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Risk assessment of accidents involving environmental high-toxicity substances

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Abstract

The introduction of new safety legislation in Russia has been accompanied by R&D into risk assessment, especially needed when dealing with high-toxicity substances. In the present article, two models for evaluation of the dose absorbed by recipients as a result of instantaneous releases and short-term continuous emissions of toxicant to the atmosphere are developed. The models have the form of definite integrals with Green's function. The numerical problem of evaluation of the absorbed dose with obtained models is reduced to the calculation of single definite integrals. It is shown that under similar initial conditions, the dose absorbed as a result of instantaneous discharge is greater than the dose resulting in a short-term continuous emission of toxicant. An interval approach is developed to estimate the sensitivity of the numerical results to the errors in empirical parameters and variables included in the models. On the base of introduced definitions of interval variables, interval vectors and interval functions, interval estimates for absorbed dose are developed. It is shown that there exists an optimal number of terms in empirical equations with inexact parameters. Numerical examples of interval analysis are given. © 2000 Published by Elsevier Science B.V.

Keywords: Risk assessment; Major accident hazards; Toxic dose; Consequence models; Interval analysis

1. Introduction

The release of dioxine at the industrial plant near Seveso (North Italy) on June 10, 1976 resulted in severe environment pollution and soil contamination. Many people

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were affected by the dioxine. After this accident, a general concern by the population of Western Europe resulted in a critical analysis by the European Community of legislation, codes and acts related with industrial risk, accident hazards, prevention and mitigation. As a result of this work, the Seveso-1 Directive[1] has been prepared and published in 1982 and came into effect in 1984. In 1996, the European Union has adopted a new Directive[2] regulating major chemical accident hazards, which was to be enforced in early 1999. The Directive implementation has resulted in essential improvements in the control of accident hazards in the EU.

But also all over Europe, the Seveso Directive was giving the incentive to safety promotion, and further international agreements in the frame of UN-ECE co-operation.[3] As a result, the national law "On industrial safety" of the Russian Federation is similar to the Seveso-2 Directive and came into effect on June 21, 1997. This law interdicts to construct, maintain and restructure any industrial plant without the certificate of industrial safety issued by the authoritative expert commission. This certificate requires detailed evaluation of accident risks in a given plant and the availability of the sets of measures needed for accident prevention and risk reduction. However, scientific works on the development of mathematical models and respective software have been started by Russian scientists long before the introduction of the above-mentioned certificate. They take into account both international results and experience matured within the Russian Federation.

The investigations related to this subject are carried out in the State Research Institute on Organic Chemistry (SRIOCT) of the Russian Federation with financial support of the Russian government and the International Scientific and Technology Center (ISTC) at Moscow. Risk analysis has been adopted as the conceptual framework to approach the regulatory requirements. This includes the following steps:

- initial analysis of the main hazards of contamination and accidents in a given industrial plant;
- analysis of the consequences of possible accidents;
- evaluation of frequency and/or probability of accidents;
- risk assessment and development of measures of prevention and mitigation.

The second step of this procedure is based on the dynamic mathematical models for the description of the accident as a function of time. These models include explicit and implicit relationships, differential equations, definite integrals, etc. To evaluate the risk, it is necessary to solve linear and non-linear equations, to determine the extreme of functions, etc. All these problems need to be solved despite of inadequate empirical data, i.e. under uncertainty.

[1] Directive 82/501/EEC.
[2] Seveso-2 Directive 96/82/EC.
[3] United Nations: Convention on the Transboundary Effects of Industrial Accidents done at Helsinki, on 17 March 1992. E/ECE/1268.

The suggested procedure has been applied to the evaluation of risk connected with the storage and facilities for the destruction of the chemical weapons.

Chemical weapons have been mostly stored and accumulated in the USA and the former Soviet Union. They constitute a severe hazard for all humankind. On April 1997, the International Convention on the Interdiction of the Design, Production, Accumulation and Use of the Chemical Weapons come to the force. On November 7, 1997, it was ratified by the Russian Federation. Moreover, the Russian Federation has taken the obligation during 10 years to completely destroy all chemical weapons, which have been accumulated in seven arsenals in the different regions of Russia. Of course, the destruction of chemical weapons in an environmental friendly way is a problem with which many other countries are presently confronted. The interested reader is referred to a recent NATO/ISTC workshop on the subject [1].

In Russia, the State Scientific Institute on Organic Chemistry is defined as a leading research institute on the technology and equipment design of plants related with the annihilation of the chemical weapons. The SRIOCT team played a leading role during evaluation of the risk resulting in accumulation and annihilation of chemical weapon. Particularly, within the years 1998–1999, the team has developed the certificate of industrial safety for the chemical plant for annihilation of chemical weapons in Kizner (Udmurt Republic of Russian Federation).

At the present, this project is offering a good opportunity to test and improve the methodology for evaluation and prediction of the risks from accidents. In certain cases, the methodological development has resulted in approaches, which differ somewhat from the ones generally used elsewhere. Indeed the present article describes two models for evaluation of the dose absorbed by recipients as a result of instantaneous releases and short-term continuous emissions of toxicant to the atmosphere, which allows the evaluation of the absorbed dose by the calculation of single definite integrals. Furthermore, an interval approach is developed to estimate the sensitivity of the numerical results to the uncertainties in empirical parameters and variables included in the models. Numerical examples of interval analysis are given.

2. Models for instantaneous and short-term toxicant emissions in the air

Harmful effects to people by toxic substances are possible as a result of both instantaneous release and short-term continuous emission of toxicant to the atmosphere. The severity of the damage depends on the absorbed inhalation dose.

Let us consider a concentration c_m of toxicant in the atmosphere at the point $\vec{x} = (x_1, x_2, x_3)^T$ at the time t. Suppose that the source of instantaneous discharge allocated at the point $\vec{x}' = (x_1', x_2', x_3')^T$ releases a toxicant mass (M) at the time t'. Under these assumptions, the concentration c_m can be written as a function [2]:

$$c_m(\vec{x}, t) = MG(\vec{x}, \vec{x}', t - t'), \tag{1}$$

where $G(\vec{x}, \vec{x}', t - t')$ is a factor of meteorological dilution that coincides with the Green's function [3].

