A METHOD FOR EVALUATING HAZARDS OF LOW VOLATILITY TOXIC LIQUIDS

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ABSTRACT

Although spills of low volatility toxic liquids do not receive the public attention given to releases of high volatility or flammable liquids, releases of low volatility toxic chemicals may present a hazard to facility personnel and the public. The purpose of this paper is to develop a method of ranking and evaluating the hazard presented to the public by a low volatility toxic chemical or a low volatility mixture of toxic chemicals. The ranking system, named *LOVRS* (LOw Volatility hazards Ranking System), can be used to determine if currently stored chemicals present a hazard to the public, or to screen the list of chemicals that might be stored at a proposed facility. For example, this type of information could be used to determine whether a mixture of chemicals stored at a toxic waste incineration site presents a hazard to the public.

LOVRS employs readily available chemical properties, such as vapor pressure, molecular weight, Short Term Exposure Limit (*STEL*), Time Weighted Average (*TWA*), or other selected measure of toxicity, to compute a numerical value that is related to the hazard potential of each chemical. Commonly available sources of the required chemical properties are the CCPS DIPPR data base, NIOSH, etc.

This paper presents ten toxic chemicals which were ranked using *LOVRS* and compares the results with other ranking methods. Extension of the pure-component ranking equations to multi-component mixtures of hazardous chemicals is developed.

Evaporation rate and dispersion calculations were made for the ten chemicals ranked using *LOVRS*. The results of the calculations for worst-case conditions (Pasquill F stability, 1.5 m/s wind speed) with an assumed distance of 16,500 ft (5,030 m) to an area of concern are presented. Using the computed results, a relationship is shown to exist between the *LOVRS* Toxic Index value and the maximum mole fraction of a component that can be present in the released mixture. This relationship can be used to determine the maximum mole fraction at which a toxic chemical can be stored in a low volatility mixture without presenting a hazard to the public.

INTRODUCTION

The determination of the possible risk of toxic chemical storage facilities to the public often involves many hazard zone calculations for the various chemicals and chemical mixtures that may be present in a facility. When new chemicals are added to the inventory, calculations of the extent of any hazards must be performed for those new chemicals and for any subsequent mixtures of the new chemicals with existing chemicals. Even with a constant number of toxic chemicals present, the large number of possible combinations quickly makes the task of quantifying the risk that the mixtures pose to the public quite daunting. In this paper, we seek to develop a method to allow the quantification of the hazards that chemicals or chemical mixtures with low volatility pose to the public with as few calculations as necessary. To do this, we first develop a ranking system that takes into consideration both the toxicity of the chemical as well as its ability to place its vapor into the air. This ranking is called the Toxic Index (*TI*). Next, we develop a method for determining whether a chemical, when stored as a pure substance, can generate concentrations over the toxic endpoints at the nearest public receptor to the facility. Finally, the *LOVRS* parameter is developed which allows chemicals to be screened for their ability to generate hazardous conditions at the public receptor whether stored as a pure substance or in a mixture.

DEVELOPMENT OF A TOXIC INDEX FOR CHEMICALS

A method of ranking hazardous (toxic) chemicals, termed the Toxic Index (*TI*), will be developed. The purpose of the *TI* is to rank a list of chemicals with respect to their potential hazard to the public. The ranking methodology employs readily available information, such as the Short Term Exposure Limit (*STEL*), the Threshold Limit Value (*TLV*), the vapor pressure of each chemical at 65EF (291.5 K), and molecular weight. The Toxic Index is computed by dividing the estimated vapor concentration at the liquid interface by the *STEL* (or any other suitable value). Both the vapor concentration and the *STEL* are expressed in concentration units of milligrams per cubic meter (mg/m^3).

$$TI = \frac{C_i}{STEL} \tag{1}$$

where: TI = Toxic Index (dimensionless)
C_i = vapor concentration at the liquid interface, mg/m^3
$STEL$ = Short Term Exposure Limit, mg/m^3

STEL values for compounds with only *TLVs* available are estimated using the equation $STEL = 3 \cdot TLV$. This is based on FEMA guidance.)

The interface concentration, C_i, is computed by assuming the vapor above the liquid obeys the ideal gas equation of state. This assumption yields:

$$C_i = P_{vp} \cdot \frac{M_w}{R \cdot T} \tag{2}$$

where: P_{vp} = vapor pressure at 291.5 K (65°F), Pascal (Pa)
M_w = molecular weight, mg/mg-mole
R = gas constant, 8.314 x 10^{-3} [Pascal$\cdot$m^3]/[mg-mole$\cdot$K]
T = vapor temperature, 291.5 K

The Toxic Index for a chemical mixture can be computed using a generalized form of Equation (1).

