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A method to relate chemical accident properties and expert judgements in order to derive useful information for the development of Environment-Accident Index

Åsa Scott Andersson [a,b,*], Mats Tysklind [b], Ingrid Fängmark [a]

[a] *Swedish Defence Research Agency, Division of NBC Defence, SE-901 82 Umeå, Sweden*
[b] *Environmental Chemistry, Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden*

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Abstract

The environment consists of a variety of different compartments and processes that act together in a complex system that complicate the environmental risk assessment after a chemical accident. The Environment-Accident Index (EAI) is an example of a tool based on a strategy to join the properties of a chemical with site-specific properties to facilitate this assessment and to be used in the planning process. In the development of the EAI it is necessary to make an unbiased judgement of relevant variables to include in the formula and to estimate their relative importance. The development of EAI has so far included the assimilation of chemical accidents, selection of a representative set of chemical accidents, and response values (representing effects in the environment after a chemical accident) have been developed by means of an expert panel. The developed responses were then related to the chemical and site-specific properties, through a mathematical model based on multivariate modelling (PLS), to create an improved EAI model. This resulted in EAI_{new}, a PLS based EAI model connected to a new classification scale. The advantages of EAI_{new} compared to the old EAI (EAI_{old}) is that it can be calculated without the use of tables, it can estimate the effects for all included responses and make a rough classification of chemical accidents according to the new classification scale. Finally EAI_{new} is a more stable model than EAI_{old}, built on a valid base of accident scenarios which makes it more reliable to use for a variety of chemicals and situations as it covers a broader spectra of accident scenarios. EAI_{new} can be expressed as a regression model to facilitate the calculation of the index for persons that do not have access to PLS. Future work can be; an external validation of EAI_{new}; to complete the formula structure; to adjust the classification scale; and to make a real life evaluation of EAI_{new}.

Keywords: Environment-Accident Index; Expert judgements; Environmental effects; Chemical accidents; Chemical properties; Site-specific properties; PLS

1. Introduction

After a chemical accident has occurred it is necessary to make a rapid decision about proper actions. This is a complicated task because of the number of processes affecting the environmental effects. Moreover, assessing a future effect of a hypothetical accident, as a step in a planning process, is even more difficult. In our society large effort has been put into developing different models to predict environmental consequences from chemical spill. However, the majority of these models make no attempt to bring together site-specific variables (e.g., soil and water variables) with chemical inherent properties (e.g., toxicity, density and volatility), but focus only on the chemical itself and its inherent capacity to harm the environment. The Environment-Accident Index (EAI) is an example of a tool based on the strategy to join the properties of a chemical with site-specific properties.

The EAI was originally proposed as a simple equation [1] (see Eq. (1)), based on a few chemical property descriptors and some properties of the surroundings at the site of the accident such as soil- and groundwater conditions.

$$EAI = Tox \cdot Am \cdot (Con + Sol + Sur) \quad (1)$$

The EAI consists of three parts: viz., (i) the acute toxicity to water living organisms (Tox), (ii) the stored or transported amount

* Corresponding author at: Swedish Defence Research Agency, Division of NBC Defence, SE-901 82 Umeå, Sweden. Tel.: +46 90 10 68 29; fax: +46 90 10 68 02.
E-mail address: asa.scott@foi.se (Å. Scott Andersson).

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of the chemical (Am) and (iii) factors controlling the spreading of a chemical. The latter part, the so-called *spreading part* (consistency, solubility and properties of the surrounding environment) contains chemical–physical properties of the chemical, the possibility of soil penetration and the depth and mobility of groundwater (Con, Sol and Sur). The calculation of EAI is based on points for the different variables [2] and hence the sum of the calculated EAI is a sum with no unit, and it is the sum calculated for one accident site compared to the sum of another accident site that is in focus. In essence the index is to be used as a simple tool to judge and rank the consequences for the environment in order to take proper actions in the planning process or at an accident site.

Con (mm^2/s) is the consistency or viscosity/physical state of the chemical, Sol (wt.%) is the water solubility of the chemical.

Sur is the properties of the surrounding environment such as

(1) distance, in meters, to nearest well, watercourse or lake (DNW),
(2) depth of groundwater in meters (DGS),
(3) whether the groundwater surface is inclined towards a well, lake or watercourse or if it is horizontal (SGS),
(4) the thickness, in meters, of the soil and the material it consists of, for example, gravel, sand, moraine, silt, clay or frozen ground.

As a result of the first validation [2,3] a more focused approach was taken on the development of EAI. Firstly, a decision was taken to focus only on accidents involving organic chemicals [6]. The reason is that the first results showed that one model could not handle both inorganic and organic chemicals. In addition, two new descriptor variables for inherent chemical properties were added to the data set: viz., density, D (kg/m^3) and vapour pressure, P_v (kPa). These new variables are important for describing the vertical transportation of the chemical in water and soil, together with evaporative losses to the air. Another change was that type of soil was replaced by two new variables: the hydraulic conductivity for each chemical and soil, K' (m/day) and porosity of the soil, n (%). Hence the index describes negative effects *in the environment* of a chemical release to soil, groundwater or water but *not* to air.

In order to avoid focusing on petroleum products and to increase the chemical diversity in the dataset used in the development of EAI, a selection of a representative subset of accidents was made [4]. In the absence of data on environmental consequences that not apply solely to one specific measured parameter an expert panel was, based on a designed questionnaire, asked to judge the environmental consequences after chemical accidents [5]. The expert panel judgements were then used as response variables.

