.6	Patince	1754.8	0.057	0.079	0.063	0.077	0.061	0.087	0.060
16.8	Radvaň - Neszmely	1749.5	0.056	0.073	0.061	0.071	0.059	0.079	0.058
26	Kravany - Labaztjan	1738	0.054	0.067	0.058	0.066	0.057	0.072	0.056
46	Štúrovo - Esztergom	1720	0.053	0.062	0.055	0.061	0.055	0.065	0.054
55.6	Chľaba - Szob	1710	0.053	0.060	0.055	0.059	0.054	0.063	0.054

Slovak Geol. Mag., 12, 2 (2006), 103 – 116

Km from oil spill site	Site	Rkm	Var. 4b 530 kg FO	Var. 5 98 kg FO	Var. 6 35 kg P	Var. 7a 199 t FO	Var. 7b 79.7 t FO	Var. 8 180 t P
1.1	Szony	1765	**0.170**	0.072	0.058	***4.568***	***1.857***	***4.133***
3.2	Szony	1763	**0.114**	0.062	0.054	***2.444***	**1.008**	***2.214***
7.3	Iža - Almasfuzito	1758.8	0.093	0.058	0.053	**1.682**	**0.703**	**1.525**
11.6	Patince	1754.8	0.084	0.056	0.052	**1.315**	**0.556**	**1.193**
16.8	Radvaň - Neszmely	1749.5	0.077	0.055	0.052	**1.050**	**0.450**	**0.954**
26	Kravany - Labaztjan	1738	0.070	0.054	0.051	**0.807**	**0.353**	**0.734**
46	Štúrovo - Esztergom	1720	0.063	0.052	0.051	**0.548**	**0.249**	**0.500**
55.6	Chľaba - Szob	1710	0.062	0.052	0.051	**0.487**	**0.225**	**0.445**

Explanations: **0.10** – exceedance of limit concentration 0.1 mg/l in accordance with Act Nr. 296/2005; *2.6 mg/l – toxic effects on water organisms can be assume;* FO – fuel oil, P - petrol

Tab. 10. Maximum values of petroleum hydrocarbons (mg.l^{-1}) in Danube, discharge 9000 $m^3.s^{-1}$

Km from oil spill site	Site	Rkm	Var. 1a 117 kg FO	Var. 1b 460 kg FO	Var. 2a 212 kg P	Var. 2b 420 kg P	Var. 3a 180 kg FO	Var. 3b 587 kg FO	Var. 4a 163 kg FO
1.1	Szony	1765	0.071	**0.132**	0.088	**0.125**	0.082	**0.154**	0.079
3.2	Szony	1763	0.061	0.094	0.070	0.090	0.067	**0.106**	0.065
7.3	Iža - Almasfuzito	1758.8	0.058	0.080	0.064	0.077	0.062	0.088	0.061
11.6	Patince	1754.8	0.056	0.073	0.061	0.071	0.059	0.080	0.058
16.8	Radvaň - Neszmely	1749.5	0.055	0.069	0.059	0.067	0.057	0.074	0.057
26	Kravany - Labaztjan	1738	0.054	0.064	0.057	0.063	0.056	0.068	0.055
46	Štúrovo - Esztergom	1720	0.052	0.060	0.054	0.059	0.054	0.062	0.053
55.6	Chľaba - Szob	1710	0.052	0.058	0.054	0.058	0.053	0.061	0.053

Km from oil spill site	Site	Rkm	Var. 4b 530 kg FO	Var. 5 98 kg FO	Var. 6 35 kg P	Var. 7a 199 t FO	Var. 7b 79.7 t FO	Var. 8 180 t P
1.1	Szony	1765	**0.144**	0.067	0.056	***3.596***	**1.468**	***3.254***
3.2	Szony	1763	**0.100**	0.059	0.053	***1.934***	**0.804**	***1.752***
7.3	Iža - Almasfuzito	1758.8	0.085	0.056	0.052	**1.351**	**0.571**	**1.226**
11.6	Patince	1754.8	0.077	0.055	0.052	**1.064**	**0.456**	**0.966**
16.8	Radvaň - Neszmely	1749.5	0.072	0.054	0.051	**0.861**	**0.374**	**0.783**
26	Kravany - Labaztjan	1738	0.066	0.053	0.051	**0.662**	**0.295**	**0.603**
46	Štúrovo - Esztergom	1720	0.061	0.052	0.051	**0.465**	**0.216**	**0.425**
55.6	Chľaba - Szob	1710	0.060	0.052	0.051	**0.417**	**0.197**	**0.382**

