Analysis of the transport of cyanide spill on the Tisza River

L. Koncsos and G. Fonyó

Budapest University of Technology and Economics, Department of Sanitary and Environmental Engineering, Müegyetem rkp. 3. UV Building, Budapest, H-1111 Hungary
(E-mail: *koncsos@vcst.bme.hu*; *fonyo@vcst.bme.hu*)

Abstract The present paper deals with the wastewater pond accident in Nagybánya (Romania) in 2000 of which the result was an about 100 tons of highly toxic cyanide spill into the River Tisza. Measurements and laboratory tests were performed during the toxic wave transport. On the basis of this data set mass balance calculations were performed by hydraulic and transport models to investigate and better understand the effect of the accident and to calculate the possible heavy metal sedimentation process in Tisza River bed. This paper deals with calculations for cyanide and copper which are mostly associated to cyanide pollution.
Keywords Cyanide; heavy metal; transport model

Objectives

The accident at the wastewater pond in Nagybánya (Romania) on 30 January 2000 led to the spill of about 100 tons of highly toxic cyanide within approximately half a day (Lakatos *et al*., 2003; Macklin *et al*., 2003). The contamination reached via the River Szamos the Tisza-Danube system and caused damage to the ecosystem never seen before; the consequences and the time of restoration are not yet known. The cyanide pollution was associated with heavy metals, primarily copper and zinc. The case (and its evaluation) was further complicated by snow melting and rainfall, and temporal changes in water level and the streamflow resulting.

The primary objective of the present assessment is to perform on the basis of observations available detailed mass balance calculations by using hydraulic and transport models, and to estimate – for various cross sections of the River Tisza – the amount of pollutants transported in the water phase and that portion which might be deposited in the sediment. The latter plays a crucial role from the viewpoint of long-term impacts.

Methodology

Data and information

The river system studied is illustrated in Figure 1. This includes those cross sections for which water level, streamflow and water quality observations were available for the period in question.

Flow data are known on a daily time scale also for tributaries (for a more detailed assessment hourly data are also accessible), while the frequency of water quality data varies from section to section as sampling more or less followed the transport of the accidental pollution. Accuracy of the data may vary since analyses were performed by different laboratories (and in the case of frequently applied quick tests results also had to be utilized). This fact should be stressed since the total amount of the cyanide (or copper) spilled into the river system is only known roughly. One of our goals is to refine the estimate on the basis of Tisza observations performed, while the main question is to determine longitudinal changes of the amount of pollutants in the water phase. We note that morphological data obviously needed for our analyses were available for the entire Hungarian stretch of the Tisza River.

Water Science and Technology **Vol 50 No 5 pp 101–107** © 2004 IWA Publishing and the authors

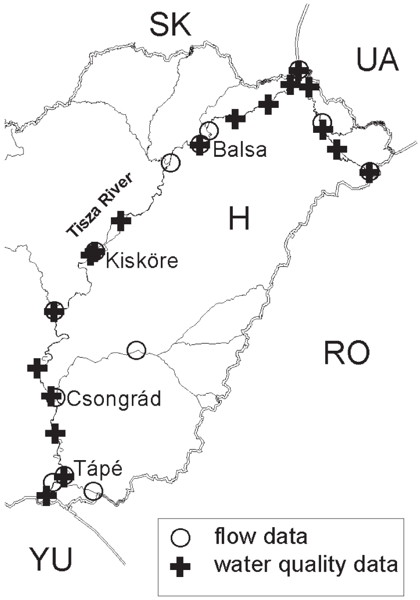

Figure 1 Hungarian section of River Tisza. Regular flow rate monitoring points and cyanide concentration sampling points for the January 2000. accident are marked

Hydraulic computations

The fate of the pollutants is basically determined by longitudinal and temporal changes of the cross-section mean velocity. As the spill accident happened approximately 200 km upstream, at the Hungarian border section the cyanide contamination has completely mixed in the cross-section. Therefore a 1D description can be applied for the transport of the cyanide wave (Eq. (3)) of which the hydraulic part was solved first. For the 1D transport derivation the unsteady Saint-Venant equation was applied (the use of the full equation was suggested by the available period of short time) (Chalfen *et al.*, 1986) as follows:

$$\frac{\partial Q}{\partial x}+\frac{\partial A}{\partial t}-q=0 \tag{1}$$

$$\frac{\partial z}{\partial x}+\frac{\alpha' Q^2}{gA^3}\frac{\partial A}{\partial x}-\frac{\alpha'' Q}{gA^2}\frac{\partial A}{\partial t}+\frac{\alpha' Q}{gA^2}\frac{\partial Q}{\partial x}+\frac{\alpha''}{gA}\frac{\partial Q}{\partial t}+\frac{Q^2}{K^2}=0 \tag{2}$$

where:

Q water discharge
A cross section area
x coordinate
t time
z absolute height of water surface
g gravity acceleration
α', α'' dispersion coefficients for the impulse transfer
$K = AcR^{(1/2)}$
c Chezy coefficient
R hydraulic gradient

The numerical solution for (Eq. (1)) and (Eq. (2)) was the double-sweep method (Chalfen *et al.*, 1986). Boundary conditions were obtained from daily observations of discharge and water level, see the monitoring network in Figure 1. For a given river stretch (between two subsequent cross sections with observations) the upstream condition was discharge (Q) while the downstream condition was water level (h) data time series. The above approximation gives good agreement between observations and computation. Roughness coefficient of the model was estimated for each river segment by using literature experiences, as well as flow and water level data.

Transport of the pollutant wave

Assuming complete mixing, transport of the pollution can be described by the well-known 1D transport equation (Somlyódy, 1985; Somlyódy *et al.*, 1985). We note that under the given hydraulic conditions the mixing length of the Tisza River can be estimated as about 10 km for tributaries, which can be neglected in comparison to the total length of the river investigated. Additionally the intensive mixing does not allow significant non-uniformities in water quality downstream to tributaries (minor discrepancies can occur in the computation of the pollution wave transport due to the peak operation mode of the Tiszalök Barrage and three dimensional impacts of the Kisköre Reservoir not necessarily reflecting properly by a 1D approach; see later) (Fontaine, 1983). The 1D convection-dispersion equation can be written as follows:

$$\frac{\partial(AC)}{\partial t}+\frac{\partial(AvC)}{\partial x}=\frac{\partial}{\partial x}(D_L A\frac{\partial C}{\partial x})-kAC \tag{3}$$

where

C	cross section average concentration
D_{L}	longitudinal dispersion coefficient
v	longitudinal velocity
k	retention coefficient

The last (first order kinetic) term on the right hand side of the equation expresses that due to deposition or adsorption the amount of contamination may vary longitudinally. If, for instance $k = 0$ (or it is small) the pollutant behaves as a conservative one. If $k > 0$, retention takes please, while in the opposite case there is a release, primarily from the sediment.

The dispersion coefficient can be estimated from empirical relationships:

$$D_{\mathrm{L}} = k_1 Ru \tag{4}$$

and

$$D_{\mathrm{L}} = k_2\,(v^2 B^2/Ru), \tag{5}$$

where:

u	bottom shear velocity (to be derived from hydraulic computations)
R	hydraulic radius (approximately equal to the mean depth),
k_1 and k_2	parameters.

Due to linearity the solution of the 1D equation (Eq. (3)) between two neighboring cross sections can be obtained by convolution (see Eq. (8)), from a sequence of analytical solutions: on the basis of the principle of superposition the wave of a "length" of T can be composed of point sources of Δt duration shifted by time, τ. For each of the point sources the well known Gaussian solution (Somlyódy, 1985) can be applied. The result of the convolution is as follows:

$$C = \sum_{i=1}^{n} \frac{M_i \Delta t}{2A(\Pi D_x (t-(i-1)\Delta t)^{1/2}} \exp(\frac{-(x - v\ \ (t-(i-1)\Delta t))^2}{4D_x (t-(i-1)\Delta t)}) \tag{6}$$

where:

M	mass load during a given period of time
i	index
Δt	time step
$t = \Delta x / u$	travel time between subsequent cross sections

Water quality components

Two parameters are investigated: cyanide and copper (see Figures 2, 3, 4 and 5). Parameters were estimated for both reach by reach (dispersion and retention coefficients). Our hypothesis is that cyanide remains completely in dissolved phase which is due to forming a complex with copper. As a result of release from the sediment, the amount of copper probably increases longitudinally (k<0).

