## Evaluation of Risk Zones Over a River Pathway, Downstream a Release Point, Under Seasonal Pollutant Biodegradability

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Original scientific paper Received: January 26, 2006 Accepted: May 26, 2006

In order to simulate the scenario of an accidental pollutant release in a river pathway, and to evaluate the pollution risk downstream the source, an advective-dispersive stationary model has been used. By accounting for the recorded data on the water quality parameters over one year, and for the seasonal variation of the pollutant biodegradability, the model prediction accuracy has been improved. By applying a probabilistic analytical method, that includes the release statistics from a municipal wastewater treatment plant (WWTP), together with the dispersion model predictions, the risk zones along the river are identified for every month of the year. The probabilistic analysis can be used to derive site-specific assessments and can support the WWTP failure prevention measures.

Key words:

Risk assessment, pollutant riverine dispersion

### Introduction

Municipal wastewaters contain a large variety of contaminants (organic, inorganic, micro-organisms, suspended solids), coming from variate sources and presenting important fluctuations, both in flow-rates and composition. A WWTP is a dis design to remove all pollutants and to improve the water quality quantities, i.e. pH, turbidity, dissolved oxygen ( $\gamma_{02}$ ), temperature, hardness, suspended solids, and chemical/biological compounds (organics, inorganics, oil & greases, toxics, belonging to (non-)conventional or priority chemicals classes).<sup>1</sup> The pollutant mass concentrations (or loads) in the WWTP effluent have to conform to the current regulations on maximum admissible values (e.g. the Romanian national NTPA<sup>2</sup>).

A classical WWTP consists of a series of sections: primary (mechanical and chemical), secondary (biological) and, in modern configurations, a tertiary (advanced) pollutant treatment. The most important and sensitive is the biological treatment on an acclimatised activated sludge, on coupled aeration basin – sludge settler interconnected units. This step is able to remove organics (BOD<sub>5</sub>) and inorganic pollutants from wastewaters, with the expense of higher costs than other steps, because of the need to supply molecular oxygen (air) to the micro-organisms, using energy-intensive mechanical aerators.

The biological treatment step is very sensitive to input-flow oscillations, operating conditions and biomass evolution. That is because the removal of pollutants is achieved through a combination of biological metabolism, adsorption, and entrapment in the suspended biological flocks, i.e. a complex process of low flexibility, slow kinetics following the influent characteristics, fluctuating over the year seasons, and lacking of reproducibility. Sudden increases in substrate concentration, some inhibitory substances, deterioration of the biomass, inadequate mixing, or low operating flexibility of the aerator-settler unit, all these can lead to a difficult process control and can increase the risk of an accidental release.<sup>3-6</sup> WWTP risks, related to the influent over-loading (exceeding the plant processing capacity) or biomass degradation can be minimized by using a complex (effective) treatment schema, an adequate control, intermediate storage tanks, design precautions, etc. For instance, several constructive and operating solutions have been implemented:<sup>1,3,7</sup> (i) the use of sequential WWT-units to enhance bio-transformation, by accumulating the desired micro-organisms via operation modes, alternating oxic (aerobic AE), anaerobic (AN) and anoxic (AX) cycles; (ii) improve WWTP flexibility by using a complex removal schema involving serial-parallel AE, AX, AN clarifiers, interconnected via multiple sludge / mixed liquor recycling loops; (iii) integration of chemical and biological processes for inducing an increased bio-availability by means of a pre-

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liminary chemical oxidation of recalcitrant or inhibitory compounds; (iv) improvement of the WWT-bioreactor performance by means of suitable constructive solutions (e.g. high-rate biofilms, membrane bioreactors); (v) advanced operating control policies,<sup>6–8,10–13</sup> complex AE, AN, AX operating cycles<sup>9</sup> in multi-unit optimised systems.<sup>7,14</sup>

In spite of the mentioned modern solutions, the WWTP safe operation still remains a critical issue. The probability of an accidental WWTP failure has to be considered in all risk assessments, accounting for receptors (usually a river), past failures causes and frequency, pollution magnitude, and dispersion area.<sup>15</sup> Simulation of an accidental discharge scenario over the river control section, combined with a probabilistic failure analysis, is an important part of any WWTP risk analysis.