conditions (from low flow to flood flow) in the Danube (Szolgay et al., 1994; Mišík et al., 1994; Szolgay et al., 1996). On the other hand, pollution decay and influence of tributaries (Váh, Hron, Stará Žitava, Ipeľ) were not considered.

5. Conclusion

Travel times computed in the first scenario of pollution migration, when contaminant (oil substances phase/film) migrates at the water surface depending on the flow velocity, represent average values, which were determined by simulated average cross-sectional flow velocities. They have to be treated with care, as approximate values. Real distribution of flow velocity in the cross-section is uneven. Maximum flow velocities in the river streamline may differ substantially from the average value. More reliable estimate of travel times would require simulations with detailed 2-dimensional numerical model, which provides better information on the flow velocity distribution and flow direction.

The results of simulations of contaminant dissolved component migration, presented in Tabs. 8 to 10 and Figs. 6a, b, c and 7a, b, c can be concluded as follows:

- Oil spills from pipelines or hoses (from 35 kg up to 587 kg - further marked as variants 1-6) can be indicated as "minor oil spills", the total occurrence frequency of which ranges in the interval 1.2 . 10^{-3}/year-6.1 . 10^{-4}/year.

- Oil spills from vessels (mobile tanks) (from 80 t up to 199 t - further marked as variants 7-8) can be indicated as "major oil spills", the total occurrence frequency of which is around 4.1 . 10^{-7}/year.

In the cases of "minor" oil spills (from pipelines and hoses) model simulations indicated maximum concentrations of petroleum hydrocarbons in the range of about *0.27-0.06 mg.l^{-1}*, in the distance *around 1.1 km from the oil spill site* (see Fig. 6a, b, c). Concentrations of contaminant decreased gradually with increasing distance from the pollution source, due to dissolution in the water (see Tabs. 8-10). Such values are similar to annual maximums, when comparing with statistical evaluation of Danube water quality (Danube water quality monitoring in the period 2002-2005 – see Tabs. 3-4). In several sections of Danube the maximum values of petroleum hydrocarbons$_{UV}$ concentrations in the range 0.1-0.4 mg.l^{-1}, locally even 0.6-0.7 mg.l^{-1} were recorded every year (Mucha et al., 2003-2006; see Tab.3).