In summary, the following strategy was proposed for the development of the EAI:

(I) To collect a larger database of accidents, together with relevant numerical descriptors to be used in the development of the index.
(II) To condense the large number of dependent descriptors in the database into a few orthogonal independent descriptors.
(III) To use the new latent descriptors in a statistical experimental and multivariate design to select a minimum number of representative accidents.
(IV) To evaluate the environmental consequences of chemical accidents by an expert panel.
(V) To create a PLS model to analyse the included accident descriptors and responses in comparison with the originally proposed EAI.
(VI) Model validation.

This paper deals with part V in the proposed strategy.

2. Objective

The objective of this paper is to:

(1) develop a mathematical relationship between the x-variables (chemical and site-specific properties of the accidents) and the y-variables (judgements of nine responses made by the expert panel);
(2) use the relationship to derive variable information on the weight and importance of the x-variables.

3. Material

The material used in this paper is the 18 selected chemical accidents divided in two subsets; a training set (TS), and a validation set (VS) consisting of nine accidents each [4]. In this study the accidents are described by chemical and site-specific properties (x-matrix), and modelled together with response variables from the expert judgements (y-matrix).

3.1. Chemical- and site-specific properties

The chemical accidents are described by 10 variables (x-variables), consisting of chemical and site-specific properties (descriptors), see Table 1.

Toxicity and amount are important variables to judge effects in the environment after chemical accidents. However, the toxicity associated with the amount released is the crucial factor governing the environmental effects of a chemical at an accident site. A weakly toxic chemical in large amounts can cause as much damage to the environment as well as a small amount of a highly toxic chemical. Therefore, the amount to toxicity ratio, m/Tox was calculated and used in the selection procedure. Properties related to the chemicals were gathered from various literature sources and databases [7–17]. The hydraulic conductivity values were calculated assuming saturated soil conditions, according to Freeze and Cherry (1979) [18] in Eq. (2).

$$K' = \frac{v_w}{v'} \cdot Kw \tag{2}$$

Table 1
Chemical accidents described by the chemical and site-specific properties in the training and validation set, respectively

Accident	Chemical	CAS-no.	Chemical properties					Site-specific properties				
			P_v	v	D	S_w	m/Tox	DNW	DGS	SGS	K'	n
TS1	Dieselfuel/heating oil No. 1	68334-30-5	0.5	2.75	820	0.1	9.5E+09	100	5	1	3	35
TS2	Dieselfuel/heating oil No. 1	68334-30-5	0.5	2.75	820	0.1	9.5E+09	5	0.2	1	1	15
TS3	Gasoline	86290-81-5	70	1	750	0.01	7.8E+09	100	0.01	1	3	33
TS4	Gasoline	86290-81-5	70	1	750	0.01	7.8E+09	2	1.9	0.5	1	43
TS5	Methanol	67-56-1	12.8	0.8	790	90	2.7E+06	125	33	1	1	55
TS6	Phenol	108-95-2	0.05	3.2	1070	8	2.7E+10	4	4.1	0.5	–	–
TS7	*n*-Butylacetate	123-86-4	1.2	1	880	0.01	2.7E+08	25	23	0.5	3	33
TS8	Styrene	100-42-5	0.6	0.9	910	0.01	6.6E+09	1	3.1	1	3	33
TS9	4-Chloro-*m*-cresol	59-50-7	–	2.25	1370	0.001	2.6E+05	200	1.5	0.5	1	15
VS1	Kerosine/Jet fuel	8008-20-6	0.1	1.50	808	0.1	7.8E+09	15	1.5	1	3	35
VS2	Dieselfuel/heating oil No. 1	68334-30-5	0.5	2.75	820	0.1	1.4E+10	7	0.4	1	1	15
VS3	Dieselfuel/heating oil No. 1	68334-30-5	0.5	2.75	820	0.1	5.0E+09	5	8	1	1	55
VS4	Gasoline	86290-81-5	70	1	750	0.01	5.8E+09	25	0.01	1	2	35
VS5	Gasoline	86290-81-5	70	1	750	0.01	7.2E+09	2	16	1	1	43
VS6	*Iso*-propanol	67-63-0	4.2	3	790	90	7.9E+04	300	2	1	2	35
VS7	Chlorobenzene	108-90-7	1.2	1	1110	0.05	2.1E+11	30	2.3	1	1	15
VS8	Vinylacetate	108-05-4	12	1	930	0.02	1.7E+09	7	7.6	0.5	2	35
VS9	Formic acid	64-18-6	4.3	1.5	1220	90	8.7E+07	30	3.2	0.5	1	15

The descriptor variables are: kinematic viscosity (v, mm^2/s); water solubility (S_w, wt.%); amount (m, metric tonnes) of the stored or transported chemical; acute toxicity (Tox, mg/L); the amount to toxicity ratio (m/Tox, L); the density (D, kg/m^3); vapour pressure (P_v, kPa); the distance to nearest well, lake or watercourse (DNW, m); the depth to groundwater surface (DGS, m); the slope of the groundwater surface and the flow direction (SGS, leaning towards a well lake or watercourse = 1, horizontal surface = 0.5 and no well lake or watercourse in the flow direction = 0.1); hydraulic conductivity for each chemical and soil (K', m/day); and porosity of the soil (n, %).

The descriptors can be considered as consisting of two groups: v, S_w, D and P_v describing the inherent properties of a chemical; and DNW, DGS, SGS, K' and n describing site-specific properties. The amount of a chemical involved in an accident, and thus also the m/Tox ratio, are properties which does not belong to any of the two groups.

3.2. Response variables

The expert panel was divided into two groups, one judging the chemical accidents in the training set (TS), and one judging the accidents in the validation set (VS) [5]. The experts judged both the short- and long-term effects of each accident on:

(1A) Animal life in the aquatic environment,
(1B) Ground-living animals and microorganisms,
(1C) Animals in the terrestrial (above ground) environment,
(2A) Vegetation in the aquatic environment,
(2B) Vegetation in the terrestrial environment,
(3A) The potential for using groundwater and surface water for drinking water,
(3B) The potential for using land and water for economic activities, such as growing crops, forestry, commercial fishing and building,
(4) Vital installations such as wells, cables, sewage systems, and water treatment plants, etc.,
(5) The potential of the site for outdoor life and recreational pursuits such as fishing (angling), walking, trekking and swimming.