The present study aims at exemplifying the methodology to simulate an accidental release scenario in a riverine receptor (of known characteristics) from a WWTP, and to construct the so-called Limit State Functions (LSF) associated with the violation of polluting constraints over a certain river control section, downstream the release point. By introducing the random variables, and defining the risk as the probability that a given location hazard exceeds a set of defined limits, the LSF-functions are then re-calculated in probabilistic terms together with the 'probability of failure'  $(P_f)$  and risk contours over the river control section. The paper also illustrates how the analysis accuracy can be improved by using recorded river-water quality data, and by accounting for the seasonal variation of pollutant biodegradability in the advective-dispersive model.

### **Risk assessment measures**

Risk assessments are already routine methods to evaluate the failure probability of an engineering system. The risk is usually defined as the product between the failure probability ( $P_f$ ) and the consequences of a future event. Generally, the 'risk' is a quantifiable measure of the 'safety' of a system and, because it refers to a future (possible) event, it is subjected to uncertainties being always defined in probabilistic terms. The system reliability (R) is defined as the probability that the 'system stress' (inducing the failures) will not exceed the 'system strength' (capacity to resist to failures), and  $R \le 1 - P_f$ .<sup>16,17,20</sup>

Risk assessment usually uses two classes of methods: sampling or analytical probabilistic methods.<sup>17–20,29</sup> Analytical techniques (namely, the first-order FORM, and the second-order SORM reliability methods) use the first- and second mo-

ments of the random variable distribution to evaluate the nonlinear LSF and  $P_{\rm f}$ . This probabilistic structural analysis of the system needs simulation of the process by means of a mechanistic or an empirical model (e.g. neural networks, adaptive interpolation). The random sampling methods, such as Monte-Carlo, stratified sampling (e.g. Latin Hypercube sampling), importance sampling, and adaptive importance sampling replace the continuous average of the uncertainty variable (u) by a discrete approximation using a large number of process simulations. Because the computational effort is often prohibitively large, some variants try to improve the accuracy by keeping a reasonable computational level, by explicitly accounting for the system reliability sensitivity vs. independent variables, or by applying an adaptive sampling.

In the analytical methods (approached in this paper), one starts from definition of *n*-dimensional random variable vector **u** on which the system performance and risk depend (e.g. discharged flow-rates and WWTP operating parameters causing the river pollution). If a normally distribution is assumed, the system uncertainty models can be based on the known means  $(\mu_{u_i})$  and standard deviations  $(\sigma_{u_i})$  of variables u (e.g. determined from the WWTP accidental release statistics, if any). The advantage of such an approach in estimating the system reliability is that it only depends on the first and second moment properties of individual random variables and not on their distribution type.<sup>17</sup> The disadvantage is that, for non-normal random variables, the model prediction accuracy is diminished.

Then, a set of *m*-functions g(u) can be formulated such that violation of the defined constraints, of type g(u) < 0, will be assimilated with the system failure. By accounting for multiple failure sources, the system reliability is related to the *m*-failure events  $F_1, \ldots, F_m$ . Thus, the probability of failure  $(P_f)$  is defined as the joint probability that the *g*-constraints be violated by the random variation of the variables u, i.e.:

$$P_{f} = P[F_{1} \cup F_{2} \cup \dots F_{m}] = P\{g(\boldsymbol{u}) < 0\} =$$

$$= \int \dots \int f(\boldsymbol{u}) d\boldsymbol{u},$$
(1)

(where f(u) is the joint probability density function of u). For independent or weakly correlated events, an approximate formula for  $P_{\rm f}$  is:<sup>19</sup>  $P_{\rm f} = \sum_i P_i$ (where  $P_i$  = the *i*-th individual failure occurrence probability). Usually, g(u) can be explicitly defined as the deviation of output  $\gamma$  random variables vs. some imposed limits (i.e. the 'dangerous or failure dose'), being denoted as LSF:

$$LSF(\boldsymbol{u}) = \boldsymbol{g}(\boldsymbol{u}) = \gamma_{adm} - \gamma.$$
(2)