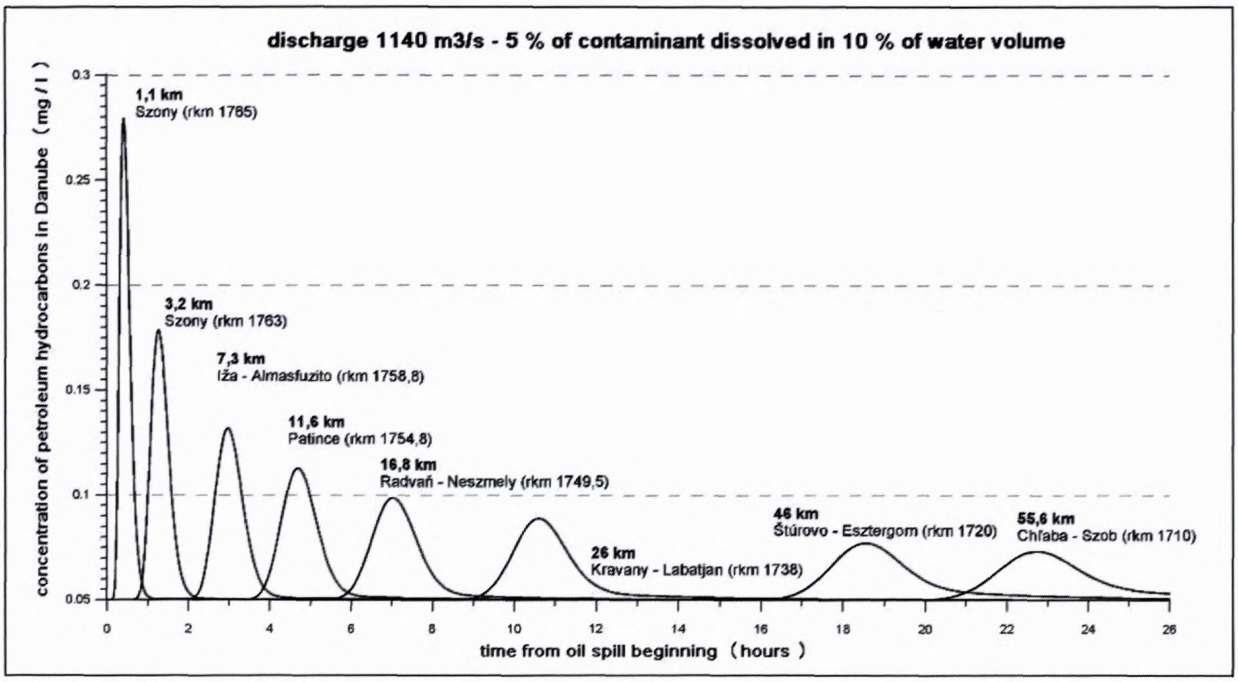

Fig. 6a. Calculated concentrations of petroleum hydrocarbons in Danube as a result of fuel oil spill in the quantity of 587 kg.

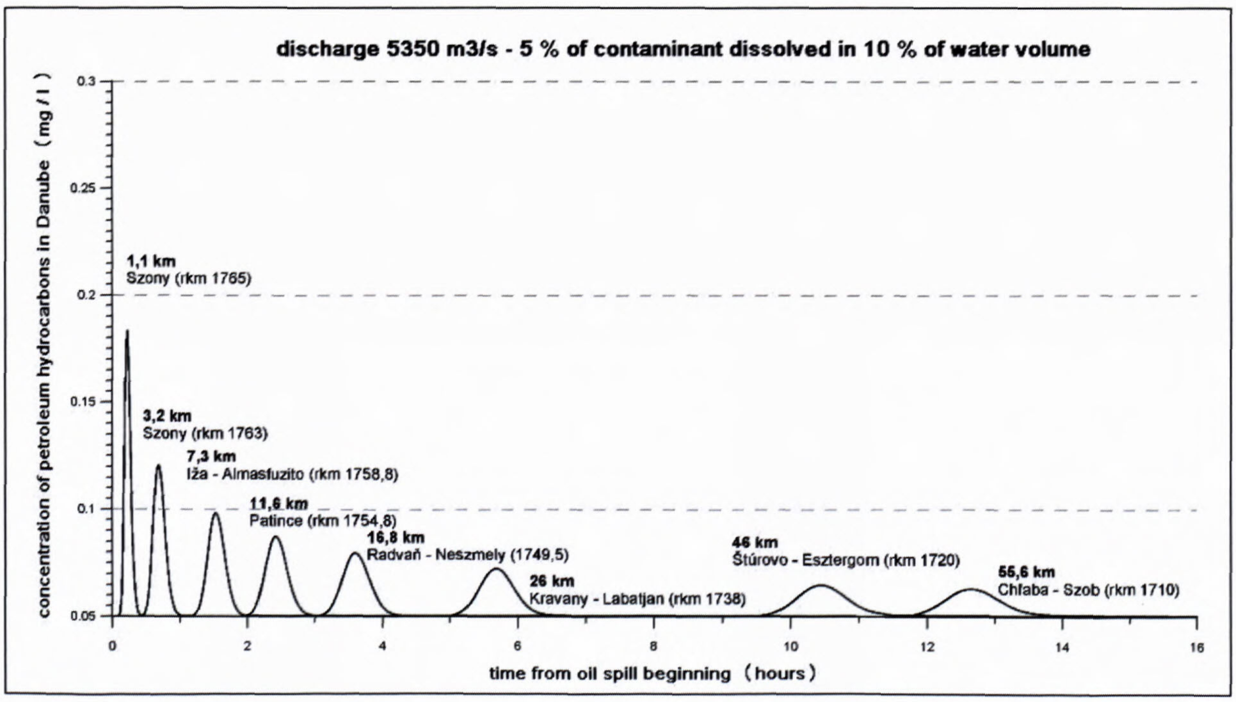

Fig. 6b. Calculated concentrations of petroleum hydrocarbons in Danube as a result of fuel oil spill in the quantity of 587 kg.