The experts made their judgements for each response on a continuous scale. Markings at 0% (no effects), 25% (small effects), 50% (moderate effects), 75% (large effects), and 100% (very large effects) served as guidance to the expert panel. Hence, the judgements were expressed as a numerical value between 0 and 100%. The judgements of these questions were used as responses (y-variables) and modelled together (see Section 4 below).

The expert panel study [5] showed that the responses were correlated. The responses showed a time dependence were the largest effects were judged after 0–1 year and smaller effects with time (Fig. 1). As expected, the experts found it difficult to judge the environmental effects after more than 1 year, and therefore only the first time interval, 0–1 year, was modelled.

The expert panels consisted of 10 experts judging the accidents in the training set, and 7 experts, judging the accidents in the validation set. This means that single expert judgements of an accident in one panel could not be directly compared to single judgements of an accident in the other panel. To get comparable measures of the judgements between the two expert panels the median judgements in each group were used (response variables in Table 2). Consequently, each accident was assigned a median value for each response to be used in the modelling. The medians of the responses for the 18 chemical accidents in the training- and validation set can be seen in Table 2.

3.3. Pre-treatment of data

Variable S_w was log transformed and the variables P_v, v, D, m/Tox, DNW and DGS in the X matrix were power transformed

Table 2
Summary of the judgements of the expert panel expressed as the median of the judgements for each response and accident (*y*-variables)

Accidents	Expert judgements of environmental effects								
	1A	1B	1C	2A	2B	3A	3B	4	5
T1	75	75	32	51	51	96	55	15	75
T2	85	70	49	69	53	95	92	87	87
T3	90	75	50	74	68	77	74	26	94
T4	75	56	49	50	41	26	50	4	49
T5	55	26	35	36	38	25	26	4	37
T6	83	48	25	74	25	83	74	98	82
T7	40	52	26	23	48	25	25	61	50
T8	60	71	26	29	35	22	25	6	38
T9	25	57	13	18	25	31	18	3	6
V1	75	75	25	75	50	75	50	50	75
V2	75	75	50	75	75	75	50	50	75
V3	75	75	50	75	75	50	75	25	75
V4	75	75	25	75	50	50	75	25	50
V5	97	75	50	75	75	75	75	50	75
V6	25	25	1	25	25	25	1	1	1
V7	100	100	50	100	75	75	100	50	100
V8	50	50	25	25	25	75	25	1	25
V9	25	25	25	25	25	25	1	50	12

in order to approach a normal distribution, as described below.

S_w : $10 - \log$

P_v : $(X)^{-0.25}$

v : $(X)^{0.5}$

D : $(X)^{-2}$

m/Tox, DNW and DGS : $(X)^{0.25}$

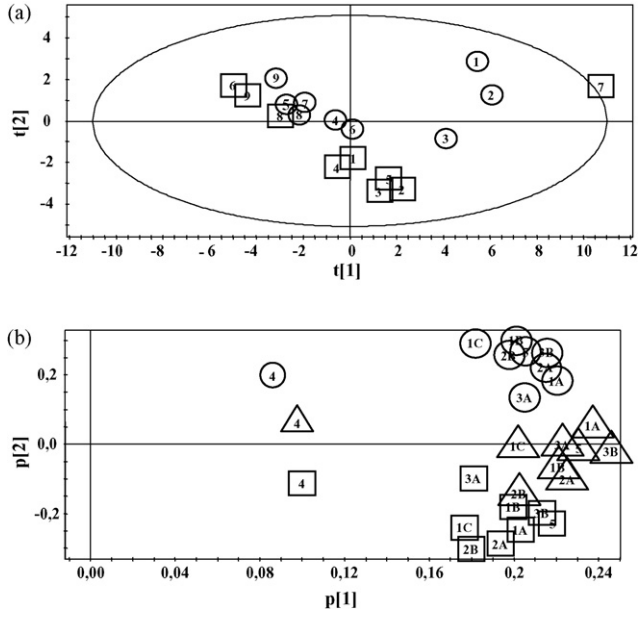

Fig. 1. Chemical accidents described by the medians of the judged response values. (a) Variable scores $t[2]/t[1]$ for the accidents. Accidents in the TS are marked with circles and accidents in the VS are marked with squares. (b) Variable loadings $p[2]/p[1]$ for the responses. Responses for years 0–1, 1–5 and >5 are marked with squares, triangles and circles, respectively.

Before calculation the variables in the *x* and *y* matrices were mean centred and scaled to unit variance in order to allow each variable equal opportunity to influence the model.

4. PLS-modelling

Partial least squares projections to latent structures, PLS, is a data analysis technique that can handle data matrices with correlated variables like expert judgements, chemical properties, etc. The method is also capable of handling large data matrices and is better than traditional methods for handling noisy and missing data [19,20]. PLS relates two data matrices: *X* (containing the properties of the chemicals involved and the site-specific properties of each accident) and *Y* (containing the responses, in this study the environmental consequences of each accident as judged by the experts) to each other (see Fig. 2). The method can be used to predict a response value, *y*, for a known set of *x*-variables.