One approximate route to evaluate  $P_f$  is the first-order second moment method developed by *Hasofer & Lind*,<sup>17</sup> i.e. the so-called 'Most Probable Failure Point' (MPP) method. MPP is based on a safety index  $\beta > 0$ , which is defined as the shortest distance between the origin of the reduced coordinate system (in terms of  $u'_i$ ) and the failure surface defined for every constraint by  $g(\mathbf{u}) = 0$ :<sup>17</sup>

 $P_{\rm f} = \Phi(-\beta(u')),$ 

where:

$$u'_{i} = \frac{u_{i} - \mu_{u_{i}}}{\sigma_{u_{i}}}; \quad u'_{i} = -\alpha_{i}^{*}\beta;$$

$$\alpha_{i}^{*} = \operatorname{sign}(\partial g / \partial u'_{i}) |\partial g / \partial u'_{i}| / \sqrt{\Sigma_{i}(\partial g / \partial u'_{i})^{2}}; \quad (3)$$

$$i = 1, \dots, n.$$

In the previous relationship,  $\alpha_i^*$  denotes the direction *i* cosines in such a reduced variable representation, while  $\Phi$  denotes the cumulative distribution function for the standard normal. The independent random variables, normally distributed  $u_i \sim N(\mu_{u_i}, \sigma_{u_i}^2)$ , have been considered in their scaled form  $u'_i$ . The safety index  $\beta$  is in fact a measure of the 'structural reliability' of the system, being related to the nonlinear response of the system to the independent variables u.

In the MPP method, independent variables are assumed to be normally distributed, with known mean and variance. As proved, the safety index  $\beta$  is less influenced by the distribution type, but very dependent on the failure magnitude.<sup>17</sup> Starting from the definition, the  $\beta$ -index can be evaluated numerically by solving the implicit equation:

$$g(u_1, \dots, u_n) = 0; \quad u_i = \mu_{u_i} - \alpha_i^* \sigma_{u_i} \beta;$$
  

$$(\partial g / \partial u'_i) = (\partial g / \partial u_i) \sigma_{u_i}; \quad i = 1, \dots, n.$$
(4)

Evaluation of g(u) implies repeated simulations of the system by means of a mathematical model. A convenient way is to consider, in a first step, the deterministic process and to simulate the system by using the average values  $\mu_u$ . Then, by replacing in the model the average values with the random variables, in the form of  $u_i = \mu_{u_i} - \alpha_i^* \sigma_{u_i} \beta$ , the stochastic LSF solution is generated, leading to evaluate the safety index  $\beta$ .

Application of the MPP method is (self-understood) relevant only if g(u) and  $\beta$  are 'sensitive' to the failure factors (in terms of u), that is for significant sensitivity coefficients  $\partial\beta/\partial\mu_{u_i}$  and  $\partial\beta/\partial\sigma_{u_i}$ . Otherwise, other factors causing the system failure have to be identified. In general, LSF depend on the process characteristics, on the influential variable distribution, but also on the set of constraints (physico-chemical, technological, or safety regulations).

# Pollutant dispersion model in a riverine pathway

To simulate the pollutant dispersion in a river, downstream a release point, dispersion models of various complexity have been developed. According to the pollution source and river characteristics, dynamic or stationary models, one-dimensional (i.e. longitudinal direction x), bi-dimensional (i.e. longitudinal and lateral directions x, y), or tri-dimensional (i.e. longitudinal, lateral, and vertical directions x, y, z) have been reported.<sup>21-23</sup> Besides, even if not included in the present analysis, separate models have been developed to simulate the surface or submerse releases in the river (in form of jets or plumes), and the transient zone where the jet energy is progressively diminished until its velocity becomes practically the same with those of the river.<sup>21</sup> Starting from these basic models, successive developments tried to include supplementary features of the phenomenon, such as: absorption of certain gases from atmosphere (oxygen) through the river surface; chemical and biological pollutant degradation; multiple receptors from the environment; pollutant adsorption in suspended solids, river bed, or living organisms; etc.