For example, suppose that the wind is directed with the velocity u_1 along the x_1 axis, and the pollutant is a neutral gas, which is completely reflected from the soil. Then the function $G(\vec{x},\vec{x}',t-t')$, can be written in the form

$$G(\vec{x},\vec{x}',t-t') = \frac{1}{(2\pi)^{3/2}\prod_{i=1}^{3}\sigma_i(t-t')}\exp\left\{-\frac{[x_1-x_1'-u_1(t-t')]^2}{2\sigma_1^2(t-t')}\right\} \times \exp\left[-\frac{(x_2-x_2')^2}{2\sigma_2^2(t-t')}\right]\left\{\exp\left[-\frac{(x_3-x_3')^2}{2\sigma_3^2(t-t')}\right]+\exp\left[-\frac{(x_3+x_3')^2}{2\sigma_3^2(t-t')}\right]\right\}, \quad (2)$$

where $\sigma_i^2(t-t')$ is a variance describing the toxic cloud dispersion in the direction of the i-th axis. The variance σ_i^2 as a function of its arguments can be found by fitting experimental data.

Let us assume now that the point-allocated source of short-term emissions of toxicant acts during the time interval, $0 \le t \le T$ with a constant rate m_0. Then the concentration field at the point x can be described by the equation

$$c_H(\vec{x},t) = \begin{cases} m_0\int_0^t G(\vec{x},\vec{x}',t-t')\,\mathrm{d}t, & \text{if } t<T \\ m_0\int_0^T G(\vec{x},\vec{x}',t-t')\,\mathrm{d}t, & \text{if } t\ge T. \end{cases} \quad (3)$$

In the case of an instantaneous discharge at the time $t'=0$, the maximum possible absorbed dose within the interval $[t_H,t_K]$ at the point $\vec{x}$ is described by the definite integral

$$d_m(\vec{x}) = M\int_{t_H}^{t_K} G(\vec{x},\vec{x}',t-t')\,\mathrm{d}t. \quad (4)$$

To evaluate the dose absorbed as a result of short-term emissions of toxicant, it is necessary to distinguish two cases, according to the end time t_{Ki} for exposure to the toxicant: (1) $t_{K1}<T$, and (2) $t_{K2}\ge T$.

In case (1), the dose absorbed by the recipient is evaluated as

$$d_{H1}(\vec{x}) = m_0\int_{t_H}^{t_{K1}}\int_{t'=0}^{t} G(\vec{x},\vec{x}',t-t')\,\mathrm{d}t'\,\mathrm{d}t. \quad (5)$$

In case (2), the following equation holds true

$$d_{H2}(\vec{x}) = m_0\int_{t_H}^{T}\int_{t'=0}^{t} G(\vec{x},\vec{x}',t-t')\,\mathrm{d}t'\,\mathrm{d}t + m_0\int_{T}^{t_{K2}}\int_{t'=0}^{T} G(\vec{x},\vec{x}',t-t')\,\mathrm{d}t'\,\mathrm{d}t. \quad (6)$$

In this case, the absorbed dose consists of two parts: the mass of toxicant absorbed during the emission time interval $[t_H,T]$ and the mass absorbed after that the emission has ceased at its source $[T,t_{K2}]$.

Calculation of the absorbed dose for the short-term emission is more complicated than for instantaneous release of toxicant because of double integrals in Eqs. (5) and (6). However, it is possible to reduce the double integrals to single ones by variable substitutions because the functions in Eqs. (5) and (6) depend only on the difference $t - t'$. This allows us first to combine the double integrals (5) and (6) into the general equation

$$I = \iint_{(D)} f(t,t')\,\mathrm{d}t'\,\mathrm{d}t, \tag{7}$$

where D is the respective region of integration and $f(t,t') = G(\vec{x},\vec{x}',t - t')$.

Then it is possible to simplify integral (7) by substituting t and t' with the new variables ν and μ, in one-to-one relationships with the original ones, as follows:

$$t = t(\nu,\mu), \quad t' = t'(\nu,\mu). \tag{8}$$

Substituting Eq. (8) into Eq. (7), we have [4]

$$I = \iint_{(D)} f(t(\nu,\mu),t'(\nu,\mu))\,|J(\nu,\mu)|\,\mathrm{d}\nu\,\mathrm{d}\mu, \tag{9}$$

where D' is the region of integration in terms of the new variables ν and μ, and $|J(\nu,\mu)|$ denotes the absolute value of Jacobian $J(\nu,\mu)$

$$J(\nu,\mu) = \det\begin{pmatrix} \dfrac{\partial t}{\partial \nu} & \dfrac{\partial t}{\partial \mu} \\ \dfrac{\partial t'}{\partial \nu} & \dfrac{\partial t'}{\partial \mu} \end{pmatrix},$$

which is a factor of plane mapping.

Using the following substitution in the double integrals

$$t = \frac{\sqrt{2}}{2}(\nu + \mu) \quad \text{and} \quad t' = \frac{\sqrt{2}}{2}(\nu - \mu), \tag{10}$$

we get $|J(\nu,\mu)| = 1$, and Eq. (9) is reduced to the form

$$I = \iint_{(D)} f(t(\nu,\mu),t'(\nu,\mu))\,\mathrm{d}\nu\,\mathrm{d}\mu. \tag{11}$$

Substitution (10) is equivalent to the mapping from the co-ordinate system (t,t') to the new system (ν,μ), as shown in Fig. 1 that also shows the integration regions.

Region D'_1 (i.e. the trapezium $t_H ABt_{K1}$) corresponds to integral (5). The sum of integral (6) has a common region of integration $t_H ACKt_{K2}$ (D'_2) consisting of two sub-regions: trapezium $t_H ACT$ and rectangle $TCKt_{K2}$.