PLS is built on projection of each data matrix to latent structures where the correlation between the matrices is investigated. The new projected *latent variables* or vectors are calculated so that the first vector describes the highest correlation between *X* and *Y*, the second vector describes the second highest correlation

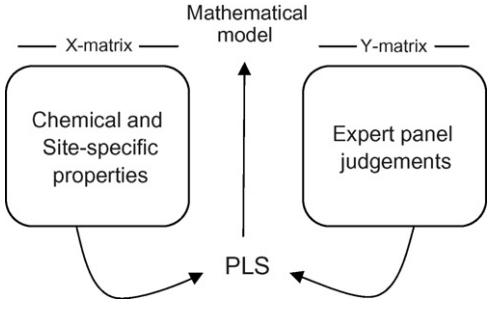

Fig. 2. A schematic picture of the modelling process.

and so on. The vector is a straight line through the average point of each point (observation) swarm that is fitted to the observations. Through projection of the points (observations) on this vector the so-called score values are obtained and the score values of all observations form the first *X*-score vector *t*[1]. The same procedure is applied to the *Y* matrix where the best correlation from *Y* to *X* is described with the first *Y* score vector, *u*[1]. Then vectors *t*[2] (always orthogonal to *t*[1]), and *u*[2] (not necessarily orthogonal to *u*[1]), can be calculated in the same way for maximum correlation.

Having done this, *t*[1] and *u*[1] are related to each other with the inner correlation, $ui[1]=ti[1]+h_i$, where h_i is the residual. After this, predictions can be made by inserting *x*-variables from an observation into the model and using the inner relation between *t* and *u*, to predict the unknown *y* response value. The number of significant PLS-components calculated of the model, described by the goodness of fit (R^2) and the goodness of prediction (Q^2) for each PLS-component, are used to evaluate the models. R^2 and Q^2 range between 0 and 1. A high value of both is preferable and the difference between R^2 and Q^2 should not be too large, if possible not above 0.2–0.3.

A PLS model may be re-expressed as a solution consisting of PLS regression coefficients, *B*, according to Eq. (3)

$$Y = XB \tag{3}$$

Here, *X* refers to the *X* matrix, including squared and/or cross-terms (if included), and *Y* is the response matrix. If *X* and *Y* are unscaled and uncentered, the regression coefficients are expressed as Eq. (4):

$$y_m = b_0 + b_1x_1 + \cdots b_kx_k \cdots, \text{ etc.} \tag{4}$$

This solution is favourable when the purpose is to present the model to other people, who are not familiar with the latent way of thinking [21].

The number of significant PLS components are usually determined using a method called cross-validation (CV). With CV the dataset is divided into *X* groups of typically 5–10 objects [21]. A model is fitted for the dataset with one group excluded. The excluded group is predicted by the model and the difference between the actual and the predicted value is calculated. This process is repeated *X* times and then all partial predictions are summarised, providing a measure of the predictive power, which can be expressed as the goodness of prediction (Q^2) for each component of the model. In PLS modelling, an external validation is preferred, i.e., prediction of an external set of data with known *y*-responses by the model, based solely on the training set. The difference between the predicted and known *y* values will indicate the predictive power of the model.

5. Results and discussion

The dataset of chemical accidents was initially divided in two subsets; a training set (TS) and a validation set (VS), in order to allow an external validation of a model built on the TS. However, during the first modelling phase it was found that there were too few accidents in the TS to represent the variation in the VS and to build a model that covered a broad spectrum of chemical accident situations. Therefore, we considered both the training and validation sets as a single, combined set for the modelling and to restrict the validation procedures to internal validation (cross-validation).

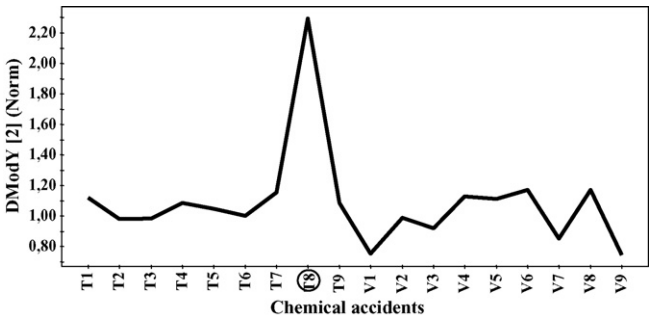

Fig. 3. The objects (accidents) distance to the model in the *Y*-space (DModY).

5.1. Results of the modelling

The modelling resulted in a one-component PLS model for the time interval 0–1 year with R^2 and Q^2 values of 0.758 and 0.648, respectively. This model was obtained through several steps (described in more detail below) in which one accident (T8), three responses (1C, 2B and 4) and three property variables (K', *n* and *v*) were excluded from the calculations for the following reasons.

Firstly, accident T8 was found to be an outlier in its relation between *X* and *Y* as shown in Fig. 3. The reason for this anomaly is that for this particular accident the expert judgements concerning the effects in the aquatic environment varied extensively (0–96% effects). Thus, in this case, the median value (29%) was a bad estimate of the judgements made. For that reason, the accident T8 was excluded.

Secondly, it had already been observed that response 4 (effects on vital installations) behaved differently from the other responses (see Fig. 1 above) and so was also excluded, resulting in a two component model with R^2 and Q^2 values of 0.749 and 0.518, respectively. Thirdly, responses 1C (effects on animals in the terrestrial environment) and 2B (effects on vegetation in the terrestrial environment), proved to have a lower predictive capacity (Fig. 4) than the other responses and to investigate if the predictive power of the model would be better without these responses they were excluded, resulting in a model with R^2 and Q^2 values of 0.756 and 0.593, respectively.

Finally, three property descriptors (K', hydraulic conductivity; *n*, porosity; and *v*, viscosity), were excluded since they were of low importance for the model, as shown in the VIP[1]-plot in Fig. 5. In Fig. 5, the variable S_w has a large confidence interval (jack knifing), but its contribution to the model is still significant (close to one in the VIP plot). It was therefore considered

[1] The variable influence on projection parameter (VIP) shows how each variable influences the model. Variables with large VIP are the most relevant for the model.