$$TI_m = \sum_{j=1}^{N} TI_j = \sum_{j=1}^{N} \frac{C_{ij}}{STEL_j} \tag{3}$$

where: C_{ij} = interface concentration of each component in the mixture
$STEL_j$ = *STEL* for each component in the mixture

Utilizing the assumption that the liquid is an ideal mixture (i.e., $P_j = X_j \cdot P_{vp_j}$) yields:

$$TI_m = \sum_{j=1}^{N} \frac{\left(\dfrac{X_j \cdot P_{vp_j} \cdot M_{wj}}{R \cdot T} \right)}{STEL_j} = \frac{1}{R \cdot T} \sum_{j=1}^{N} \frac{\left(X_j \cdot P_{vp_j} \cdot M_{wj} \right)}{STEL_j} \tag{4}$$

where: P_j = partial pressure of component *j*, Pascal
X_j = mole fraction of component *j*, in liquid
P_{vp_j} = vapor pressure of component *j*, at 291.5 K
M_{wj} = molecular weight of component *j*

Given the assumptions under which Equation (4) was developed, the mixture Toxic Index will be directly comparable with the pure component index.

The Toxic Index is dimensionless and represents the ratio of the potential of the chemical to evaporate from the liquid pool (i.e., to enter the air stream) and the toxicity of each compound as measured by the *STEL*. The index uses readily available chemical properties and does not involve complex calculations.

RANKING OF CHEMICALS

For this study, ten chemicals were selected that had varying degrees of volatility and toxicity. All ten chemicals listed here are listed in 40 CFR 261, Appendix VIII. These chemicals are ranked in order of descending toxicity and vapor pressure, the two simplest methods of ranking, in Table 1. When these chemicals are ranked according to their *TI*, however, to reflect both the toxicity of the compound and its ability to leave the pool and enter the toxic vapor cloud, their order changes dramatically, as illustrated in Table 2.

CALCULATION OF EVAPORATION RATES

In order to compute the dispersion distances resulting from a chemical spill, the rate of evaporation of the chemical must be determined. The evaporation rate from a liquid pool is a function of several variables.

- Composition of the liquid
- Temperature of the liquid
- Ambient atmospheric conditions
- Area of the liquid surface
- Depth of the liquid
- Diffusivity of the vapor
- Temperature of the ground

Table 1
Selected Chemicals Ranked by Toxicity and Vapor Pressure

Rank by		Name	*STEL* (mg/m^3)	Vapor Pressure (Pa)
Toxicity	Vapor Pressure			
1	4	Methyl isocyanate	0.15	46,953.0
2	8	Warfarin	0.30	11.997
3	10	Parathion	0.30	0.00107
4	7	Hydrazine	0.39	1,271.4
5	9	Nicotine	1.50	10.62
6	2	Formaldehyde	2.50	419,270.0
7	3	Hydrogen cyanide	5.00	84,116.0
8	5	Carbon tetrachloride	126.00	11,238.0
9	1	Methyl chloride	207.00	471,260.0
10	6	Toluene	565.00	2,666.2

Table 2
Selected Chemicals Ranked by Toxic Index

Rank	Name	P_{vp} (Pa)	*STEL* (mg/m^3)	C_i (mg/m^3)	*TI*
1	Methyl isocyanate	46,953.0	0.15	1,105,472.1	7,369,800.0
2	Formaldehyde	419,270.0	2.50	5,195,163.6	2,078,100.0
3	Hydrogen cyanide	84,116.0	5.00	933,643.3	186,730.0
4	Methyl chloride	471,260.0	207.00	9,819,712.8	47,438.0
5	Hydrazine	1,271.4	0.39	16,818.7	43,125.0
6	Carbon tetrachloride	11,238.0	126.00	713,248.8	5,660.7
7	Warfarin	11.997	0.30	1,526.1	5,087.1
8	Nicotine	10.618	1.50	719.6	473.7
9	Toluene	2,666.2	565.00	101,376.8	17.9
10	Parathion	0.300	0.30	0.13	0.4

The modeling of the evaporation rate can be a complex process involving the simultaneous solution of heat and material balances. Additional complications arise if the liquid is not uniform in temperature and composition.

For demonstration purposes, a simple, yet conservative, approach was taken to develop a method of computing evaporation rates from a liquid pool. The pool was assumed to be uniform in composition over the pool volume. Cooling of the pool due to evaporation was also ignored, leaving the pool temperature constant and equal to the surrounding temperature. These assumptions increase the evaporation rate, yielding a conservative estimate.