By using the new co-ordinate system, the equation for dose evaluation can be rewritten as

$$d_{H1}(\vec{x}) = m_0 \int\int_{(D'_1)} G\left(\vec{x},\vec{x}',\sqrt{2}\,\mu\right)\mathrm{d}\mu\,\mathrm{d}\nu. \tag{12}$$

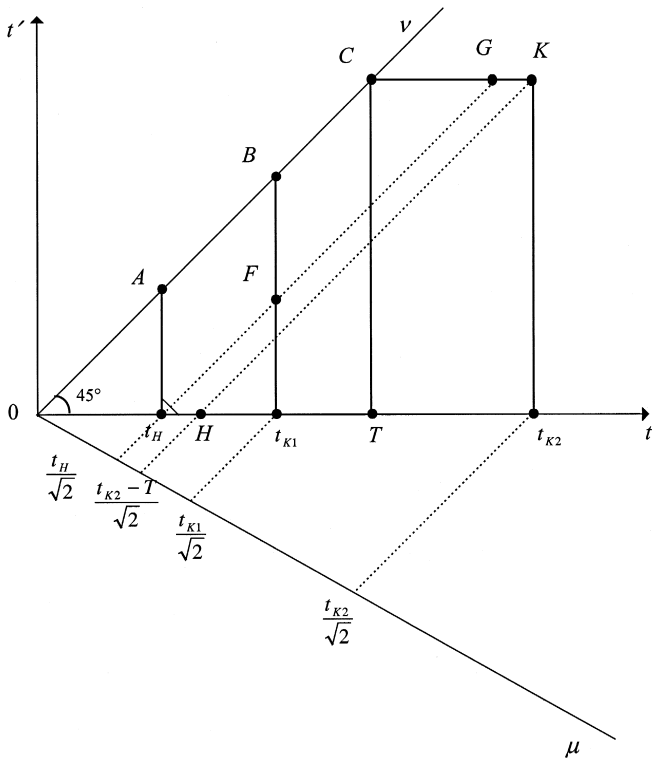

Fig. 1. Mapping of co-ordinate system for absorbed dose evaluation.

It follows from Eq. (12) that: (1) function $G(\vec{x},\vec{x}',\sqrt{2}\,\mu)$ does not depend on variable ν; and (2) region $t_H ABt_{K1}$ in the new co-ordinate system is a sum of two regions, namely rectangle $t_H ABF$ and triangle $t_H Ft_{K1}$. By taking these properties into account, we finally write the model for the evaluation of the absorbed dose of toxicant when $t_{K1} < T$ as

$$
\begin{aligned}
&d_{H1}(\vec{x}) \\
&\quad = m_0 \int_0^{\frac{t_H}{\sqrt{2}}} \mathrm{d}\mu \int_{\sqrt{2}\,t_H-\mu}^{\sqrt{2}\,t_{K1}-\mu} G\big(\vec{x},\vec{x}',\sqrt{2}\,\mu\big)\mathrm{d}\nu \\
&\qquad + m_0 \int_{\frac{t_H}{\sqrt{2}}}^{\frac{t_{K1}}{\sqrt{2}}} \mathrm{d}\mu \int_{\mu}^{\sqrt{2}\,t_{K1}-\mu} G\big(\vec{x},\vec{x}',\sqrt{2}\,\mu\big)\mathrm{d}\nu \\
&\quad = m_0\big(t_{K1}-t_H\big)\int_0^{t_H} G\big(\vec{x},\vec{x}',\lambda\big)\mathrm{d}\lambda + m_0 \int_{t_H}^{t_{K1}} G\big(\vec{x},\vec{x}',\lambda\big)\big(t_{K1}-\lambda\big)\mathrm{d}\lambda, \qquad (13)
\end{aligned}
$$

where $\lambda = \sqrt{2}\,\mu = t - t',\ \lambda \geq 0$.

For the particular case when $t_H = 0$, we have

$$d_{H1}(\vec{x}) = m_0 \int_0^{t_{K1}} G(\vec{x},\vec{x}',G\lambda)(t_{K1} - \lambda)\mathrm{d}\lambda. \tag{14}$$

To calculate absorbed dose $d_{H2}(\vec{x})$, the region of integration D_2' should be considered. From Fig. 1, region D_2' is a polygon $t_H ACKt_{K2}$ consisting of trapezium $t_H ACG$, parallelogram $t_H GKH$, and triangle HKt_{K2}. Using this splitting, we get the following equation for dose $d_{H2}(\vec{x})$:

$$d_{H2}(\vec{x}) = m_0 \int_0^{t_H} G(\vec{x},\vec{x}',\lambda)(T - t_H + \lambda)\mathrm{d}\lambda + m_0 T \int_{t_H}^{t_{K2}-T} G(\vec{x},\vec{x}',\lambda)\mathrm{d}\lambda + m_0 \int_{t_{K2}-T}^{t_{K2}} G(\vec{x},\vec{x}',\lambda)(t_{K2} - \lambda)\mathrm{d}\lambda. \tag{15}$$

When $t_H = 0$, we get

$$d_{H2}(\vec{x}) = m_0 T \int_0^{t_{K2}-T} G(\vec{x},\vec{x}',\lambda)\mathrm{d}\lambda + \int_{t_{K2}-T}^{t_{K2}} G(\vec{x},\vec{x}',\lambda)(t_{K2} - \lambda)\mathrm{d}\lambda. \tag{16}$$

Thus, the evaluation of the maximum possible absorbed dose under short-term continuous emission of toxicant is reduced to the calculation of single intervals (13) and (14) if $t_{K1} < T$ and to the integrals (15) and (16) in the case $t_{K2} \geq T$.

The obtained models allow the comparison of the dose of the same toxicant absorbed by a recipient after an instantaneous release with the dose absorbed after a short-term continuous emission.

Suppose that the mass M is released at the moment $t = 0$. Then in accordance with Eq. (4), the dose absorbed by the recipient during the time $0 \leq t \leq t_{K1}$ is evaluated as

$$d_m(\vec{x}) = M \int_0^{t_{K1}} G(\vec{x},\vec{x}',\lambda)\mathrm{d}\lambda. \tag{17}$$

Now suppose that there is a short-term continuous emission of toxicant with rate $m_0 = M/t_{K1}$ during the same time $0 \leq t \leq t_{K1}$ ($t_{K1} < T$) as before. Due to Eq. (14) in this case, we get the following estimate of the absorbed dose

$$d_{H1}(\vec{x}) = M \int_0^{t_{K1}} G(\vec{x},\vec{x}',\lambda)\mathrm{d}\lambda - m_0 \int_0^{t_{K1}} G(\vec{x},\vec{x}',\lambda)\,\lambda\mathrm{d}\lambda. \tag{18}$$

Comparing Eqs. (17) and (18), we get the inequality

$$d_m(\vec{x}) > d_{H1}(\vec{x}), \tag{19}$$

which is valid because function $G(\vec{x},\vec{x}',\lambda)\lambda$ is always positive. Thus, under the given conditions, the absorbed dose after an instantaneous release of toxicant is greater than the dose absorbed after a short-term continuous emission of it.