Calibration of the model system

The roughness coefficient of the hydraulic model was estimated by fine tuning. Dispersion and retention coefficients were estimated for both cyanide and copper observations by a Monte Carlo method based optimization (Koncsos, 1994). First estimates were made from cross section to cross section, which step was followed by a calibration for the entire river system. The retention coefficients and dispersion coefficient (D_L, k_1 and k_2) were calculated for cyanide and copper separately, and jointly alike. A D_L related sensitivity analysis was performed since its estimation is becoming increasingly uncertain as the gradient is diminishing.

Results and discussion

Hydraulic model

Without discussing any details we note that roughness coefficients were in agreement with literature data. (Manning coefficient falls in the range of 35–45 $m^{1/3}/s$). The calibration of the model is successful and it describes well water level, velocity and travel time conditions of the period studied. The latter one is the main input of calculating convolution and retention of the transport model.

Transport of cyanide and copper waves

The comparison of observed and computed cyanide concentrations can be seen in Figure 2. Figure 3 demonstrates the same for copper.

Both Figure 2 and Figure 3 show temporal variations for two subsequent cross sections from upstream to downstream. The initial section for cyanide was Tunyogmatolcs at the River Szamos, while the last one Tapé close to Szeged (Csenger and Csongrád for copper). All the results were obtained by using solely the measured initial upstream condition, i.e. no updating was made on the basis of observations. An exception was the Kisköre section where monitoring showed a somewhat skewed pattern than the calculations. Nevertheless, from a practical viewpoint the difference is not significant. Figure 4 and Figure 5 summarize the model results for all the examined Tisza River sections.

From the figures and analyses performed we draw the following conclusions:

1. The average longitudinal dispersion coefficient is 60–70 m^2/s, which is in agreement with Eqs (4) and (5). Parameter estimates obtained via optimization are somewhat uncertain for the downstream river reach due to the small concentration gradient already referred to. Cyanide and copper led to similar values;

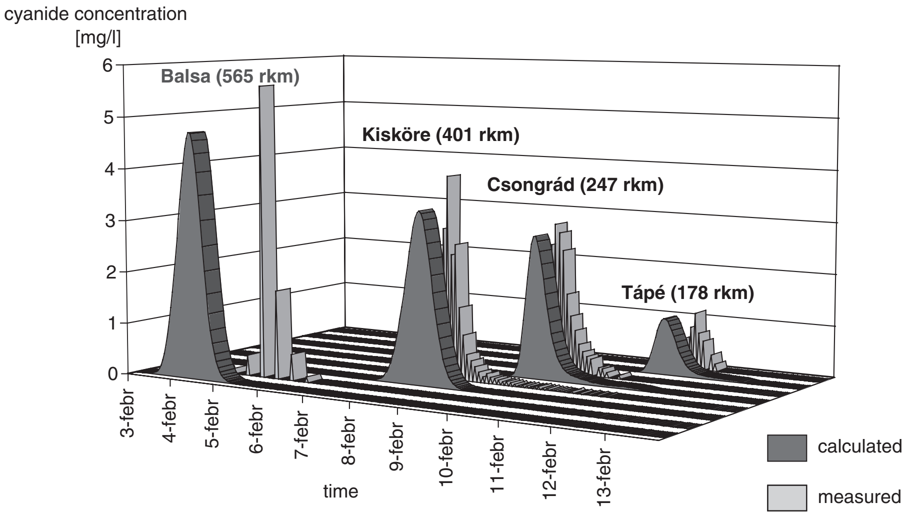

Figure 2 Measured and calculated cyanide concentrations of the January 2000 accident for River Tisza sections. River kilometres are marked in brackets