Slovak Geol. Mag., 12, 2 (2006), 103 – 116

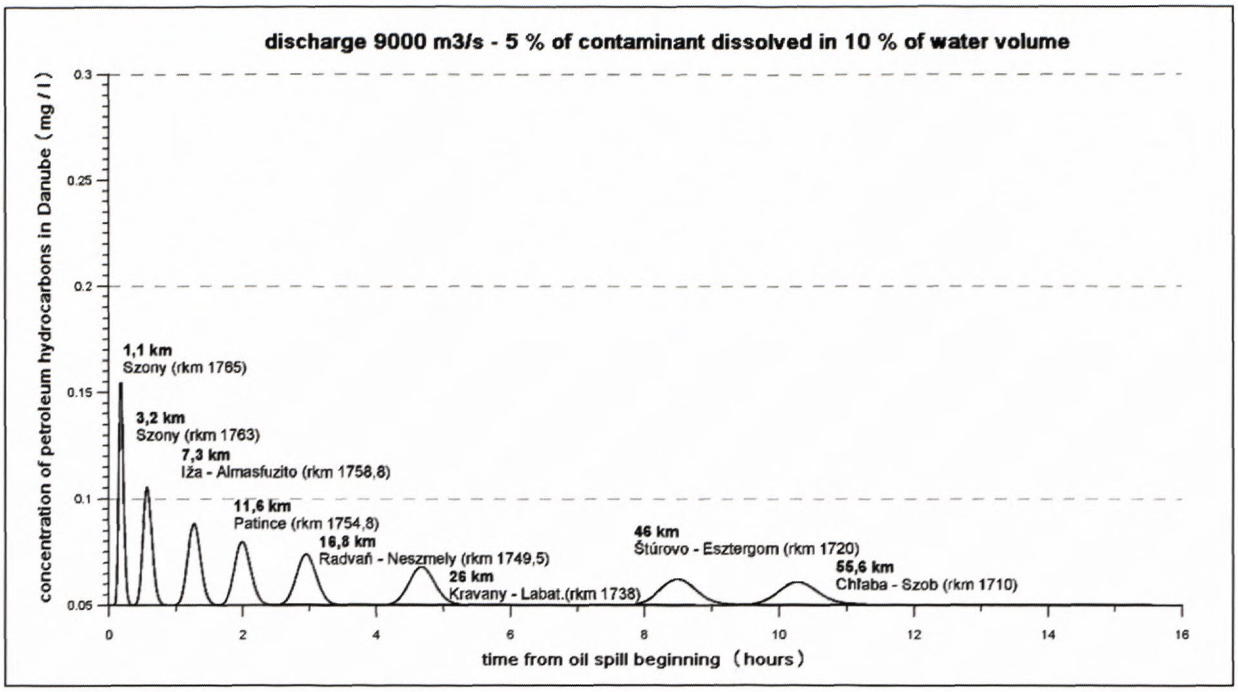

Fig. 6c. Calculated concentrations of petroleum hydrocarbons in Danube as a result of fuel oil spill in the quantity of 587 kg.

In the cases of "minor" oil spills (from pipelines and hoses, quantity of about 35-600 kg of oil substances) total frequency of these events reaches relatively higher values $F=1.2\ .\ 10^{-3}$-$6.1\ .\ 10^{-4}$/year according to the analysis of "failure trees" (Kminiaková and Jelemenský, 2006). Serious harmful effects on water organisms life are not assumed. Values in the range *0.06-0.27* $m.l^{-1}$ (see Tabs. 8-10) are comparable with normal maximum values in each year. Higher concentrations of petroleum hydrocarbons in the order of several mg/l can be expected in the close surrounding (around 500 m) of the oil spill site. Toxic effects of such pollution can not be excluded from considerations.