Let us discuss the result (19). First, it is necessary to stress that Eq. (19) is valid for any kind of function $G(\vec{x},\vec{x}',t-t')$ under only two assumptions, namely that:

- function G does not depend on the two separate arguments t and t', but only depends on the difference $t-t'$ $(=\lambda)$;
- function G is positive and tends to zero when $t-t'$ tends to infinity.

Thus, the obtained results are valid not only for the functions described by Eq. (2) but also for all functions that satisfy the constraints given above. In particular, they are valid for different models of covariance σ^2 as a function of time and environmental conditions, such as the models by Pasquill–Gifford, Briggs or Smith–Hosker.

Second, the above given equations are based on the suggestion that maximum possible absorbed dose as a function of concentration is described by the equation

$$d(\vec{x}) = \int_t c(\vec{x},t)\,\mathrm{d}t. \tag{20}$$

However, it is possible to prove that inequality (19) is also valid for the more general case when

$$d(\vec{x}) = \int_t c^n(\vec{x},t)\,\mathrm{d}t, \tag{21}$$

where n is an empirical coefficient that can vary from 1 to 3.

Third, it can be proven that, when the total mass released is equal to that of an instantaneous emission, inequality (19) is valid also in the case of a continuous release at changing rate $m(t)$ and in the case of a sequence of instantaneous discharges of toxicant.

Further, such results and conclusions hold true not only for point-allocated sources of toxicant but also for distributed sources of different shape (see Ref. [5]).

3. An introduction to interval analysis

To assess the risk connected with a specific accident, the following analysis steps should be performed:

- Choice of adequate models for the release and diffusion of the toxicant;
- Determination of the empirical parameters of the chosen models;
- Calculation of the maximum possible absorbed dose and the vulnerability;
- Quantification of the risk;
- Analysis of the uncertainties and reliability of the final results for the decision making.

Unfortunately, the last step of this procedure is frequently ignored by the practitioners, though it should play a very important role. The goal of this step is to determine the confidence interval for the risk figure, which allows making a better-informed decision.

The uncertainty in the risk assessment depends on both errors in experimental data and inaccuracies of the chosen models. For example, let the “true” value of the risk be

expressed by a function $z_0 = f_0(x,b)$, where x is a set of variables and b a set of parameters. Then the following sources of errors/uncertainties can be defined:

Accuracy error of the model $z = f(x,b)$ chosen from the set of existing empirical models $z_i = f_i(x,b)$ describing the diffusion of the toxicant. Generally, neither of these models coincides exactly with "true" model $z_0 = f_0(x,b)$;
Approximation error of the model $z = f(x,b)$ because of ignoring a number of variables affecting the diffusion process;
Errors of measurements of the variables x;
Errors of empirical parameters b (e.g. resulting particularly from the clustering of the environmental conditions into a finite number of clusters);
Round-off errors.

At present, two basic approaches are applied to the analysis of the uncertainty of the results, namely, statistical methods and interval analysis [6]. Statistical approaches usually assume that errors of models are related mainly to uncertainties in experimental data and empirical parameters b, which are defined as random variables with known density functions $w(b)$. Under this assumption, the resulting z is also a random value with distribution $\varphi(z)$. If the models are simple enough and linear (for example to be expressed as a linear combination of variables and parameters) and all variables are normally distributed, the resulting z will have also a normal distribution. Therefore, it would be possible to write a confidence interval for the unknown "true" value z_0 as $\bar{z} - 2\sigma_z \le z_0 \le \bar{z} + 2\sigma_z$, where $\bar{z}$ is the mean and σ_z is the standard deviation of random value z. This interval covers the "true" risk value with a 95% confidence probability. The main advantage of the statistical approach is its analytical formulation and availability of effective software packages. However, the application of the statistical methods to the problem of risk assessment is related with a number of difficulties. First, simple statistical formulation is based on the assumption of additive errors with normal distribution, which frequently is not fulfilled. The model $z = f(x,b)$ for risk evaluation is essentially a non-linear one. Under these circumstances, the problem of determining the density function $\varphi(z)$ has no analytical solution. Generally, the statistical approach does not allow taking into account in a differentiated way systematic and non-statistical errors, such as round-off errors and clustering approximations, accuracy errors of the models, etc. The interval approach has no such restrictions. It allows taking into account errors of any nature, with finite known ranges. For this reason, interval analysis may be a good alternative to the statistical methods.

The interval analysis introduced below is based on the definition of an interval variable [6]. Given some numerical constant or variable a whose exact value is unknown but there are given lower and upper bounds a^-, a^+ of its possible values, then interval

$$[a] = [a^-; a^+] = [a : a^- \le a \le a^+], \tag{22}$$

is called *interval variable* denoted as $[a]$.

From this definition, it is easy to conclude that the "true" value of a certainly belongs to the interval that is formed by all its possible, i.e. $a \in [a]$. Certainly, this is valid under the assumption that the bounds of interval are defined correctly. Thus,

within interval analysis, the initial object of any operation is not a number as in usual arithmetic and algebra, but interval $[a]$. It is necessary to stress that no probabilistic measure needs to be defined on interval $[a]$.

Different models can be applied for determining the interval bounds depending on a priori information that is available to the investigator. Sometimes, the point estimate $\hat{a}$ of the unknown "true" value parameter a and the absolute error Δ are given such that $|\hat{a} - a| \leq \Delta$. More frequently, the point estimate $\hat{a}$ and fractional error $\delta = \Delta/\hat{a}$ are given. Thus, for the determination of the lower and upper bounds of interval $[a]$, one of the following equations can be applied

$$[a] = [\hat{a} - \Delta; \hat{a} + \Delta] = [\hat{a}(1 - \delta); \hat{a}(1 + \delta)] = [a^-; a^+]. \tag{23}$$

Certainly, there exists one-to-one correspondence between all representations of interval. Particularly, if bounds a^-; a^+ are given, it is easy to calculate the middle point of interval $a = (a^- + a^+)/2$ and the absolute error $\Delta = (a^+ - a^-)/2$. If the point estimate and either the absolute or fractional error are given, then the bounds a^- and a^+ can be easily calculated. Definition of an interval variable $[a]$ allows the consideration of *an interval vector* $[\vec{x}] = ([x_1] \ldots [x_k])^T$, including n interval components $[x_1] \ldots [x_k]$.