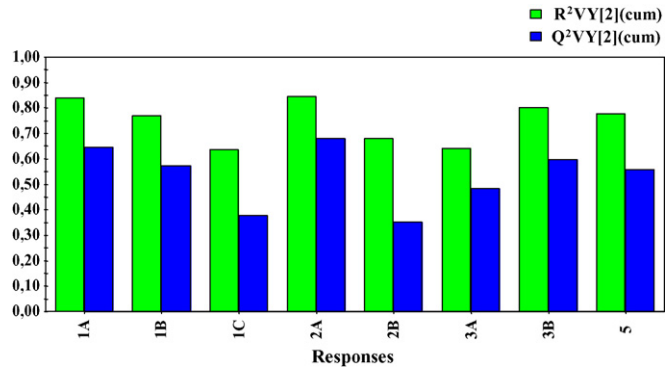

Fig. 4. The explained variance (R^2Y) and the goodness of prediction (Q^2Y) for the responses.

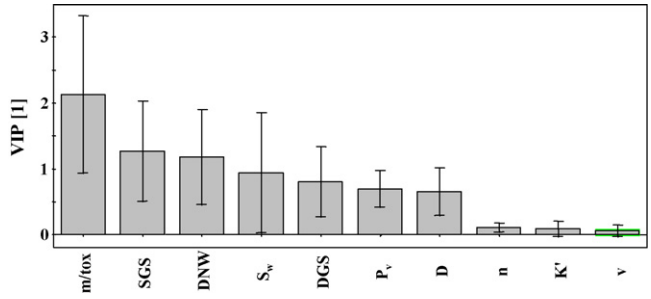

Fig. 5. Variable of importance plot (VIP) of the *x*-variables.

as significant for the model. The final model, EAI_{new} was calculated as described above.

It is of great importance to point out that the excluded variables are of low significance only for EAI_{new} and its proposed usage, and that these chemical and site-specific properties together with the responses are still important factors to consider in every type of chemical accident.

5.2. Classes

EAI_{old}, was developed for use with a three-category risk scale, with classes 0–100, 100–500 and more than 500. Each class was associated with specific recommendations regarding further investigations and measures that should be taken for the described accident scenario. This approach was satisfactory since the purpose of the EAI is to give guidelines about measures that should be taken rather than exact risk values. The new model, EAI_{new}, is mainly based on the accident describing variables of EAI_{old}, with a few additional variables. One purpose of this study was to compare the original EAI_{old} and EAI_{new} to see which descriptors were important and decide the weight they should be given in a final model.

To facilitate such a comparison, the EAI_{new} also has to use categories or classes. One possibility would have been to use the same division of effects levels as used in the questionnaires, i.e., 0–25% = no/small effects; 26–50 = small to moderate effects; 51–75 = moderate to large effects and 76–100 = very large effects. However, the classification associated with EAI_{old} was based on three categories and the initial valuation of EAI_{old} [2] indicated that the limits for these categories worked well. Given this and the fact that accidents should be neither underestimated nor overestimated, the following classification scale was proposed.

(Class I) 0–33% for small to moderate effects,
(Class II) 34–74% for moderate to large effects,
(Class III) 75–100% for large to very large effects.

Using this new classification scale, EAI_{new} can be compared to EAI_{old}.

5.3. EAI_{new} in relation to EAI_{old}

To investigate the weight and importance of the accident describing variables in the new model in relation to the variables in EAI_{old}, EAI_{new} can be re-expressed as a regression model (see below). The PLS analysis showed that the pattern of explained variance is similar among all responses (Fig. 6). This means that the responses are similar in character and, generally, one response can be selected to represent the others. Therefore, response 2A (effects on vegetation in the aquatic environment) is used as an example to study the feasibility of such an approach.

A regression model was expressed through the use of regression coefficients derived from EAI_{new} for each variable.

The result is presented in Eq. (5), in which all the variables are unscaled but transformed (see Section 3.3).

$$EAI_{new} = \underbrace{18.9 + [7.1(P_v)^{-0.25} + 8.7\times10^{6}(D)^{-2} - 3.2\log S_w]}_{\text{chemical property variables}} + 0.07(m/\text{Tox})^{0.25} - \underbrace{[6.8(\text{DNW})^{0.25} - 7.4(\text{DGS})^{0.25} + 27.9\text{SGS}]}_{\text{Site-specific property variables}} \quad (5)$$

To compare the relative weights in the model of the variable *m*/Tox and two groups of variables: the chemical properties (P_v, D and S_w) and the site-specific properties (DNW, DGS and SGS), each variable and the sum of these groups were calculated for the accidents in the dataset according to Eq. (5) The result can be seen in Table 3.

The results show that SGS is the most important of the calculated variables followed by *m*/Tox, DNW, *D*, DGS, P_v and S_w. The variables in the two groups were summed to compare their importance. In general the EAI_{new} is more strongly influenced by the chemical variable group and single variable *m*/Tox than

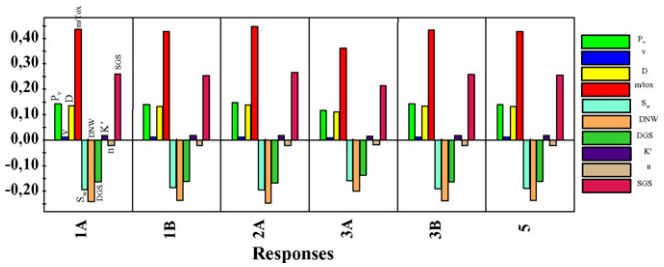

Fig. 6. The scaled and transformed weights, i.e., the coefficients, for each variable.