In the case of this scenario, assuming partial dissolution of contaminant, output concentrations of petroleum hydrocarbons in the ranges 0.05-0.09 mg/l at lower discharges and 0.05-0.07 $mg.l^{-1}$ at higher discharges were achieved (profile Chlaba-Szob, 55.6 km away from oil spill site).

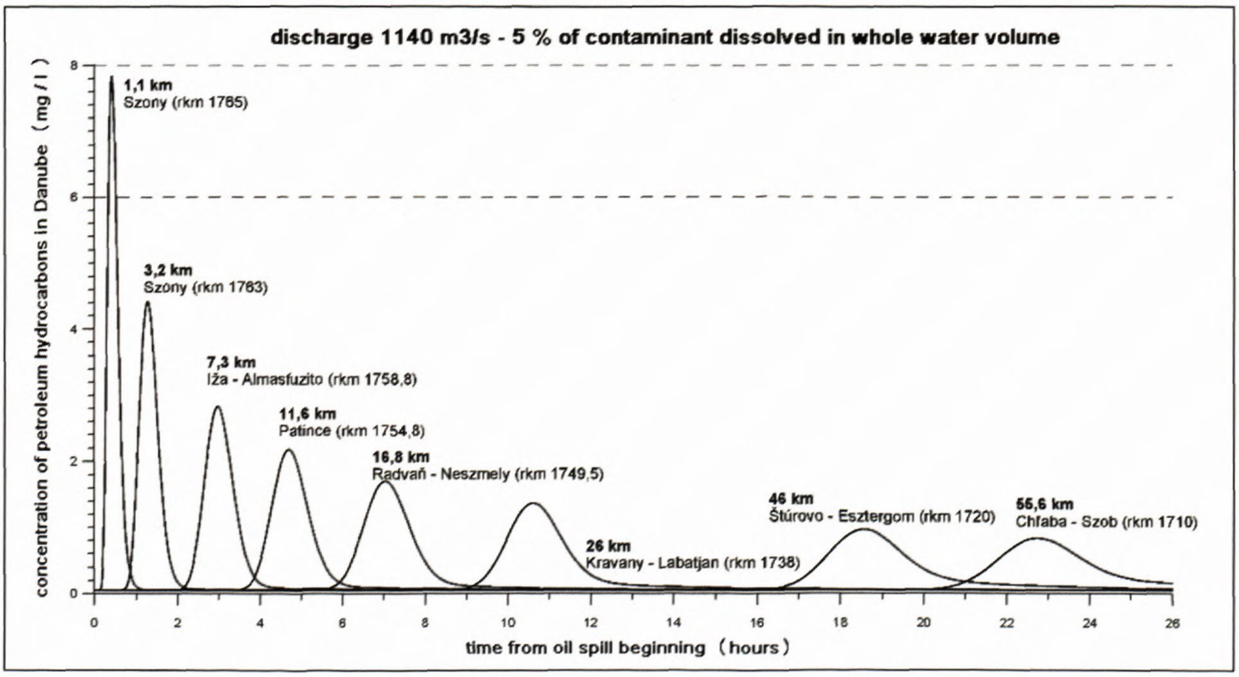

Fig. 7a. Calculated concentrations of petroleum hydrocarbons in Danube river as a result of fuel oil spill in the quantity of 199 tons.