We need also a definition of *an interval function* $[z] = f(\vec{x}, [\vec{b}])$, whose argument is an interval vector of parameters $[\vec{b}]$. At a fixed value for $\vec{x}$, the resulting interval $[z]$ is defined as

$$[z] = [z^-; z^+] = \left[\min_b \left(f(\vec{x}, \vec{b}), \vec{b} \in \left[\vec{b}\right]\right); \max_b \left(f(\vec{x}, \vec{b}), \vec{b} \in \left[\vec{b}\right]\right)\right]. \tag{24}$$

From Eq. (24), the interval bounds are defined as the two extreme values of the function $f(\vec{x}, \vec{b})$ over all possible values of the parameters b within their given intervals. For the simplest cases, these bounds can be calculated by the rules of *interval arithmetic*, as shown in Appendix A.

4. Application of interval analysis to the risk assessment problem

The general procedure for applying interval analysis to the risk assessment problem includes the following steps:

- Step 1. Determination of measurement errors/uncertainties for variables $\vec{x}, \vec{x}'$, M, u_1 in Eq. (2) and their representation in interval form $[\vec{x}]$, $[\vec{x}']$, $[M]$, $[u_1]$.
- Step 2. Choice of empirical models for standard deviations σ_1, σ_2, σ_3 entering in Eq. (2). Determination of the accuracy error of the model chosen and the errors of the empirical parameters involved. Determination of the interval functions $[\sigma_1(t)]$, $[\sigma_2(t)]$, $[\sigma_3(t)]$.
- Step 3. Interval representation of the factor of meteorological dilution $[G(\vec{x}, \vec{x}', t - t')$.
- Step 4. Calculation of interval $[d]$ for the maximum possible absorbed dose based on Eq. (15) or Eq. (16) depending on kind of release. Interval $[d]$ is a non-analytical, non-linear function of interval parameters and variables:

$$[d] = f\{[\vec{x}], [\vec{x}'], [M], [u_1], [\sigma_1], [\sigma_2], [\sigma_3], t_k, T\}.$$

- Step 5. Determination of interval value of the probit function $[Pr]$.
- Step 6. Calculation of interval $[R]$ of the risk value for the decision making.

Within the limits of the present paper, it is not possible to give a detailed description of all steps. Therefore, we focus on the most essential aspects of the algorithm.

Step 1. The vectors $\vec{x},\vec{x}'$ denoting in Eq. (2) the co-ordinates of the source of discharge and the location of the recipient can be measured within any predefined accuracy. For this reason, we will assume these variables as exact ones.[4]

The values of M — mass of toxicant and u_1 — velocity of wind in the direction of x_1 axis are major sources of uncertainty. The mass M is mostly estimated by expert judgement. The most convenient way to describe its uncertainty is to define the fractional error δ_M (%). Even being optimistic about the reliability of the judgement, we must recognise that this error can be rather large, and we assume it can vary within $5\% \le \delta_M \le 50\%$.

The value of wind velocity u_1 during the accident under consideration can be derived from meteorological monitoring. As a rule, meteorological data are determined as an average over several hours and over a large area as a town, city, etc. Therefore, the value u_1 will be known with an unavoidable error. It is reasonable to consider the fractional error of u_1 to be $1\% \le \delta_U \le 20\%$. Using Eq. (21) and assigning the fractional errors δ_M and δ_U, we can represent both variables in interval form

$$[M] = \left[M(1-\delta_M); M(1+\delta_M)\right], \quad [u_1] = \left(u_1(1-\delta_U); u_1(1+\delta_U)\right]. \tag{30}$$

Step 2. At this step, the interval models for the standard deviations σ_1, σ_2, σ_3 of the concentration field should be defined. There are at least three empirical models whose parameters depend on atmosphere stability class, roughness of spreading surface, and release features. They are represented by:

$$\sigma_i = b_{1i}(x_1)^{b_{2i}}, \qquad i = 1,2,3; \tag{31}$$

$$\sigma_1 = \sigma_2 = \frac{c_3 x_1}{\sqrt{1+0.0001\,x_1}}, \quad \sigma_3 = F(x_1,Z)\,g(x_1), \tag{32}$$

$$F(x_1,Z) = \begin{cases} \ln\dfrac{c_1(x_1)^{d_1}}{1+c_2 x_1^{d_2}}, \text{if } Z > 0.1 \\ \ln\left\{c_1 x_1^{d_1}\left(1+\dfrac{1}{c_2 x_1^{d_2}}\right)\right\}, \text{if } Z \le 0.1 \end{cases}, \quad g(x_1) = \frac{a_1 x_1^{b_1}}{\left(1+a_2 x_1^{b_2}\right)};$$

$$\sigma_i = \frac{a_{1i} x_1}{(1+a_{2i} x_1)^{a_{3i}}}, \qquad i = 2,3, \qquad \sigma_1 = \sigma_2, \tag{33}$$

where $x_1 = u_1 t$ is a current distance (measured in meters) from the release source in the direction of the wind; $F(x_1,Z)$ is a corrective factor depending on the roughness length

[4] There would be no great difficulty to consider a possible uncertainty in the exact location of the release as well.

Z (measured in meters) of the spreading surface; the coefficients a_i, b_i, c_i, d_i are given in tables as a function of release features for the different models:

model (31) is suggested in Ref. [3];
model (32), known as a model of Smith–Hosker [2], is considered as most accurate;
model (33) is discussed in Ref.[3].

To choose the most appropriate model among the available ones, it is necessary to analyse their *accuracy errors* with respect to a set of applicable reference data, and to adopt the simplest model associated with an admissible error.

In the following, we show the comparison of models (31), (32) and (33) with respect to the standard deviation σ_2 for data corresponding to an atmosphere of stability class B.

