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A Mathematical Model for Estimating the Consequences of a Dispersion of Pollutants in Water Following a Major Accident

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In the history of Major Accident Hazard, but not only, many accidents causing a spill of pollutant in surface water are reported. Transport phenomena of pollutants in watercourses are widely discussed in scientific literature, however the available models are not always applicable to such industrial realities, both for the boundary conditions and for the required number of data, which is not always available.
This paper describes a model for the rapid assessment of the consequences of pollutants spill in a river and can be used as a predictive tool in the Risk Assessment. The aim of this model is to provide an estimate of the consequences of the accident using minimal and easily available input data. Indeed, the user can choose to insert required data, when known, or leave their estimation to the model, based on easily found information (river dimensions, environment, riverbed materials, etc.).
This one-dimensional model is applicable to instantaneous or short-term spills of partially or completely soluble substances in water, as well as insoluble and less dense substances, such as oils.
In the first case, the model calculates the maximum concentration reached along the axis of the watercourse considering the transverse and longitudinal diffusion, the removal of the substance by suspended solids and the volatility of the substance. In the second case, it estimates the evolution of the substance pool, evaluating the distance it can reach and considering its evaporation.
The calculation method is based on the theories of models proposed by official publications (ISPRA, EPA, etc.), providing a solution that gives satisfactory result when compared to other models, and is included in S.T.A.R. (Safety Techniques for Assessment of Risk). S.T.A.R. is a software provided by ARTES S.r.l. and acknowledged by OECD, used to estimate the consequences of accident scenarios, such as gas/liquid dispersion, fires and explosions. The model uses the database included in the software, that enlists more than 440 substances.

1. Introduction

This article introduces a one-dimensional model for expeditious evaluation of the effects of spills of substances completely or partially soluble using minimal and easily available input data. The model is the combination of two parts. Each part describes a specific evolution mechanism of pollutants in watercourses.
The first part describes the dispersion due to the flow field. This kind of mechanism only concerns the hydrodynamics effects of the flow on the solute. From the hydrodynamics point of view, the dilution of substances occurs only due to the effects of the flow field. Hence the solute reaction with other elements of the environment is not considered.
The second part of the model fills this lack in the description of the phenomena. In fact, when chemical substances are exposed to an open environment, they could suffer a natural decay due to reactions with elements of the environment, physical changes or biological degradation. The nature of the solute and the conformation of the watercourse appear to be the main operators in the definition of the effects of accidental spills. The model for insoluble substances lighter than water cited in the abstract, is not described here. In the S.T.A.R. software was used the one proposed in Brock Neely (1992) and taken up in SNPA 92/2013 (2013).

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2. Referring models

This section introduces the two models used as basis of the proposed one.
For the description of the hydrodynamic part, the Riverine Emergency Management Model (USACE, 1993), known as REMM, is used.
The substance physical-chemical degradation is described using the model proposed by EPA (1985).

2.1 Riverine Emergency Management Model

The Riverine Emergency Management Model (REMM) is a mathematical dispersion model well tested for instant releases of soluble substances.
In this one-dimensional model the hydrodynamic dispersion weights more than diffusion phenomena and pollutant natural decay. Eq(1) is the equation provided by the REMM Technical Manual.
As a result, REMM gives the distribution of the pollutant concentration along the river centerline in a given time. This can be graphically represented as a Gaussian curve:

$$C(x,t) = \frac{M}{2\Omega\sqrt{\pi D t}} \cdot e^{\left[-\frac{(x-ut)^2}{4Dt} + k_e(t)\right]} \quad (1)$$

where *x* is the distance from the spill along the river centerline, *t* is the time passed from the spill and *u* is the current velocity. Concentration *C* has the maximum when *x* = *ut*.
The river geometry is represented by Ω and *D.* Ω is the cross-sectional area of the river effectively occupied by water. The *D* factor estimates the dispersion along the river centerline. Many equations to determine *D* factor are available in literature, all of them empirically obtained.
The main issue in using REMM is the k_e factor determination. This coefficient estimates the natural decay of the leaked substance over time according to its physico-chemical properties. k_e factor considers substance evaporation, its absorption by organic and inorganic suspended solids and the reaction with other substances which might be present in water.
The integration of REMM and the model proposed by EPA was studied in order to define this factor.

2.2 EPA model

This model was developed to estimate the concentration of a substance continuously released in a river. The model is graphically represented by an exponential curve according Eq(2) that describes how the maximum concentration decreases along the river centerline.

$$C(x) = C_0 \cdot e^{\left[-\frac{k'_v - \sum k_i}{1 + k_p S}\frac{x}{u}\right]} \quad (2)$$

Contrary to REMM, the concentration decreasing is exclusively due to natural decay.
The k'_v parameter is related to volatilization properties (vapor pressure) of the substance. *S* is the concentration of suspended solids in water. k_i and k_p values depend on the riverbed terrain.
C_0 is the initial concentration of the substance in water. In the standard application of EPA model this parameter can be found in analytic way. Applying the model to major accident consequences assessment, this parameter is hard to estimate.