By considering a turbulent field, in any point the mass concentration and velocity fluctuate around the mean values, that is:  $w = \overline{w} + w'', \gamma = \overline{\gamma} + \gamma''$ . In a tri-dimensional model, the advective and turbulent diffusion of pollutant in the river, is given by the following mass balance of a differential volume element:

$$\frac{\partial \gamma}{\partial t} + \frac{\partial (\gamma w_x)}{\partial x} + \frac{\partial (\gamma w_y)}{\partial y} + \frac{\partial (\gamma w_z)}{\partial z} =$$

$$= \frac{\partial}{\partial x} \left( D_x \frac{\partial \gamma}{\partial x} \right) + \frac{\partial}{\partial y} \left( D_y \frac{\partial \gamma}{\partial y} \right) + \frac{\partial}{\partial z} \left( D_z \frac{\partial \gamma}{\partial z} \right) + \sum_i r_i.$$
(5)

[where:  $\gamma$  = pollutant mean mass concentration (that is  $\overline{\gamma}$  in a turbulent motion);  $w_x$ ,  $w_y$ ,  $w_z$  = fluid velocities over movement directions;  $D_x$ ,  $D_y$ ,  $D_z$  = mass dispersion coefficients;  $r_i$  = reaction rates responsible to the pollutant degradation in the river (chemical, biological, or physical transformation)].

For a rapid simulation of the pollutant dispersion, downstream a small-size release point (see Fig. 1), a reduced bi-dimensional advective-dispersive stationary model has been adopted:<sup>24</sup>



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Fig. 1 – Schematic representation of a riverine pathway contamination with a pollutant release from a WWTP (small size release point located in the middle of the river; adapted from Whelan & McDonald<sup>24</sup>)

$$w \frac{\partial \gamma}{\partial x} = D_y \frac{\partial^2 \gamma}{\partial y^2} - r(\gamma);$$
  
$$\frac{\partial \gamma}{\partial y} = 0, \text{ for } y = 0, \text{ and } y = b;$$
  
$$\gamma = 0, \text{ for } y = b;$$
  
$$\gamma = \gamma_0, \text{ for } x = 0, y = 0,$$
 (6)

[where y = lateral distance from middle-river; b = river half-width;  $w = \overline{w}_x =$  water mean velocity in the flow direction;  $D_y =$  apparent lateral dispersion coefficient; r = pollutant (bio)degradation rate]. Such a model is based on several simplificatory assumptions:

i) a small size discharge source, with a continuous and stationary release flow-rate ( $Q_{ef}$ ), and a pollutant flow-rate ( $Q_m$ ), located in the middle of the river (y = 0); the release water temperature and  $\gamma_{O_2}$ are approximately the same with those of the river;

ii) contaminant release time in the riverine pathway is much longer than the travel time  $(\bar{t})$  in the control section (from the source to a receptor located at a certain distance from the source;  $\bar{t} = x/w$ ); the transient time-intervals are much shorter comparatively to the discharge time;

iii) uniform longitudinal flow with a constant flow-rate (Q) and velocity (w) over the analysed period (recorded data are usually mediated on a monthly basis);

iv) river-geometry is approximated by a prismatic one in the considered pollution control section, of constant rectangular cross-section (of width b and depth h);

v) a constant pollutant biodegradation rate, temperature (*T*), pH,  $\gamma_{O_2}$ , and other water quality quantities in the analysed river section;

vi) negligible contaminant adsorption/desorption to/from the river particles or sediments; if these are proved to be important, a supplementary pollutant disappearance rate (r') must be added to the mass balance;

vii) an advection which dominates dispersion in the longitudinal direction  $(D_x = 0)$ ;

viii) a fully mixed contaminant plume over the river depth (i.e. vertically-integral mass balance);

ix) a constant lateral dispersion coefficient  $(D_y)$  that includes the lateral turbulent mixing and diffusion; a value of  $D_y = 0.06 h w$  is adopted following the recommendations of Fischer.<sup>25</sup>

x) other pollutant losses in the riverine pathway (such as volatilisation, adsorption) are neglected or included in the overall degradation constant.