Table 3
Calculated variables, and calculated sums of both chemical property variables and site-specific variables, according to EAI_{new}

Accident:	P_v	D	S_w	m/Tox	DNW	DGS	SGS	∑Chem.prop.var	∑Site-spec.var
TS1	8.4	12.9	3.2	21.9	-21.5	-11.1	27.9	24.5	-4.7
TS2	8.4	12.9	3.2	21.9	-10.2	-4.9	27.9	24.5	12.8
TS3	2.5	15.5	6.4	20.8	-21.5	-2.3	27.9	24.4	4.1
TS4	2.5	15.5	6.4	20.8	-8.1	-8.7	14	24.4	-2.8
TS5	3.8	13.9	-6.3	2.8	-22.7	-17.7	27.9	11.4	-12.5
TS6	15	7.6	-2.9	28.4	-9.6	-10.5	14	19.7	-6.1
TS7	6.8	11.2	6.4	9	-15.2	-16.2	14	24.4	-17.4
TS8	8.1	10.5	6.4	20	-6.8	-9.8	27.9	25	11.3
TS9	-	4.6	9.6	1.6	-25.6	-8.2	14	14.2	-19.8
VS1	12.6	13.3	3.2	20.8	-13.4	-8.2	27.9	29.1	6.3
VS2	8.4	12.9	3.2	24.1	-11.1	-5.9	27.9	24.5	10.9
VS3	8.4	12.9	3.2	18.6	-10.2	-12.4	27.9	24.5	5.3
VS4	2.5	15.5	6.4	19.3	-15.2	-2.3	27.9	24.4	10.4
VS5	2.5	15.5	6.4	20.4	-8.1	-14.8	27.9	24.4	5
VS6	5	13.9	-6.3	1.2	-28.3	-8.8	27.9	12.6	-9.2
VS7	6.8	7.1	4.2	47.4	-15.9	-9.1	27.9	18.1	2.9
VS8	3.8	10.1	5.4	14.2	-11.1	-12.3	14	19.3	-9.4
VS9	4.9	5.8	-6.3	6.8	-15.9	-9.9	14	4.4	-11.8

the site-specific variable group (these groups and the variable *m*/Tox are coloured grey in the table).

Regarding how each variable influence the magnitude of EAI_{new} compared to how they influenced EAI_{old}, the results show that *m*/Tox (compared to Am and Tox), DNW, DGS and SGS (all of which contribute to variable Sur) influenced the magnitude of EAI in the same way in both the old and new models. For example: high values of *m*/Tox (due to very large amount of chemicals or very toxic chemicals, or both) give high values when calculated in EAI_{new}, and also high values for Am and Tox, in special tables used to calculate EAI_{old} [2]. High values mean, for both indices, larger effects in the environment.

However, the influence of one variable, S_w, on the two models is qualitatively different. Low water solubility gives a high value in EAI_{new} and a low value in EAI_{old}, which means that highly soluble chemicals give the highest value calculating EAI_{old} while highly soluble chemicals have a negative influence on the magnitude of EAI_{new}. This difference between the models is probably due to the fact that EAI_{old} contained inorganic chemicals that could both be highly soluble and toxic. The difference can also be due to the judgements related to EAI_{new}, since the experts probably considered the largest environmental effects to be associated with accidents involving chemicals with low water solubility. For variables P_v and D, which were added to EAI_{new}, a high vapour pressure (P_v), and a high density (D) gives a low value in EAI_{new}, indicating smaller effects in the environment and vice versa. As chemicals with a low P_v will stay in the water and soil environment for a longer time they can have a more negative (toxic) influence on this environment than chemicals with a high P_v. Chemicals with a higher density can be more difficult to clean up and they can therefore have larger negative effects on the environment than a low density chemicals.

5.4. Observed versus predicted effects

To evaluate the PLS model the estimated predictions of model EAI_{new} were analysed. In Table 4, the observed versus the estimated (or "predicted") values for each accident and response can be seen, the classified accidents being coloured grey. It has to be remembered that there is a confidence interval for every observed and, hence also every predicted response value. In Table 4, borderline response values (defined as those within a confidence interval of ±2 of the limit between two classes), are marked with circles, and underestimated values are marked with squares.

The fact that many of the non-classified response values (41) were borderline values (26) and few were underestimated (7) is a satisfactory result. Even if some of the response values are close to class limits, and therefore the classification has a fairly high degree of uncertainty these results show that the model gives class predictions close to corresponding observed response values.

It is also clear, from Table 4, that the highest number of accidents (71%) can be classified by responses 1A (effects on water living organisms) and 3B (the potential for using land and water resources). Similarly, the lowest number of accidents can be classified according to responses 3A and 5 (53 and 47%, respectively), while 59% can be classified by responses 1B and 2A. Summarising the distribution of the accidents into classes based on the responses, seven were classified as Class II, while Class I and III included four and six accidents, respectively. This is very