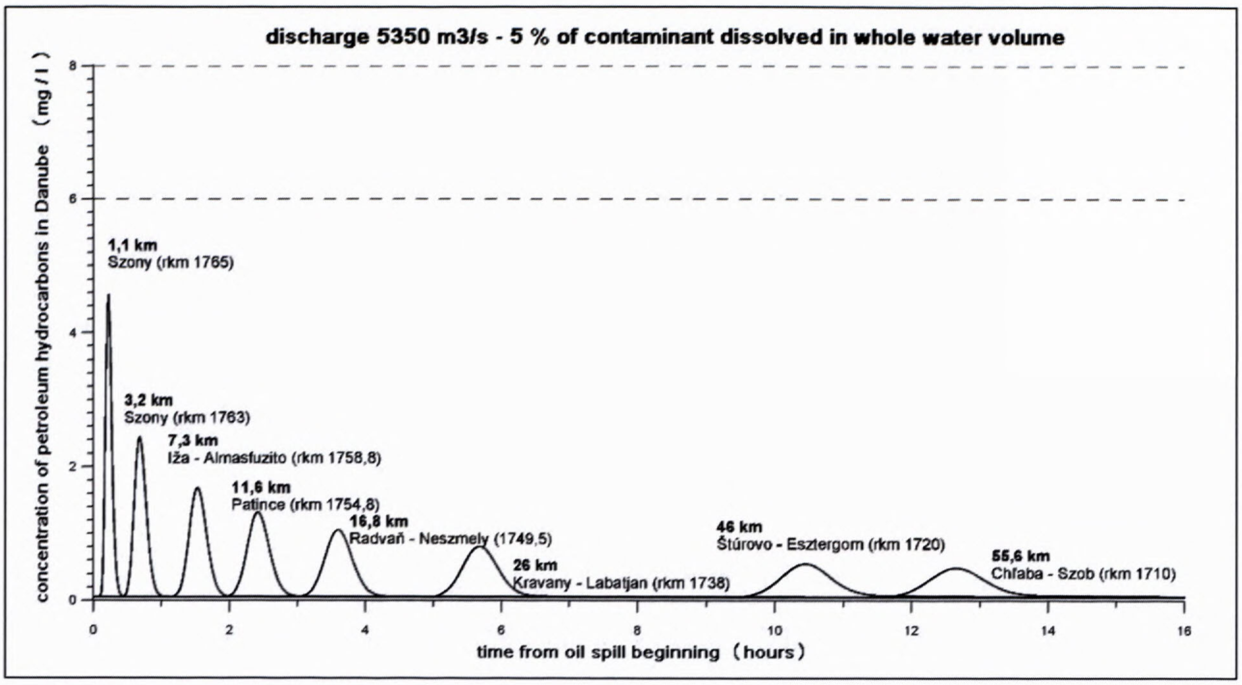

Fig. 7b. Calculated concentrations of petroleum hydrocarbons in Danube as a result of fuel oil spill in the quantity of 199 tons.