If a first-order pollutant biodegradation kinetics is assumed, i.e.  $r = k_M \gamma$  (where  $k_M$  is the overall McKinney rate constant<sup>26</sup>), an analytical solution of model (6) is possible to be derived of the form:<sup>24,30</sup>

$$\gamma(x, y, t) = (\gamma_{\text{fond}} + \gamma_{\text{disp}}) \exp(-k_{\text{M}} t);$$
  

$$\gamma_{\text{disp}} = \frac{Q_m}{(Q + Q_{\text{ef}})} \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{2n-1} \exp\left(-n_1^2 \frac{\pi^2}{b^2} \frac{D_y}{w} x\right) \cos\left(n_1 \frac{\pi}{b} y\right);$$
  

$$n_1 = \frac{2n-1}{2},$$
(7)

[where:  $\gamma_{\text{fond}}$  = pre-existent pollutant mass concentration (if different from zero), before the release point;  $\gamma_{\text{disp}}$  = dispersed pollutant mass concentration at various locations downstream the river]. If a Monod-type,<sup>4</sup> or a more complex pollutant biodegradation kinetics is considered,<sup>27</sup> a numerical solution of model (6) can be obtained by using the finite difference methods.<sup>28,31</sup>

# Risk assessment for an accidental pollutant release – A case study

In order to exemplify the pollution risk analysis by means of the 2D dispersion model, a case study of an accidental pollutant ( $BOD_5$  – organics) release has been approached. The input data, including the river characteristics and the so-called 'nominal' (normal) releases from a WWTP, are indicated in Table 1.

Input data include the receptor river water-quality parameters recorded over one year (2002), averaged on a monthly basis. The recorded parameters are: river flow-rate, temperature *T*, pH,  $\gamma_{O_2}$ , water hardness (temporally, permanent, total), BOD<sub>5</sub> (biochemical oxygen demand over 5-days at 20 °C), COD (chemical oxygen demand), filterable residue (soluble compounds), suspended solids, anion concentrations (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CN<sup>-</sup>, Symbol Significance Value (Correlation) longitudinal flow-direction  $0 \le x \le x_{\max}$  (m) x (x = 0 indicate the pollutant release location) lateral distance from the  $0 \le y \le b$  (m) V middle of the river (v = 0)to a lateral receptor vertical distance from the  $0 \le z \le h$  (m) Ζ water surface (z = 0)b half of the river width 30/2 (m) h average river depth in the  $h = (Q + Q_{\text{eff}})/(2 bw)$ control section  $\gamma(x,y)$  2D mass concentration field dispersion model of the pollutant, downstream solution (kg m<sup>-3</sup>) the release point (averaged on the depth) river mean velocity in the  $0.3 \text{ m s}^{-1}$ w flow direction monthly value ( $m^3 s^{-1}$ ) Q river average flow-rate 0.05 kg s<sup>-1</sup> (nominal)  $Q_m$ discharged pollutant / contaminant flow-rate  $\sigma_{\mathcal{Q}_m}$  $0.60 \text{ kg s}^{-1}$ standard deviation of  $Q_m$ (from accident records)  $2.5 \ m^3 \ s^{-1}$ discharged water flow-rate  $Q_{\rm ef}$ (at x = 0) $\gamma_{\rm ef} = Q_{\rm m}/Q_{\rm ef} =$ 20 g m<sup>-3</sup> (nominal) pollutant mass concentration  $\gamma_{\rm ef}$ in the discharged water (before mixing) 5 g m<sup>-3</sup> (average) pollutant mass concentration  $\gamma_{\rm fond}$ before the release point (x < 0) $15 \text{ g m}^{-3} \text{ BOD}_5$ maximum admissible pollutant  $\gamma_{\rm adm}$ concentration in the river (given by the current regulations) Т water temperature (°C) (monthly average) pН pH-index of the river water (monthly average) dissolved oxygen mass  $(mg L^{-1})$ 202 (monthly average) concentration overall rate constant complex correlation  $k_{\rm M}$ (McKinney) for pollutant  $(s^{-1})$ biodegradation  $D_v = 0.06 \ h \ u \ m^2 \ s^{-1}$  $D_{v}$ lateral dispersion coefficient  $\bar{t} = x/u$  (s) t pollutant residence time in the control section β complex correlation, Hasofer-Lind safety index  $\beta \ge 0$  $P_{\rm f}$ probability of failure complex correlation,