The reference data set contained 10 points (x_{1i}, σ_{2i}, $i = 1 \ldots 10$) that have been determined by a numerical simulation of the actual case. For sake of simplicity, these points hereinafter will be referred to as "theoretical data" and considered as an exact theoretical data set. By multiple regression analysis, the estimates a_i, b_i, c_3 that deliver the best fitting of theoretical data have been calculated. The resulting values are given below.

$$\text{Model 1: } \sigma_2(1) = 0.156(x_1)^{0.996}$$

$$\text{Model 2: } \sigma_2(2) = \frac{0.16\,x_1}{\sqrt{1 + 0.0001\,x_1}},$$

$$\text{Model 3: } \sigma_2(3) = \frac{0.166\,x_1}{(1 + 0.00016\,x_1)^{0.41}}.$$

The value predicted by these models and the theoretical data set (labelled by squares) are shown in Fig. 2. By comparing the three models, we can state that Model 1 yields a large deviation from theoretical points for large values of x_1. For example, for the last point $x_1 = 10^5$ m, the fractional error of this model is 48%. Models 2 and 3 are very close to both the theoretical points and each other. To select a single model out the latter ones, their fractional deviation has been calculated by

$$\delta_{23}(i) = 2\frac{|\sigma_{2i}(2) - \sigma_{2i}(3)|}{|\sigma_{2i}(2) + \sigma_{2i}(3)|}100\%, \qquad i = 1 \ldots 10. \tag{34}$$

We found that models 2 and 3 are very close at the points x_4 and x_6 where their fractional deviation is less than 0.2%. The maximum deviation, equal to 3.7%, was found at the point $x_1 = 10^5$ m. It was also found that neither models have a systematic error. Therefore, we can accept that the *accuracy error* of each model is less than $\delta(\sigma_2) \cong 0.5\delta_{23}(i) \cong 2\%$. Since model (32) with one parameter has the same accuracy as model (33) with three parameters, it is reasonable to choose model (32) for the calculation of variables σ_1 and σ_2.

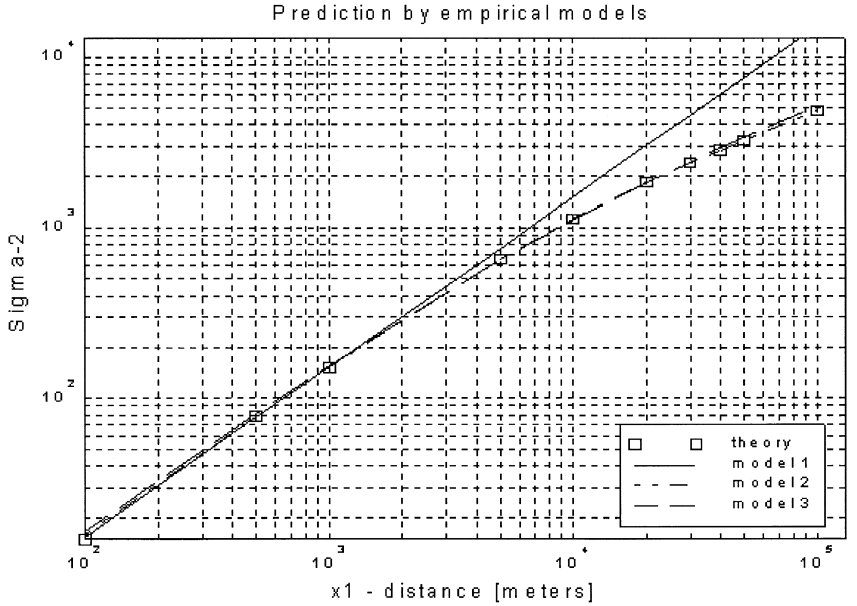

Fig. 2. Standard deviations for different empirical models.

Besides the accuracy error of the chosen empirical model, the results of its application depend on the approximation error of needed empirical parameters. One main source of these errors is the clustering of the environmental conditions into discrete classes. As a result, a same single vector of parameters is given to all situations belonging to a same class.

For example, suppose that an accident occurs during the day time under moderate insolation ($25 \le R_d \le 50$). The parameter c_3 in Eq. (32) is defined from tables in Ref. [2] depending on the wind velocity u [m/s], for the following classes: class A–B if $u < 2$, class B if $2 \le u < 3$, class C–D if $3 \le u < 4$, class C–D if $4 \le u < 6$, D if $6 \le u$. The values of the dotted line that connects the middle point of the classes (see Fig. 3) can be seen as "true" relation between function parameter c_3 and wind velocity u. The difference between this line and the discretised values is an error of clustering. For example, for the stability class B (ranging over a few discrete values in Fig. 3), the fractional clustering error of parameter c_3 is $\delta_{clus}(c_3) = 25\%$. Thus, the interval of uncertainty c_3 is $[c_3] = [c_3](1 - \delta_{clus})$; $c_3(1 + \delta_{clus})] = [0.16](1 + 0.25)] = [0.12; 0.2]$.

Using the results of the previous steps, we can write the interval function corresponding to Eq. (32) as

$$[\sigma_1(t)] = [\sigma_2(t)] = \frac{[c_3][u_1]t}{\sqrt{1 + 0.0001[u_1]t}}[0.98; 1.02], \tag{35}$$

where substitution $x_1 = u_1 t$ has been made. The last term in Eq. (35) reflects the accuracy error of model (32) equal to 2%.

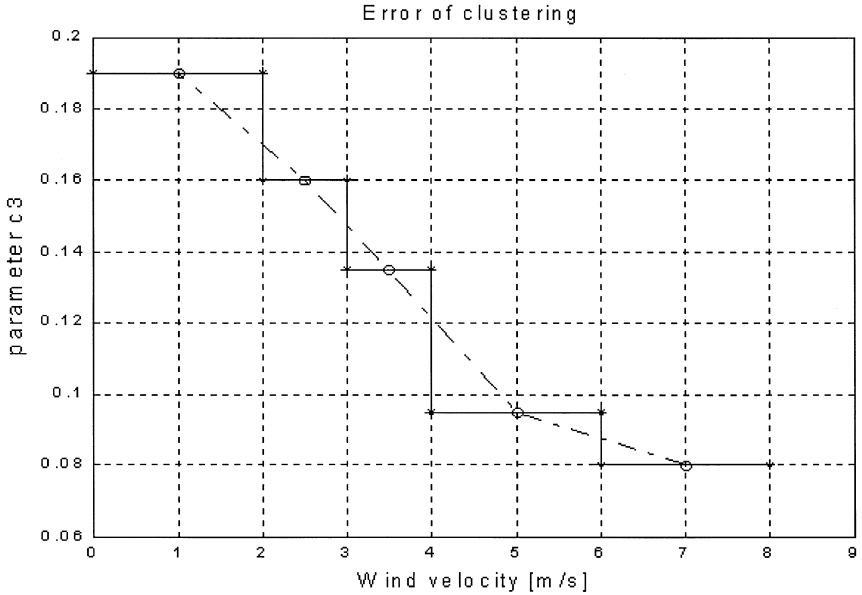

Fig. 3. The clustering error for the value of parameter c_3.