Table 4
Observed and estimated (predicted) values of model EAI_{new}

Accidents:	$1A_{obs}$	$1A_{pred}$	$1B_{obs}$	$1B_{pred}$	$2A_{obs}$	$2A_{pred}$	$3A_{obs}$	$3A_{pred}$	$3B_{obs}$	$3B_{pred}$	5_{obs}	5_{pred}
T1	(75)	71	(75)	65	51	61	96	[62]	55	57	(75)	63
T2	85	88	70	79	69	78	95	77	92	77	87	84
T3	90	78	(75)	71	74	68	(77)	68	74	66	94	[72]
T4	(75)	72	56	65	50	61	26	62	50	57	49	63
T5	55	(32)	26	33	36	[20]	25	29	26	10	37	[16]
T6	83	[72]	48	65	74	61	83	[62]	74	57	82	[63]
T7	40	47	52	45	23	(35)	25	41	25	27	50	(33)
T9	25	32	57	(32)	18	19	31	28	18	9	6	15
V1	75	85	75	76	75	75	(75)	74	50	74	75	80
V2	75	89	75	79	75	79	75	77	50	78	75	84
V3	75	78	(75)	70	(75)	68	50	68	(75)	65	(75)	71
V4	75	83	75	75	(75)	73	50	72	(75)	71	50	(77)
V5	97	79	(75)	71	(75)	69	(75)	69	(75)	66	(75)	73
V6	25	(35)	25	(35)	25	23	25	31	0	13	0	19
V7	100	97	100	86	100	88	75	84	100	88	100	94
V8	50	54	50	51	25	43	(75)	48	25	36	25	42
V9	25	30	25	31	25	18	25	27	0	7	12	13

Classified accidents are coloured grey. (a) Borderline response values, and (b) underestimated values.

close to the EAI_{old} categories calculated for the same accidents, since eight of them were placed in category 100–500, four in category 0–100, and five in category >500.

EAI_{old}, is built on cross-terms as shown in Eq. (6). To investigate how cross-terms influence EAI_{new} this approach was tested as shown in Eq. (7)

$$EAI_{old} = Am \cdot Tox(Con + Sol) + Am \cdot Tox(Sur) \quad (6)$$

If the same idea is practised on Eq. (5) the result will be an EAI_{new} with cross-terms, $EAI_{new(CT)}$, as schematically described in Eq. (7):

$$EAI_{new}(CT) = K + m/Tox(P_v + D - S_w) + m/Tox(SGS - DNW - DGS) \quad (7)$$

Calculating a PLS model including all possible cross-terms revealed that the only important cross-term was m/Tox·DNW, and according to Eq. (5), the linear model therefore would be described as Eq. (8):

$$EAI_{new} = 18.9 + [7.1(P_v)^{-0.25} + 8.7\times10^6(D)^{-2} - 3.2\log S_w] + 0.07(m/Tox)^{0.25} - \underbrace{[0.07(m/Tox)^{0.25} \cdot 6.8(DNW)^{0.25}]}_{\text{crossterm}} - [6.8(DNW)^{0.25} - 7.4(DGS)^{0.25} + 27.9SGS] \quad (8)$$

The model $EAI_{new(CT)}$ showed a lower R^2 (0.731) and Q^2 (0.603) than EAI_{new} and when $EAI_{new(CT)}$ was used to estimate predictions (the same way as described above) the result was poorer than for EAI_{new}. This indicates that the usage of cross-terms might be restricted in the final EAI formula.

5.5. Prediction of responses for 37 chemical accidents

Despite the fact that no external validation set could be used for predictions, EAI_{new} was used to predict responses for 37 chemical accidents. These 37 accidents were part of the dataset in the selection procedure [4]. The responses related to these accidents are not known since they were not part of the expert panel study. Table 5 shows the results of the predictions.

The model membership probability, MP value, shows that most accidents, at a 95% confidence level, belong to the model. This findings show that the accidents selected to build the model (EAI_{new}) adequately covered all of the accidents in the original dataset. Only one accident, No. 23, has a model membership probability lower than 5%. This accident also shows a DModX value (1.93) above the critical limit for a 95% confidence level (1.838) which means that this accident is regarded as an outlier and does not belong to the model.

When all the predicted responses (1A, 1B, 2A, 3A, 3B and 5) are taken into account each accident can be placed in a class according to the classification scale in Section 5.2. The results showed that five accidents were placed in Class I, 25 accidents in Class II, and seven accidents in Class III. This can be regarded as a normal distribution.

5.6. Potential use of EAI_{new} in the future

EAI_{new} has several advantages compared to EAI_{old}. Firstly, EAI_{new} does not require nine tables for its calculation, instead it can be directly calculated from raw data. This is advantageous, since the use of tables is not only time consuming, but there is also a risk that wrong values may be taken from the tables when calculating EAI_{old}. Secondly, the calculated PLS version

Table 5
Predictions of responses for 37 accidents [3]

Accidents	MP	DModX	1A	1B	2A	3A	3B	5	Class
1	0.76	0.74	83	75	73	73	72	78	II
2	0.45	1.02	77	70	67	68	65	71	II
4	0.65	0.84	95	84	85	83	85	92	III
5	0.62	0.87	80	72	70	70	67	73	II
6	0.15	1.45	39	38	27	34	18	24	I
7	0.88	0.61	73	67	63	64	59	65	II
8	0.95	0.49	108	95	99	94	101	108	III
10	1.00	0.28	85	76	75	74	74	80	III
11	0.86	0.64	59	55	48	52	42	48	II
12	0.96	0.47	81	73	71	71	69	75	II
13	0.97	0.44	72	66	62	63	58	64	II
14	0.67	0.83	58	54	48	51	42	48	II
17	1.00	0.24	85	76	75	74	74	80	III
18	0.38	1.10	83	75	73	73	72	78	III
19	0.13	1.50	55	51	43	48	37	43	II
20	0.06	1.78	36	36	24	32	15	20	I
22	0.87	0.63	80	72	70	70	67	73	II
23	0.04	1.93	9	14	-4	9	-18	-12	I
24	0.43	1.04	65	60	54	57	49	55	II
25	0.07	1.71	134	116	126	116	133	139	III
26	0.93	0.54	65	60	55	57	50	56	II
27	0.42	1.05	78	70	68	68	65	71	II
28	0.88	0.61	71	64	60	62	56	62	II
29	0.70	0.80	80	72	70	69	67	73	II
33	0.47	1.01	56	52	45	49	38	44	II
34	0.33	1.16	84	76	74	73	73	79	II
36	0.15	1.45	49	47	37	43	30	36	II
37	0.43	1.05	63	58	52	55	47	53	II
38	0.54	0.94	68	62	57	59	53	59	II
39	0.75	0.75	78	71	68	68	66	72	II
40	0.74	0.76	80	72	69	69	67	73	II
43	0.45	1.03	102	90	92	88	94	100	III
46	0.83	0.67	60	56	49	53	44	50	II
51	0.47	1.00	49	47	38	43	30	36	II
52	0.70	0.77	56	52	45	49	39	45	II
53	0.30	1.19	31	32	19	28	9	15	I
54	0.86	0.63	41	40	29	36	20	26	I