(accidental pollution)

 $0 \le P_{\rm f} \le 1$ 

Table 1 – Input data for the risk analysis of the pollutant discharge case study

HCO<sub>3</sub><sup>-</sup>), cation concentrations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Fe<sup>3+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>), total mercury (Hg), total phosphorous (P<sub>T</sub>), phenols, detergents, and oil products. Most of these parameters present a seasonal fluctuation over the year, as displayed in Fig. 2. For instance,  $\gamma_{O2}$  varies with the *T*, but its deficit ( $\gamma_{O2sat} - \gamma_{O2}$ ) is negligible (where  $\gamma_{O2} \approx 14.652 - 0.41T + 0.008T^2$ , *T* in °C).<sup>11</sup> The recorded data from Fig. 2 are used as input parameters in evaluating the biodegradation kinetic parameters (Eq. 8) and as input model variables (such as *Q*,  $\gamma_{fond}$ , see Table 1).

Solution of the dispersion model (6), being dependent on the mentioned input parameters and data, was derived for two extreme situations of the river conditions:

- AUG: the case of an accidental release of BOD<sub>5</sub>-organics from a WWTP at the month of August, when the river flow-rate is at its lowest level; the river parameters are:  $Q_m = 0.05$  (nominal) + 0.60 (accidental) kg s<sup>-1</sup>; Q = 10.5 m<sup>3</sup> s<sup>-1</sup>; T = 23 °C; pH 7.6;  $\gamma_{02} = 8.8$  mg L<sup>-1</sup>;

- JAN: the case of an accidental release of BOD<sub>5</sub>-organics from a WWTP at the month of January, when the river flow-rate is at its highest level; the river parameters are:  $Q_c = 0.05$  (nominal) + 0.60 (accidental) kg s<sup>-1</sup>; Q = 52.5 m<sup>3</sup> s<sup>-1</sup>; T = 3 °C; pH 7.7;  $\gamma_{02} = 13.1$  mg L<sup>-1</sup>.

The value of the biodegradation constant  $k_{\rm M}$  at 20 °C reported in the literature for BOD<sub>5</sub>-organic pollutants, is: 6 d<sup>-1</sup> (in aerated lagoons);<sup>4</sup> 1-1.3 d<sup>-1</sup>;<sup>26</sup> 0.24 d<sup>-1</sup>.<sup>11</sup> Own determinations indicated an average value of  $k_{\rm M} = 0.2$  d<sup>-1</sup> at optimal conditions of 20 °C, pH = 7.2;  $\gamma_{\rm O2} >> 2$  mg L<sup>-1</sup>. This value, adopted in this study, has been correlated with the temperature, pH, and  $\gamma_{\rm O2}$ , in the form:<sup>4</sup>

$$k_{\rm M} \approx 0.2\varphi_{\rm T}\varphi_{\rm pH}\varphi_{\gamma_{02}};$$
  
$$\varphi_{\rm T} = \theta^{(T-20)}; (\theta = 1.08; T \text{ in }^{\circ}\text{C});$$

 $\varphi_{pH} = [1 - 0.833(7.2 - pH)];$ (similarly to nitrification with suspended cells);

$${}^{\varphi_{\gamma O_2}} = \frac{\gamma_{O_2}}{K_{O_2} + \gamma_{O_2}};$$
(8)

 $(K_{O_2} = 1.3 \text{ mg } \text{L}^{-1};$  similarly to nitrification with suspended cells).