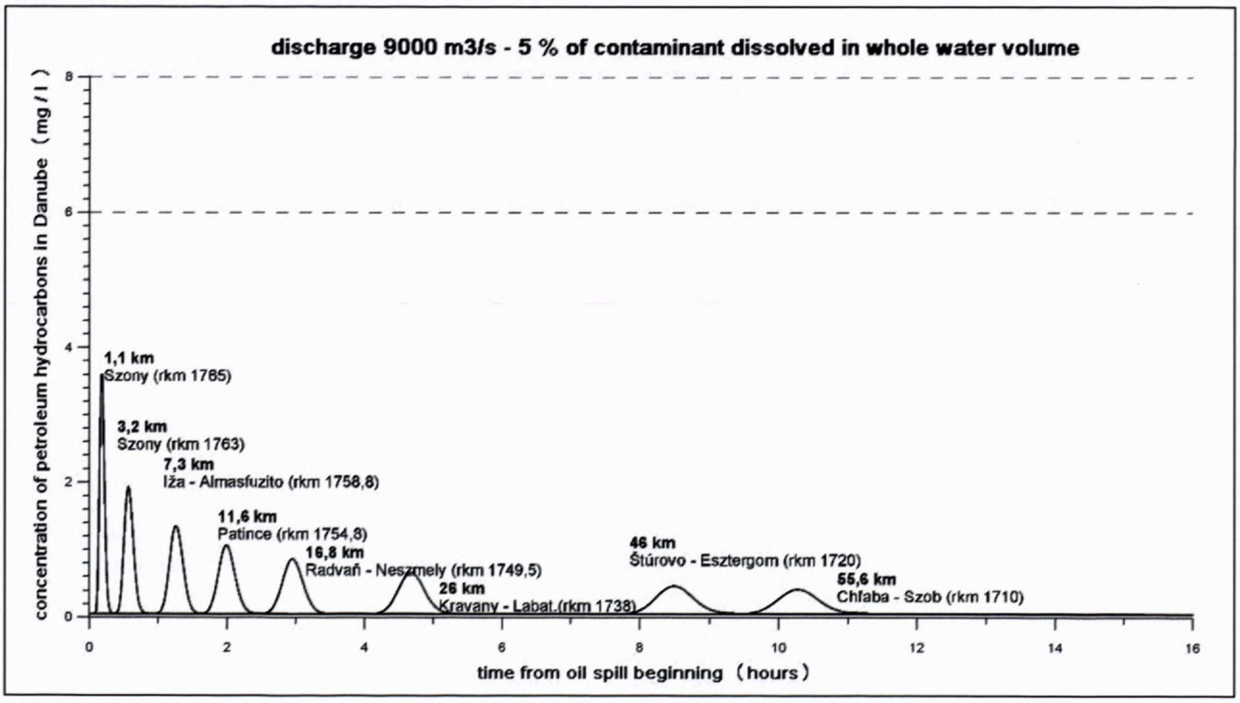

Fig. 7c. Calculated concentrations of petroleum hydrocarbons in Danube as a result of fuel oil spill in the quantity of 199 tons.

In the cases *of "major" oil spills* (from mobile tanks – vessels, assumed quantities 80-199 t) model simulations indicate maximum concentrations of petroleum hydrocarbons in the range 1.5–7.8 $mg.l^{-1}$ at various discharges, around 1.1 km away from oil spill site (see Fig. 7a, b, c). As in the previous cases, concentration will decrease gradually with increasing distance from oil spill site, due to dissolution of contaminant in the water (see Tabs. 8-10). Assuming partial dissolution of contaminant, output concentrations of petroleum hydrocarbons in the ranges 0.36-0.84 $mg.l^{-1}$ at lower discharges and 0.2-0.42 $mg.l^{-1}$ at higher discharges were achieved (profile Chlaba-Szob, 55.6 km away from oil spill site).

Harmful effects of contamination with regard to *assumed toxic impacts at water organisms* (concentrations of petroleum hydrocarbons in the range 2-3 $mg.l^{-1}$ and higher) can be expected:

- in 11 km long river section from oil spill site (profile Patince) at the discharge of 1140 $m^3.s^{-1}$ (petroleum hydrocarbons concentrations in the range 2.0-7.8 $mg.l^{-1}$)

- in 3 km long river section from oil spill site (profile Szony) at the flood discharges 5350–9000 $m^3.s^{-1}$ (petroleum hydrocarbons concentrations in the range 2.0-4.6 $mg.l^{-1}$)
- in the close surrounding of oil spill site (around 500 m) even higher concentrations of petroleum hydrocarbons can be expected.

Total frequency of "major" oil spills in the estimated quantity 80–199 t as a consequence of the mobile tanks (vessels) failure (collision with other vessel, or leakage) is substantially lower than in the case of "minor" spills. Analysis of "failure tree" (Kminiaková and Jelemenský, 2006) indicates that all possible sources of basic failures are of very low probability (frequency in the order $F=n.10^{-7}$ up to $n.10^{-8}$/year), comparable with meteor impact.

It has to be pointed out, that all mobile tanks (vessels) meet all necessary technical requirements for transport and manipulation with dangerous substances (of ADN type), as well as standards according to valid legislation in the field of shipment. Vessels are certified, capable to transport dangerous load of classes III and K1n.

Transport of similar vessels with identical load (petrol, fuel oil) of comparable volume is routine, in concordance with the Agreement on the navigation regime at the Danube river. Agreement was signed on 18th August 1948 in Belgrade and put in force on 11th May 1949 after ratification with member states parliaments. Agreement declared international navigation regime along the whole Danube section between Ulm (Germany) and Danube mouth to Black Sea in Romania (via Sulina branch and Sulina canal).

International navigation safety at the Danube river should be solved in a complex way along the whole river, not only in the form of case studies for individual potential sources of oil substances contamination.

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