3. S.T.A.R. model

The proposed model, included in the S.T.A.R. software, merges the hydrodynamic elements of REMM with the EPA theory for substance natural decay, according to its physical-chemical features. The resulting equation is written in Eq(3).

$$C(x,t) = \frac{M}{2\Omega\sqrt{\pi D t}} \cdot e^{\left[-\frac{(x-ut)^2}{4Dt}\frac{k'_v - \sum k_i}{1 + k_p S}\frac{x}{u}\right]} \quad (3)$$

This model gives a solution for the main two issues of the two models previous described: the estimation of substance decay and initial concentration. The model provides reliable results in the far-field, when complete mixing is achieved. This distance *L* is calculated with the Eq(4) (Brock Neely, 1992).

$$L = 4\frac{0.1u^*W}{D} \quad (4)$$

Where *u** is the friction velocity, Eq(8), and *W* is the river width.
The *M* factor implicitly includes the solubility characteristics of the substance. For completely soluble substances, M corresponds to the total amount spilled. For partially soluble substances, the M value

decreases proportionally. The parameters for solubility calculation are included in the substance database used in the S.T.A.R. software.
Some approximation about channel geometry, morphology and environment is needed in order to give an easy-to-use tool.

3.1 Channel geometry and environment

The river conformation has a strong impact on the evaluation of the spill effects. Indeed, the hydrodynamic contribution strictly depends on the riverbed geometry.
On one hand, a complete description of channel sections, plan-elevation profile and other river morphology elements, can provide a whole representation of the river flow field. In particular, it could be possible to evaluate the effects of the substance dispersion in every main direction.
On the other hand, this level of detail is not consistent with the aim of obtaining a one-dimensional expeditious tool. Hence the geometry data required has to be as simple as possible and the model has to evaluate the hydrodynamic dispersion only along the longitudinal watercourse direction. This requirement leads to the assumption of rectangular geometry of the channel cross-section and the related formulas for area Ω, Eq(5), and hydraulic radius R_H, Eq(6).
Beside the strictly required data (channel width *W* and water depth *Y*), other data such as water speed *u*, channel slope i_f and Manning's coefficient *n* are not essential. In fact, if the value of these parameters is unknown, the user can indicate the kind of environment where the channel is located and the main material which composes the riverbed. In this way, the calculation of the missing data will occur. For example, following Table 1, the user indicates one of the environments, then the model picks a value of slope. Similarly, the indication of the material of the riverbed (Table 2) provides the value of the Manning's coefficient. At this point, the well-known relation of Gauckler-Strickler, Eq(7), gives the estimation of the water speed value.

$$\Omega = \mathrm{WY} \tag{5}$$

$$R_H = \frac{\Omega}{W + 2Y} \tag{6}$$

$$u = \frac{\sqrt{i_f}}{n} \Omega R_H^{2/3} \tag{7}$$

$$u^* = \sqrt{g R_H i_f} \tag{8}$$

Through a similar process, it is also possible to calculate the concentration of suspended solids in water. In fact, choosing the channel environment, a set of values is proposed from Table 2. In this case, the values of the concentration of suspended solids are obtained from analysis carried out on different types of Italian rivers.

3.2 Longitudinal dispersion coefficient

In order to choose a coefficient *D* among the ones available in literature, comparisons were made for rivers of different sizes. Figure 1 gives a graphic example of the results. In particular, the graph compares the coefficient D as a function of the width for 3 different river depths. Similarly, a depth-dependent comparison was made for different widths.
It was decided to adopt the coefficient proposed in Sahay et al. (2009), considering that it is based on comparisons with other authors.
In the Sahay et al.'s formula appears the river width-water depth ratio. This is a fundamental parameter in the evaluation of the river morphology. Consequently, the dispersion factor is also a function of the morphological characteristics of the river.

3.3 Soil characterization

As introduced before, the model proposed by EPA needs some soil characterization to set *ki* and *kp* parameters, but these data are frequently unavailable.
According to EPA, 3 basic information are needed to set the values for these parameters: silk/clay fraction in the soil (*F*), percentage of organic carbon in silk/clay fraction (*XOCF*) and percentage of organic carbon in sand (*XOCS*).
Given the difficulty of having these data for a specific watercourse, a statistical approach was used. A study developed by the European JRC was therefore used. This publication resumes analysis results on hundreds of soil samples collected across Europe (R. Hierderer, 2009).