Under normal (nominal) WWTP operating conditions, the BOD<sub>5</sub>-organics content in the WWTP release is of  $\gamma_{ef} = Q_m/Q_{ef} = 20$  g m<sup>-3</sup>, and does not exceed the admissible values for discharged waters. By using the input values of Table 1,



Fig. 2 – Recorded water quality characteristics of the river over a period of one year. In traces: phenols < 0.01 mg  $L^{-l}$ , detergents < 0.05 mg  $L^{-l}$ . Absents: oil products, CN(–), Mn(2+), Hg, Ni(2+), Cr(3+), Cd(2+); water hardness in German deg. ( $\gamma_{1G} = 10 \text{ mg } l^{-l}$  CaO in water)

the solution of the dispersion model  $\gamma(x, y, \bar{t})$  is plotted in Fig. 3-4 (upper-row) for the both cases, over a control section of ca. 1 km (JAN) and 4 km (AUG). The variable  $Q_m$  (considered as risk-variable) is kept at its average value of  $\mu Q_m = 0.05$  kg s<sup>-2</sup>. The 3D-plots indicate the pollutant mass concentration field downstream the release point, while the 2D-plots display the LSF contours ( $\gamma_{adm} - \gamma$ ) in the same river control section.

Before simulating the accidental pollutant release, one introduces in the model the LSF constraint functions, defined for the target pollutant  $BOD_5$ :

$$LSF(x, y, \bar{t}, u) = \gamma_{adm} - \gamma(x, y, \bar{t}, u), \qquad (9)$$

where the random independent variable causing the accident is here  $u = Q_m$ . Under nominal conditions, it is to remark that the LSF contours downstream the river do not present any negative value in the control sections (Fig. 3-4, upper-row).

When generating the accident scenario, one replaces the deterministic  $u = Q_{\gamma}$  by the random variable  $u \sim N(\mu_u, \sigma_u^2)$ , and one calculates the safety index  $\beta$  in every location of the river, downstream the release point, by numerically solving the implicit equation (4), with  $Q_m = \mu_{Q_m} - \alpha_{Q_m}^* \sigma_{Q_m} \beta$ . Here the risk is defined as the probability that a given location hazard (i.e.  $\gamma$ -value) exceeds a defined limit ( $\gamma_{adm}$ ).

The safety index  $\beta(x, y, \bar{t})$  (the  $\beta$ -contour plots are not presented here) serves to evaluate the probability  $P_f(x, y, \bar{t})$  by means of the relationship (3). The approximate  $P_f$ -risk contours in the control section are plotted in Fig. 3-4 (down-rows). The 'zig-zag' appearance is related to the adopted number of the lateral / longitudinal divisions of the river control section sides. As the  $P_f(x, y, \bar{t})$  is evaluated over an increased number of points (i.e. by using a 'finer' 2D-grid), as the  $P_f$ -risk contours are more precise, it gets closer to the monotonous shape, but obtained with the expense of an increased computational effort.

The results for the scenario AUG indicate that, in spite of high pollutant biodegradability ( $k_{\rm M} = 0.29 \, d^{-1}$ ), the pollution risk region is extended over more than 4 km downstream the release point. Oppositely, in the JAN scenario, even if the pollutant biodegradability is very low ( $k_{\rm M} = 0.07 \, d^{-1}$ ), the river high flow-rate (ca. 5 times the AUG level) is able to dilute the pollutant over less than 600 m downstream the pollution source. The LSF and  $P_{\rm f}$ plots reveal that the region of the river most affected by pollution is the central one, and the less affected is the one in proximity of the banks.



F ig. 3 – Stationary pollutant mass concentration field, LSF contours ( $\gamma_{adm} - \gamma$ ), and risk contours (probability of failure) downstream the release point in the river, for month August-AUG (Upper-row: nominal situation, before the accidental release. Down-row: situation during the accidental release of high BOD<sub>5</sub> flow-rates).

### Conclusions

pollutant mass conc., y/g m<sup>-1</sup>

pollutant mass conc., y/g m-2

40 X X 10

0

5 0

The reduced 2D dispersion model is proved to be an effective instrument in simulating the pollutant transport and fate in a riverine pathway, downstream from a contamination source. This model can then be coupled with a risk statistical analysis (e.g. MPP rule) associated to an accidental release, in order to derive the safety index and risk contours downstream the river. The release scenario usually concerns a WWTP failure, but other accidental punctual discharges, of known frequency and magnitude, can also be approached.