The basic mass transfer algorithm used in our calculations was presented by Stiver and Mackay [1983a].

$$\phi_j = \frac{k_j \cdot P_j \cdot M_{wj}}{R \cdot T} \tag{5}$$

where: ϕ_j = evaporation rate for component j, g/m^2-s
k_j = mass transfer coefficient for component j, m/s
P_j = partial pressure of component j, Pascal
M_{wj} = molecular weight of component j, g/g-mole
R = gas constant, [Pascal$\cdot$m^3]/[g-mole$\cdot$K]
T = liquid temperature, K

The partial pressure, P_j, is estimated by assuming an ideal liquid solution.

$$P_j = X_j \cdot P_{vp_j} \tag{6}$$

where: X_j = mole fraction of component j
P_{vp_j} = vapor pressure of component j at pool temperature

The mass transfer coefficient, k_j, is approximated as suggested by Stiver and Mackay [1983b] using the relationship:

$$k_j = 0.002 \cdot U_1 \tag{7}$$

where: U_1 = wind speed at a height of 1 meter, m/s

The mass transfer coefficient, k_j, is not a function of the properties of an individual mixture component and can be designated as *k*. The final equation, obtained by substituting Equation (7) into Equation (5), is:

$$\phi_j = \frac{0.002 \cdot U_1 \cdot X_j \cdot P_{vp_j} \cdot M_{wj}}{R \cdot T} \tag{8}$$

All of the terms in Equation (8) are readily available given the atmospheric parameters and liquid composition.

VAPOR DISPERSION CALCULATIONS

To illustrate how the Toxic Index reflects the relative potential for a chemical to impact the public, vapor dispersion calculations were performed for the ten chemicals that are examined in this paper. The chemicals were assumed to have been released into a 10 m by 10 m containment in rural surroundings. A population center was assumed to be located about 16,500 ft (5,030 m) from the facility. It was also assumed that local air quality standards do not allow the facility to release vapors that could result in concentrations above the *STEL* at the population center for atmospheric conditions of 1.5 m/s wind speed and Pasquill F atmospheric stability. Vapor dispersion calculations were performed for these weather conditions using an area source Gaussian dispersion model. A point source Gaussian model could also be used for the dispersion calculations, but the dispersion results might not give the same vapor concentration at short downwind distances. At distances further removed from the vapor source, both the point source and area source would be expected to give vapor concentrations in good agreement. The centerline concentration versus downwind distance for either the area or point source model is a function of the following variables.

$$C \propto \frac{Q}{\sigma_y \cdot \sigma_z \cdot U} \tag{9}$$

where: C ' concentration of release material, mg/m^3
Q ' continuous source rate, mg/s
σ_y ' lateral dispersion coefficient, m
σ_z ' vertical dispersion coefficient, m
U ' wind speed at the height of the plume, m/s

The dispersion coefficients σ_y and σ_z were calculated using equations by Briggs [1973]. The results of these calculations are shown in Table 3 and Figure 1. As can be seen from the figure, the log of the Toxic Index is proportional to the log of the distance to the *STEL*. As Figure 1 shows, any chemical having a *TI* less than 28,900 would meet the air quality guidelines and could be stored as a pure component at the site. The maximum value of the *TI* that a pure component can have is given the name of Low Volatility Hazard Ranking System (*LOVRS*) index.

If a new chemical were to be introduced at the site, its *TI* could be computed and compared to the value of 28,900. If the *TI* were below 28,900, the chemical could be stored at the site and the air quality guidelines would be met. Toxic Indices could be calculated for a large number of chemicals using a simple spreadsheet and the results used to quickly determine if a new chemical could be stored at the facility as a pure component.

MIXTURES OF CHEMICALS

At many facilities, particularly waste handling facilities, chemicals are stored as mixtures. The question arises, how can the operator determine the maximum concentration levels that each chemical may be stored and still meet air quality guidelines? Can the concept of the Toxic Index be used to determine the highest concentration that a chemical may be safely stored in a mixture? The answer is YES.

Due to the form of the liquid evaporation and vapor dispersion equations developed previously, when the maximum concentration that a material can be stored in a mixture is graphed versus the Toxic Index, the data describe the following relationship between the variables.

Table 3
Results of Dispersion Calculations for Selected Chemicals

Rank	**Name**	***STEL*** **(mg/m^3)**	***TI***	***C*** **at 5,030 m (mg/m^3)**	**Distance to** ***STEL*** **(m)**
1	Methyl isocyanate	0.15	7,369,800.0	37.15	> 10 km
2	Formaldehyde	2.50	2,078,100.0	174.60	> 10 km
3	Hydrogen cyanide	5.00	186,730.0	31.36	> 10 km
4	Methyl chloride	207.00	47,438.0	330.00	7,530.0
5	Hydrazine	0.39	43,125.0	0.56	6,900.0
6	Carbon tetrachloride	126.00	5,660.7	23.97	1,560.0
7	Warfarin	0.30	5,087.1	0.05	1,450.0
8	Nicotine	1.50	473.7	0.02	324.0
9	Toluene	565.00	17.9	3.41	117.0
10	Parathion	0.30	0.4	0.000004	0.0