Through data analysis, an estimate of the 3 parameters was reached for 5 terrain types. The analysis focused on terrain types that recur with greater frequency in the top layers of the soil. The results are summarized in Table 2. *kp* value is obtained with Eq(9).

$$k_p = k_{oc}[0.2(1 - F)XOCS + F \cdot XOCF] \quad (9)$$

Where k_{oc} is a fraction of the substance's water-octanol partition coefficient as suggested in EPA publication. The k_i parameter includes the specific rate constant for removal to sediment and the substance volatilization. The substance removal by sediment can be considered negligible for the typical simulation times of the proposed model. The volatilization parameter is included in k'_v.

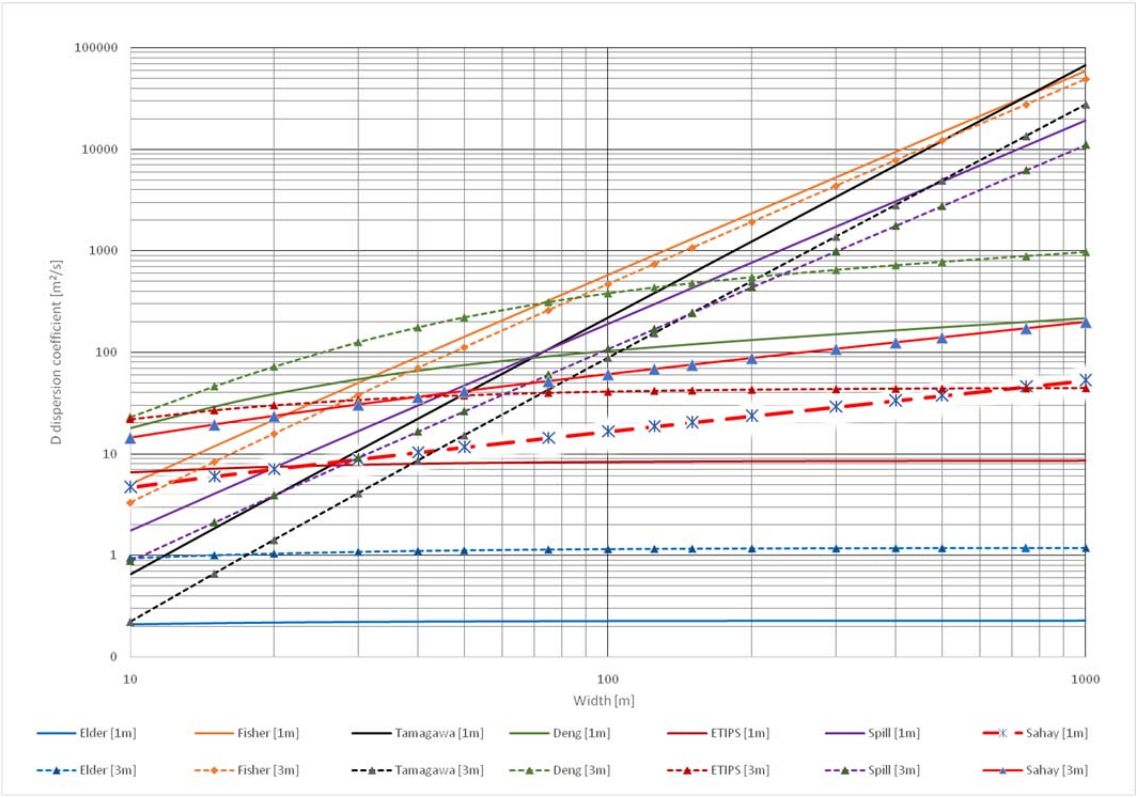

Figure 1: Comparison diagram of different dispersion coefficient estimation methods

Table 1: Proposed slope i_f and S value for different environments

Environment	i_f [%]	S [mg/L]
Mountain	1.5	3
Hills	0.5	5
High plain	0.05	10
Plain	0.015	20

Table 2: Proposed soil characterization for different terrain types

Terrain type	n	F	SOC	XOCF	XOCS
Stones and gravel	0.017	0.05	0.5	0.025	0.475
Sand and gravel	0.05	0.15	0.55	0.0825	0.4675
Clay, sand, pebbles	0.038	0.4	0.6	0.24	0.36
Dirt, mud	0.027	0.6	0.8	0.48	0.32
Concrete	0.06	0.5	0.1	0.05	0.05

4. Results comparison

The results of the proposed model were compared with 4 other ones. The chosen models are referred to as SNPA (2013), Brock Neely (1992), EnviroTechnical Information Problem Spills (1985) and USDoT (1977).
For the validation tests the example cases provided in the publications cited above were used. Each case was applied to all models and the results were compared. In Figure 2, the results of 4 of these cases are shown.
The S.T.A.R. model results are comparable to those of the other models, with a slightly conservative tendency.