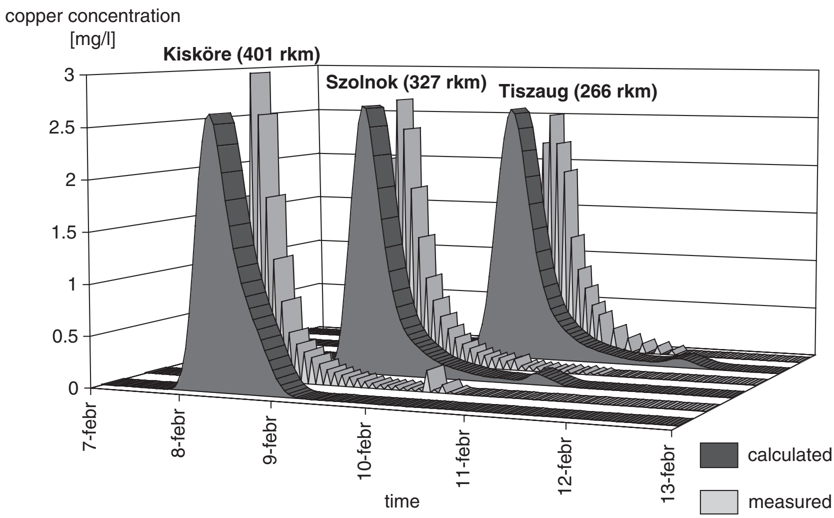

Figure 3 Measured and calculated copper concentrations of the January 2000 accident for River Tisza sections. River kilometres are marked in brackets

2. The retention coefficient was $k = 0$ practically for all the cross sections for cyanide: the pollutant behaves as a conservative one and remains in water;
3. The same statement does not apply for copper: the value of k is negative in most of the cases (– (0.05/d–0.1/d)) and it is never positive. It is likely that copper enters the water phase from the sediment (its rate varies longitudinally while its total extent can be approximated to about 30%) and enhances the formation of the dissolved cyanide complex;
4. The agreement of observations and computations – taking into account frequency and uncertainty of data, as well as overall difficulties of capturing concentration peak values – can be evaluated – in the light of the literature – as very good.

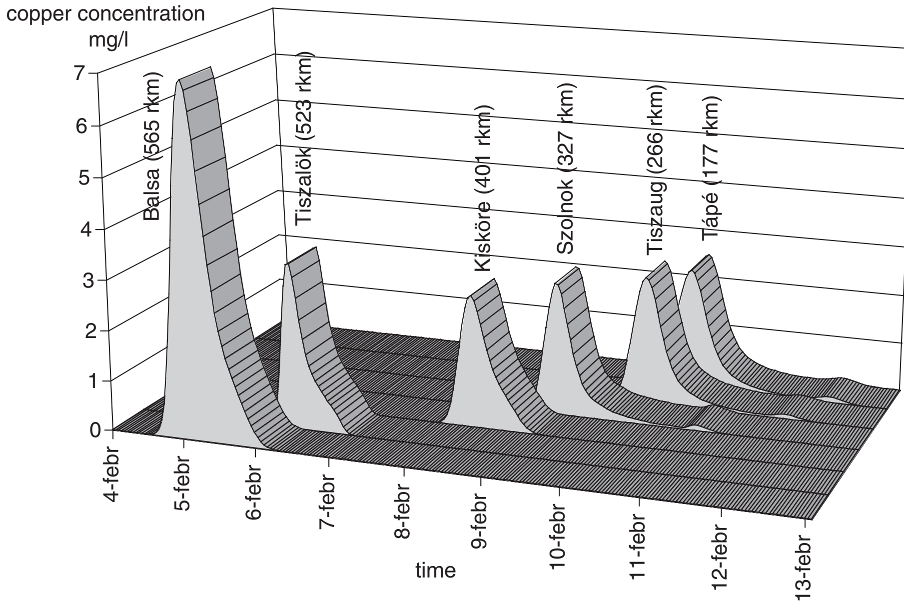

Figure 4 Calculated cyanide concentrations of the January 2000 accident for River Tisza sections. River kilometres are marked in brackets