In our sample case, we can write the analytical equations of the lower and upper bounds as a function of time

$$[\sigma_1(t)] = [\sigma_2(t)] = \left[\frac{c_3^- u_1^- t}{\sqrt{1 + 0.0001 u_1^- t}} 0.98; \frac{c_3^+ u_1^+ t}{\sqrt{1 + 0.0001 u_1^+ t}} 1.02 \right] \tag{36}$$

where the bounds u_1^- and u_1^+ have been defined in the first step of the procedure.

The procedure of determination of the interval function $[\sigma_3]$ is similar to that for $[\sigma_1]$ and $[\sigma_2]$. But in this case, the product $F(x_1, Z) \cdot g(x_1)$ in Eq. (32) depends on eight parameters c_i, d_i, a_i, b_i $(i = 1,2)$. Therefore, it results in a much wider interval of uncertainty $[\sigma_3]$ than intervals $[\sigma_1]$ and $[\sigma_2]$.

Step 3. By substituting the interval functions and variables into Eq. (2), we write the interval function $[G(\vec{x},\vec{x}',t-t')]$.

Step 4. To get an interval value $[d]$ of the dose adsorbed by recipients, it is necessary to evaluate integral (15) with interval function $[G(\vec{x},\vec{x}',t-t')]$. This can be done with application of known numerical methods and method of Monte-Carlo. For evaluation of the dose for different possible values of parameters within given intervals, a uniform distribution generator should be applied. The number of trials can be reduced by taking into account that integral (15) is a monotonous function of its upper bound, therefore, is possible to calculate integral only for the vertex of the prism formed by the interval parameters.

Step 5. The interval probit function $[Pr]$, which is usually defined as

$$[Pr] = [a] + [b] \ln [d], \tag{37}$$

is affected by a number of uncertainties, including uncertainty of the dose $[d]$ determined on step 4 and uncertainties of the parameters a, b. Furthermore, a number of different equations for a same toxicant might have been proposed. To specify interval parameter's values $[a]$ and $[b]$, or to determine a corresponding model accuracy, a procedure similar to that for step 2 can be applied.

Step 6. Usually risk is evaluated as [10]

$$R = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{Pr-5} e^{-t^2/2} \mathrm{d}t. \tag{38}$$

This integral can be written in terms of the error function $\mathrm{erf}(z)$ related with a standard normal distribution as

$$[R] = 0.5\left\{1 + \mathrm{erf}\left(\frac{[Pr] - 5}{\sqrt{2}}\right)\right\}. \tag{39}$$

To get a lower bound of the risk R^-, it is necessary to substitute into Eq. (39) the lower bound of probit Pr^-; to calculate R^+, we substitute Pr^+.

Let us consider a numerical example. In Ref. [10], the following equation for the probit function of ethylene oxide is given

$$Pr = a + \ln(ct) = -6.8 + \ln(4443t), \tag{40}$$

where t is an exposition time. Suppose that a is known and the parameter c is defined within a 20% error. Then we write its interval as $[c] = [3554; 5331]$ and the interval probit is defined as $[Pr] = -6.8 + \ln([3554; 5331])$. Substituting it into Eq. (39), we get interval risk $[R(t)]$. This interval function is shown in Fig. 4, where the solid lines show

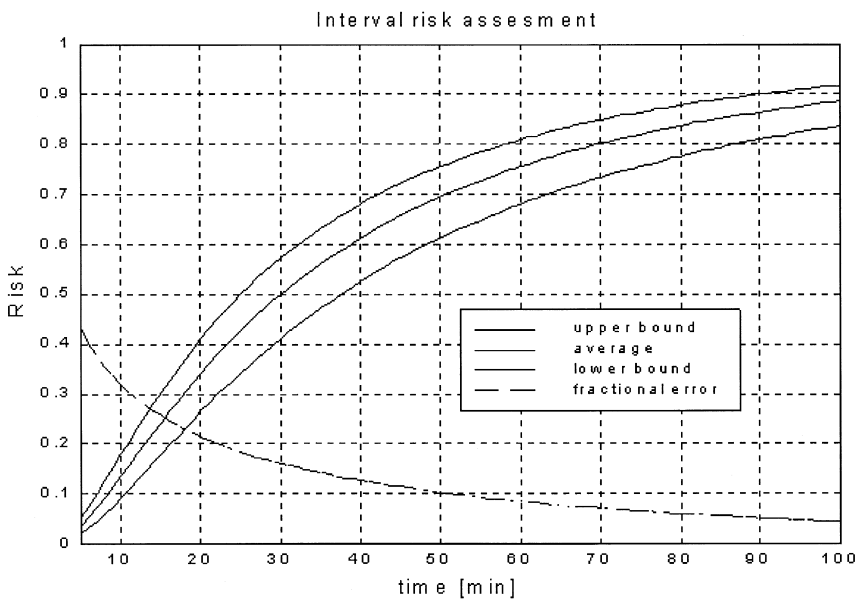

Fig. 4. Interval function for the risk value.

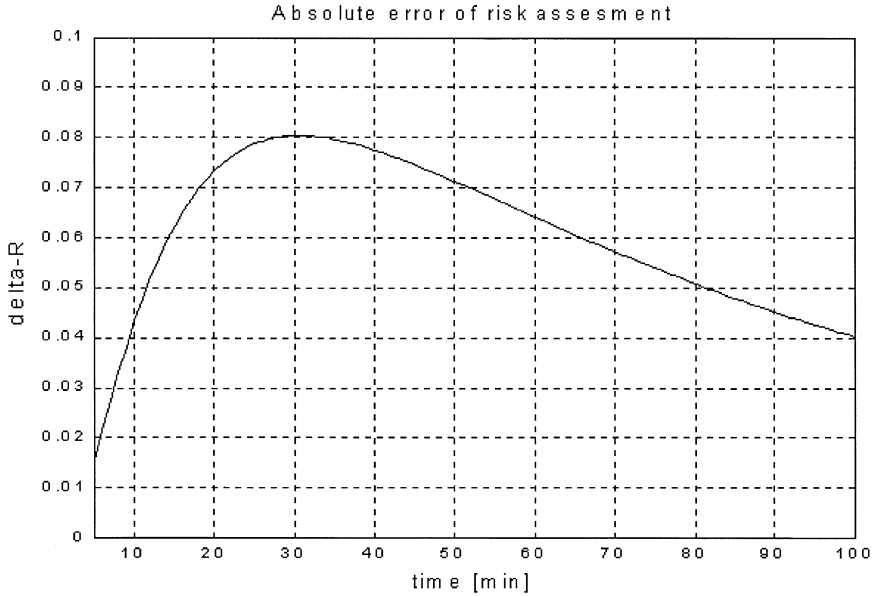

Fig. 5. Absolute error of the risk value.

the bounds of the risk value and its average. The decreasing dashed line corresponds to the fractional error of estimate calculated as $0.5\ (R^{+}-R^{-})/R_{\text{average}}$. Fig. 5 shows the absolute error $0.5\ (R^{+}-R^{-})$.