2000

length, I/m

2500

3000

3500

4000

500

1000

1500

Because the pollutant biodegradability strongly depends on the river seasonal characteristics, completion of the model with the influence of temperature, pH, and  $\gamma_{02}$  on the biodegradation constant



can improve the analysis accuracy. By repeating the same risk analysis every month during the year, superposition of the obtained risk contours can offer a clear picture about the affected sections of the river.

The derived risk measures, based on the probabilistic analysis, can be used to derive site-specific assessments, can support the failure prevention measures, plant optimization and risk management, and can indicate suitable monitoring locations of the river-pollution.

The analysis can be repeated, if necessary, in various sections of the river. In this case, the flux continuity boundary conditions among successive sections, and the travel times through the succeeding media, should be accounted in the model. Analysis can be easily extended when multiple receptors are present, by using the detailed dispersion model, or a simplified algebraic manipulation rule based on simple scale-up / scale-down criteria.<sup>24</sup>

Even, if only one pollutant has been approached in the presented case study, the risk analysis can be applied to a large category of contaminants: chemical, biological, and radionuclides. For every water contaminant, the apparent rate constant of degradation has to be evaluated by means of separate experiments. Then,  $k_{\rm M}$  can range from negligible values to large ones, by possibly including side processes such as: radionuclide decay, pollutant adsorption in the organisms and riverbed, or volatilisation through water-surface.

### Nomenclature

- b half of the river width, m
- $\gamma$  pollutant mass concentration, mg L<sup>-1</sup>
- $\gamma_{adm}$  maximum admissible pollutant mass concentration, mg  $L^{-1}$
- $\gamma_{ef}$  pollutant mass concentration in the discharged water, mg  $L^{-1}$
- $\gamma_{fond}$  pollutant mass concentration before the release point, mg  $L^{-1}$

 $D_x$ ,  $D_y$ ,  $D_z$  – mass dispersion coefficients, m<sup>2</sup> s<sup>-1</sup>

 $\gamma_{O_2}~$  – dissolved oxygen, mg  $L^{-1}$ 

 $\gamma_{\rm O_2,sat}$ - saturated  $\gamma_{\rm O_2}$ , mg L<sup>-1</sup>

 $F_i - j$ -th failure event

- f(u) joint probability density function of u
- g(u) *m*-dimensional vector of the system constraint functions

h – average river depth, m

- $K_{\rm O_2}$  oxygen Monod constant in eq. (8), mg L<sup>-1</sup>
- $k_{\rm M}$  biodegradation rate overall constant, d<sup>-1</sup>
- LSF  $(\mathbf{u})$  limit state functions
- P probability
- $P_i$  the *i*-th individual failure occurrence probability
- $P_{\rm f}$  probability of failure
- Q river average flow-rate, m<sup>3</sup> s<sup>-1</sup>
- $Q_m$  discharged pollutant/contaminant flow-rate, kg s<sup>-1</sup>
- $Q_{\rm ef}$  discharged water flow-rate, m<sup>3</sup> s<sup>-1</sup>
- *R* system reliability
- r reaction rate of pollutant degradation, mg L<sup>-1</sup> d<sup>-1</sup>
- T water temperature, °C
- $\bar{t}$  pollutant residence time in the control section, s
- *u n*-dimensional vector of independent random risk-variables causing the system failure (i.e. the river pollution)
- $u_{\text{limit}}$  imposed limitative bonds to u
- $u'_i$  scaled  $u_i$  variables
- (x, y, z) Cartesian directions of the analysed system (x = longitudinal; y = lateral; z = vertical directions)
- $w_x$ ,  $w_y$ ,  $w_z$  fluid superficial velocities over movement directions, m s<sup>-1</sup>
- $w = \overline{w}_x$  fluid superficial average velocity in the longitudinal direction, m s<sup>-1</sup>

### Greeks

- $\alpha_i^*$  direction *i* cosines in a reduced variable representation (in terms of  $u_i'$ )
- $\beta$  Hasofer-Lind safety index
- $\varphi$  correction factors in eq. (8)
- $\Phi$  cumulative distribution function for the standard normal
- $\mu_{u_i}$  mean of the random variable  $u_i$
- $\sigma_{u_i}$  standard deviation of the random variable  $u_i$
- $\theta$  constant in eq. (8)

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