The predicted response for the six responses 1A–5, the model membership probability (MP) with a 95% confidence level, the distance to the model (DModX), and the class of each accident according to the classification scale in Section 5.2.

of EAI_{new} can estimate effects for all the included responses, as well as roughly classifying accidents according to the new classification scale. Thirdly, the regression model of EAI_{new} based on a response, such as the example shown above with response 2A, can easily be calculated by anyone without the ability to perform PLS, especially if pre-calculated values of the chemical properties and toxicity are listed and only the site-specific properties have to be included. It is also very easy to make regression models for all responses in the same way as illustrated for response 2A. Finally, and most important, the EAI_{new} is based on a selected set of representative chemical accidents chosen from a larger and more diverse dataset than EAI_{old}, and was developed, via this selection, to be as unbiased as possible. This should make the EAI_{new} safer to use for many different organic chemicals and situations as it covers a broader spectrum of accident scenarios.

These advantages make it possible for concerns and interested parties in different authorities, industries or other parts of Sweden (or any other country) to calculate estimated effects in a standardised way. The only tasks they have to perform, in order to make calculations, are to select a site for investigation and then define the properties of the site (DNW, DGS and SGS) and the amount of chemical "to be spilled".

5.7. Discussion

In this study the important components are variables describing the chemical accidents on one hand and the responses judged by the expert panel on the other hand. In general, the results of this study showed (Figs. 5 and 6) that *m*/Tox clearly has the largest influence on the models, followed by SGS (slope of groundwater surface), DNW (distance to nearest well, lake or watercourse) and S_w (water solubility). Descriptors DGS (distance to groundwater surface), D (density) and P_v (vapour pressure) are less influential, and K' (hydraulic conductivity of the soil), n (porosity of the soil), and v (viscosity) have little or no influence on the models. These findings can be explained by the relative difficulty for the experts to understand and use the variables, which in turn depends on their familiarity with judging the influence of these variables.

The amount and toxicity of the chemicals involved are easy to understand and analyse, and relevant data are fairly easy to access, which means that the experts are probably trained to use such information. SGS, DNW, S_w, DGS, D and P_v are also relatively easy to analyse, although it can be harder to find information on some of these descriptors. The viscosity is probably not often used (it is harder to find data on this variable than the other chemically related variables) and is thus not considered to a large extent in the judgements.

The hydraulic conductivity (K') and porosity (n) of the soil were used in an attempt to describe the soil numerically in a way that also gave sufficient information on soil properties that influence the effects of accidents. The results show that these types of variables did not adequately describe the soil properties, and maybe the old system, relying on simple soil variables [2,3], may have provided a better way of describing these properties. It is also possible that geology and related variables were difficult to judge because many of the experts lacked formal education in hydrogeology and/or had little experience in judging these variables. Furthermore, this type of information is often difficult to obtain. All these aspects might have lead to an increased uncertainty in the judgements or caused the experts to pay less attention to these factors.

Regarding the *response variables*, response 1C, 2B and 4 were found to be less well explained (i.e., had lower R^2 values). It is possible that the experts found it difficult to judge responses related to the terrestrial environment (1C, 2B) because some relevant variables for describing these effects are not available in the EAI model and hence also a lack of experience to judge these effects.

One object, accident T8 (involving the spillage of 60 tonnes of styrene in a harbour area), was also removed from the data set as it was considered an outlier in the y-space. One reason for this is that the experts judged T8 to cause effects on vegetation in the aquatic environment (2A) varying from 0 to 96% [5] (i.e., their opinions of the effects in the environment varied greatly). The median value (29%) is in this case a poor description of the actual judgements, so the accident becomes an outlier.

6. Conclusions

By excluding less important variables and responses a better model, EAI_{new}, was obtained. EAI_{new} has the capacity to classify accidents roughly, if combined with the proposed new three-class classification scale. Further, the results of EAI_{new} showed that

- A regression model of EAI_{new} (each response), could be obtained based on the regression coefficients of the variables.
- When the contribution of each variable group to EAI_{new} is calculated, the chemical property variables (P_v, D, S_w) have greater total influence on the magnitude of EAI_{new} than the site-specific variables (DNW, DGS, SGS).
- Variables related to water solubility (S_w/Sol) have qualitatively different effects on the magnitude of EAI_{old} and EAI_{new}.
- The prediction of the accidents with unknown responses showed that EAI_{new} has been established on a valid base of accident scenarios, showing that the model can already be used in this stage of development.

7. Future work

The work with EAI_{new} will continue and the highest priority issues should be:

- to validate EAI_{new} externally to confirm its predictive power;
- to refine the structure of the formula through further consideration of:
  - S_w—how should it be handled in the formula?
  - soil variables—can simpler soil variables be used?
  - weights on the variables, especially site-specific variables.
- to further refine the classification scale, modifying the classes where necessary developing more extensive recommendations and, perhaps checklists connected to each class regarding the way the results of the EAI calculation should be treated;
- a real-life validation where EAI_{new} is tested in real-life scenarios by people working with chemical accidents.

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