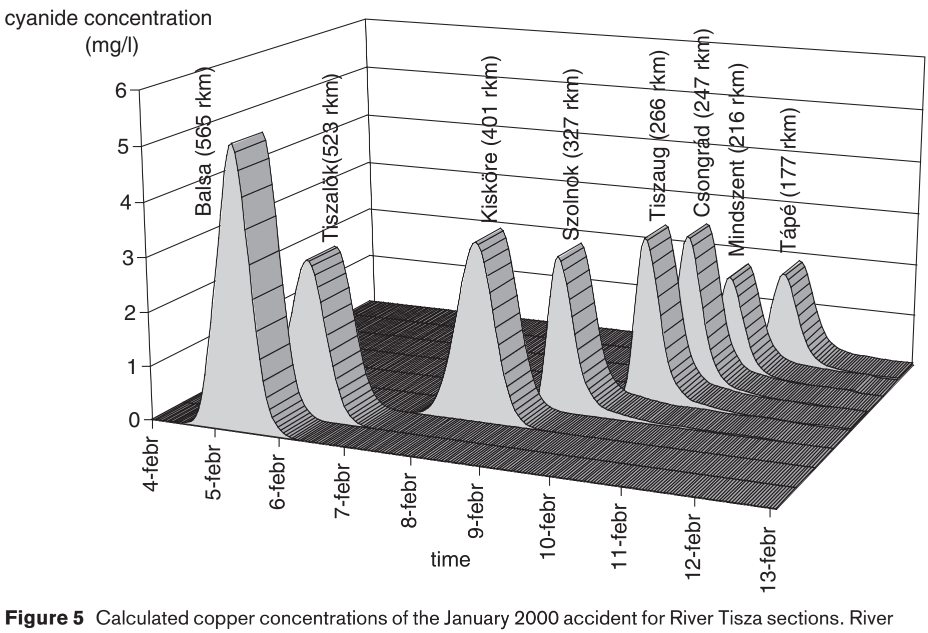

Figure 5 Calculated copper concentrations of the January 2000 accident for River Tisza sections. River kilometres are marked in brackets

Conclusions

On the basis of analyses performed we draw conclusions as follows

1. Following calibration the unsteady hydraulic model applied to subsequent river stretches characterizes well the observed changes of water level, velocity and travel time;
2. The 1D transport model describes well the fate of cyanide and copper along the Tisza River. Parameters of the model can be satisfactorily estimated on the basis of observations and literature. The linked hydraulic-transport model can be well applied in the

future for predictive purposes and the design of monitoring and early warning, as well as emergency and control actions;

3. Cyanide behaves practically as conservative material. It remains in the water (its amount is about 105–110 t) and does not accumulate in the sediment. This was proved by on-line measurements and by the monitoring activity, which is continuously on going since the accident. There is no remaining cyanide in the sediment. The likely explanation is that it forms a complex with copper. The amount of the latter increases longitudinally, due to the probable release from the sediment (the retention coefficient is negative). On the other hand the spill accident happened in wintertime when the low temperature decreased considerably the biochemical activity in the water phase. The kinetics of the process is not yet known;
4. Water quality observations exhibit a number of shortcomings. Some of the values are hard to interpret (e.g. longitudinally increasing peak concentration). Upstream to the Kisköre Reservoir – where relatively little time was available for the preparation of the monitoring plan – sampling frequency was not all the time satisfactory and/or sampling did not cover the duration of the pollution wave in the particular section (here sometimes analytical problems can be suspected, too);
5. From the viewpoint of long term ecological and water quality impacts it is favorable that the cyanide contamination traveled through the Tisza system without accumulation in the sediment. The same can hardly be stated for subsequent heavy metal spills of the past two months also originating from Romania where significant deposition is suspected which can be a serious source of future risks. For this reason it is strongly recommended to perform similar assessments as illustrated here.

References

Chalfen, M. and Niemiec, A. (1986). Analytical and numerical solution of Saint-Venant equations. *Journal of Hydrology*, **86**(1–2), 1–13.

Fontaine, T.D. (1983). Application of risk and uncertainty analysis techniques to a heavy metal specification model. *Ecological Modelling*, 1983/1984, 22, No. ¼, pp. 101–108.

Koncsos, L. (1994). REWARD User Manual, Ruhr University, Bochum.

Lakatos, Gy., Fleit, E. and Mészáros, I. (2003). Ecotoxicological studies and Risk assessment on the cyanide contamination in Tisza river. *Toxicology Letters*, 140–141, pp. 333–342.

Macklin, M.G., Brewer, P.A., Balteanu, D., Coulthard, T.J., Driga, B., Howard, A.J. and Zaharia, S. (2003) The long term fate and environmental significance of contaminant metals released by the January and March 2000 mining tailings dam failures in Maramures County, upper Tisza Basin, Romania. *Applied Geochemistry*, **18**, 241–257.

Somlyódy, L. (1985). Mixing of pollutants in rivers (in Hungarian). *Vízügyi Közlemények*, **2**, 186–201

Somlyódy, L., Licsko, I., Fehér, J. and Csányi, B. (1985). Investigation of the cadmium pollution of the Sajó river (in Hungarian). *Vízügyi Közlemények*, **67**(1), 7–35.