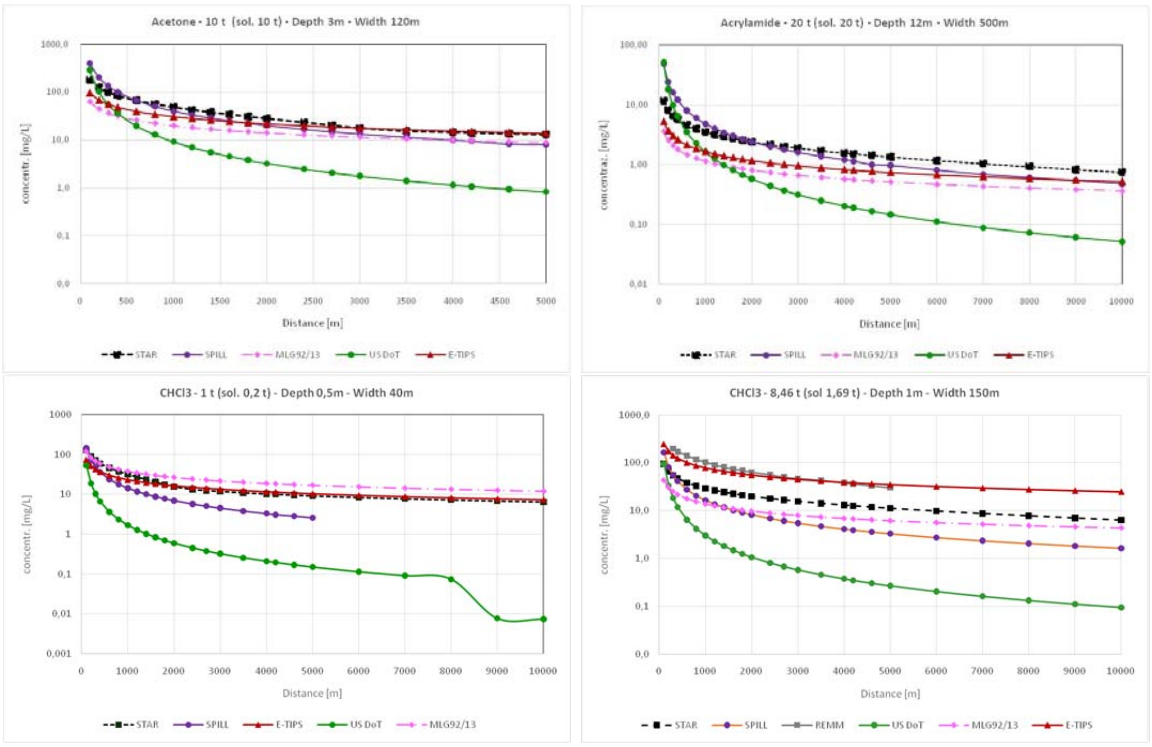

Figure 2: Results comparison with other models (4 examples)

5. Model input/output in S.T.A.R. software

The S.T.A.R. software is a tool approved by the OECD for the consequences modeling of different types of accidents (gas leaks, fires, explosions, etc.)
The strength of the software is its capability to obtain realistic results using the minimum number of user inputs.
For this water dispersion model, following inputs are required to describe river morphology:

- Environment (Table 1)
- riverbed material (Table 2)
- river width and depth

Velocity and slope can be input by the user, but the software can also estimate them, as described above.
To estimate the environmental consequences, the user needs to input:

- the substance name, chosen from the S.T.A.R. database, that includes more than 440 substances
- spilled quantity
- target distance, calculated along the river centreline from the spillage point.

The substance choice automatically involves the use of the described model or the one for insoluble substances. For partially soluble substances, the amount which is actually dissolved is calculated and used.
The user can also enter a threshold concentration (PNEC, LD50, etc.), which will be considered within the model to provide more information in the output.
The S.T.A.R. output is a table that lists the maximum concentration and the corresponding distance for each time step. The calculation is stopped when the target distance is reached.
If a threshold concentration is present, the length of the water course in which this is exceeded is provided.
In the output it is also specified if at target distance the complete mixing is achieved.

6. Conclusions

The aim of this study was to provide a tool that can help risk analysts to estimate the environmental consequences of a chemical spill in a river. The tool can be especially applied to industrial plants subjected to Directive 2012/18/EU (“Seveso III”) during the risk analysis.
A lot of similar models are proposed in literature, but all of them required specific data not always available.
The presented model aims to provide reliable results through:

- the union of two worldwide recognized models
- a simplified geometry and morphology of the river
- a statistical estimate of the most difficult to find parameters
- a populous database of chemicals

The parameters choice was made by comparing various sources and maintaining those values that provide more conservative results.
The results obtained by applying the proposed method are comparable with those of other models but using less data input.

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