By the analysis of these graphs, we can draw the following conclusions.

The fractional error of risk is rather large for small values of risk. Particularly, when $t=5$ min, it is equal to 42%. For average risk equal to 0.5 (i.e. time = 30 min), the fractional error is 16%. But the value of average risk absolute error has a maximum value (see Fig. 5). It is necessary to stress that this statement is valid for any kind of probit function $[Pr]$.

The interval curve of risk $[R(t)]$ shown in Fig. 5 allows us to solve both direct and inverse problems of risk assessment.

4.1. Direct problem

Find interval risk when exposition time is equal to 30 min. The solution can be determined from Fig. 4 for $t=30$ min, which yields $[R(30)]=[0.42; 0.58]$. In Ref. [10], it is stated that $R=0.5$ for $t=30$ min. Evidently, that interval representation of risk is more informative than point estimate.

4.2. Inverse problem

Find time of exposition such that risk will be equal 40%. From Fig. 4, drawing a horizontal line through the point $R=0.4$, we can find its intersections with interval curve $[R(t)]$. It yields the interval for exposition time equal to $[t(0.4)]=[19$ min; 28 min].

Thus, the given example shows that application of interval analysis to the risk assessment problem is an effective way to get not only point estimates but also interval of possible values of risk resulting from errors and uncertainties of empirical parameters and experimental data.

5. Conclusions

In summary, we have proposed mathematical models to evaluate the absorbed inhalation dose for both instantaneous discharge and short-term emission of toxicants released from a point-allocated source. Relations between absorbed doses for the two above given modes of exposure have been also investigated. It has been shown that under similar initial conditions, the absorbed dose resulting from an instantaneous release of toxicant is greater than the dose resulting from a short-term continuous emission of it.

The interval approach has been developed to take into account the unavoidable errors of empirical parameters included in a mathematical model. It has been shown that this allows the choice of simpler models, at a same accuracy degree, than models with larger number of inexact parameters. Numerical examples of interval analysis have been given. It has been illustrated that interval presentation of the result is much more informative and correct for problems with empirical parameters than the usual point estimate presentation.

Appendix A. Operations with interval variables

Let $[a]^*[b]$ denote a generalised arithmetic operation, i.e. the operator * means one of the $(+,-,\times,:)$ operations with intervals $[a]$, $[b]$. Then the resulting interval can be determined as

$$[c] = [\min(a * b); \max(a * b), a \in [a], b \in [b]] \tag{25}$$

Eq. (25) shows that the resulting interval $[c]$ is the set of the results of the respective arithmetic operation performed over all possible values of a and b inside their given intervals.

If the intervals do not include zero, i.e. $0 \notin [a]$, $0 \notin [b]$ and all values within the intervals are positive, then Eq. (25) results in the following rules:

$$\begin{aligned}
&2.[a] + [b] = [a^- + b^-; a^+ + b^+];\\
&3.(-1)[a] = [-a^+; -a^-];\\
&4.[a] - [b] = [a^- - b^+; a^+ - b^-], [a] - [a] = 0;\\
&5.[a][b] = [a^- b^-; a^+ b^+];\\
&6.[a]/[b] = [a^-/b^+; a^+/b^-], [a]/[a] = 1.
\end{aligned} \tag{26}$$

Applying rules (26) to $[a] = [4; 5]$ and $[b] = [2; 3]$, it is easy to get $[a] - [b] = [1; 3]$, $[a][b] = [8; 15]$, $[a]/[b] = [4/3; 5/2]$. The result of operations $[2; 3] - [2; 3]$ and $[2;$

3]/[2; 3] depends on whether we are dealing with one variable or two. In the case of two variables with equal bounds $[a] = [2; 3]$ and $[b] = [2; 3]$, we get $[2; 3] - [2; 3] = [-1; 1]$ and $[2; 3]/[2; 3] = [2/3; 3/2]$. Whereas for the same variable $[a] = [2; 3]$, we have another result: $[2; 3] - [2; 3] = 0$ and $[2; 3]/[2;3] = 1$ (the difference between the two cases is that in the last equations, the combinations $a^- - a^+$, a^+/a^- cannot occur for a single variable).

Generally, the calculation of the bounds $[z] = [z^-; z^+]$ in accordance with Eq. (26) is possible by the use of any mathematical package, for example MATLAB, which contains Optimisation-Toolbox. But for a number of functions, the bounds can be written analytically, i.e. in the case that the functions are linear with respect to parameters as:

$$[z] = [b_0] + [b_1]\varphi_1(\vec{x}) + \cdots - [b_j]\varphi_j(\vec{x}) + \cdots + [b_m]\varphi_m(\vec{x}) \tag{27}$$

where $\varphi_j(x)$ are non-negative basic functions, $[b_j]$-interval parameters. For this function, the following equation for the bounds of the resulting z as a function of vector $\vec{x}$ is valid

$$z^-(\vec{x}) = b_0^- + b_1^-\varphi_1(\vec{x}) + \cdots - b_j^+\varphi_j(\vec{x}) + \cdots + b_m^-\varphi_m(\vec{x}) \tag{28a}$$

$$z^+(\vec{x}) = b_0^+ + b_i^+\varphi_1(\vec{x}) + \cdots - b_j^-\varphi_j(\vec{x}) + \cdots + b_m^+\varphi_m(\vec{x}) \tag{28b}$$

It can be seen from Eq. (28a) for lower bound z^- that parameter b_i enters this equation with its lower bound b_i^- if the respective term in Eq. (27) is positive and with its upper b_i^+ otherwise. The inverse situation takes place when calculating upper bound z^+.

In general, in risk assessment problems, the function called posynomial with interval parameters frequently occurs [7–9]

$$[z] = (x_1)^{[b_1]}(x_2)^{[b_2]}\cdots(x_m)^{[b_m]}. \tag{29}$$

Taking a logarithm from both sides of Eq. (29), we can represent it in the form of Eq. (27).

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