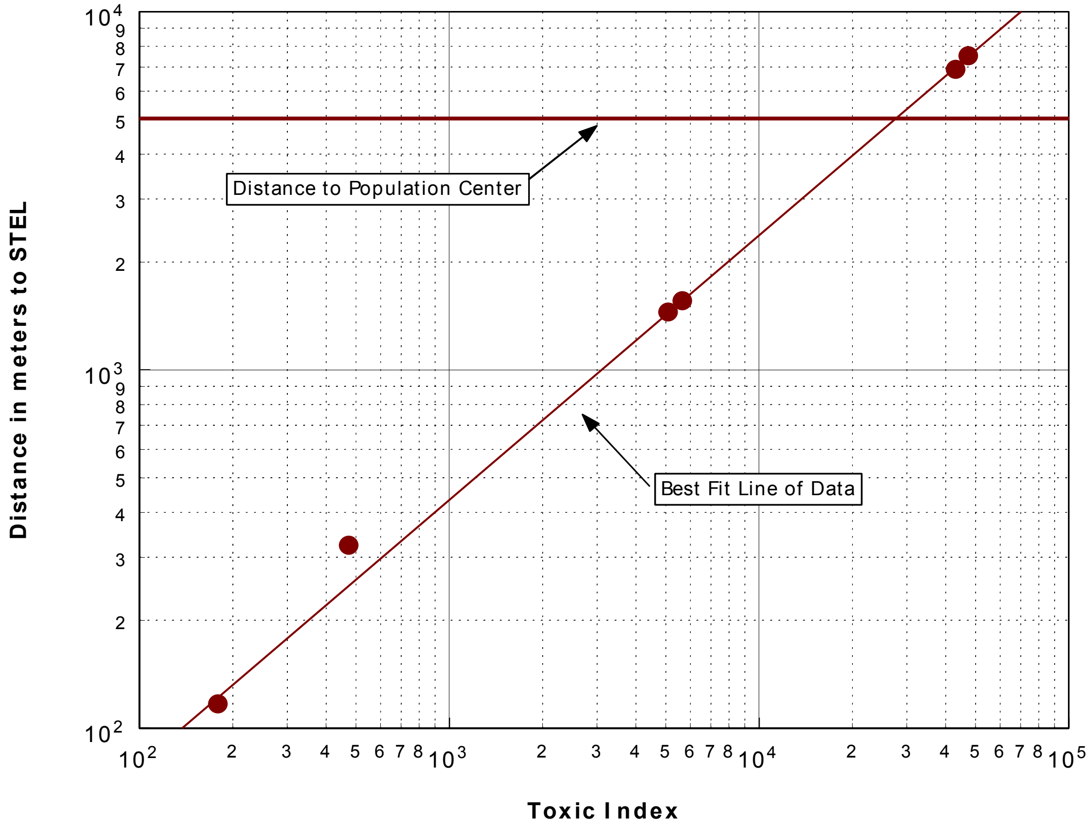

Figure 1
TI **versus Distance to** ***STEL***

$$x_{max} = \frac{LOVRS}{TI} \tag{10}$$

where: x_{max} = maximum concentration allowed in the pool, mole fraction
$LOVRS$ = Low Volatility Ranking System index

The value of *LOVRS* is specific to each facility and governing air quality standards. However, at any given facility, one value for *LOVRS* can be found that will greatly simplify determining the maximum mixture concentration that any chemical can be stored at the facility.

An example can be developed using the ten chemicals described in Table 1. For our hypothetical facility located 5,030 m from a population center and using the local air quality guidelines that require no vapor concentrations above the *STEL* under 1.5 m/s wind speed and Pasquill F atmospheric conditions, we can plot x_{max} versus TI^{-1} to determine the value of *LOVRS*. Table 4 shows the *TI* and values computed for these chemicals, and Figure 2 shows a plot of these data for the ten chemicals selected for use in this study.

Table 4
***TI* and Computed x_{max}**

Name	*TI*	x_{max}
Methyl isocyanate	7369800.0	0.0039
Formaldehyde	2078100.0	0.0139
Hydrogen cyanide	186730.0	0.1548
Methyl chloride	47438.0	0.6092
Hydrazine	43125.0	0.6701
Carbon tetrachloride	5660.7	1.0000
Warfarin	5087.1	1.0000
Nicotine	473.7	1.0000
Toluene	17.9	1.0000
Parathion	0.4	1.0000

As Figure 2 illustrates, the graph of these data is indeed linear. A linear regression on the data yields a slope of 28,900, resulting in the relationship:

$$x_{max} = \frac{28,900}{TI} \tag{11}$$

The *LOVRS* value of 28,900 is identical to the maximum value of the Toxic Index allowable for storing a pure component. When the computed value of x_{max} is greater than 1.0, the chemical can be stored pure; when the value is less than 1.0, x_{max} represents the highest mole fraction at which the chemical can be stored.

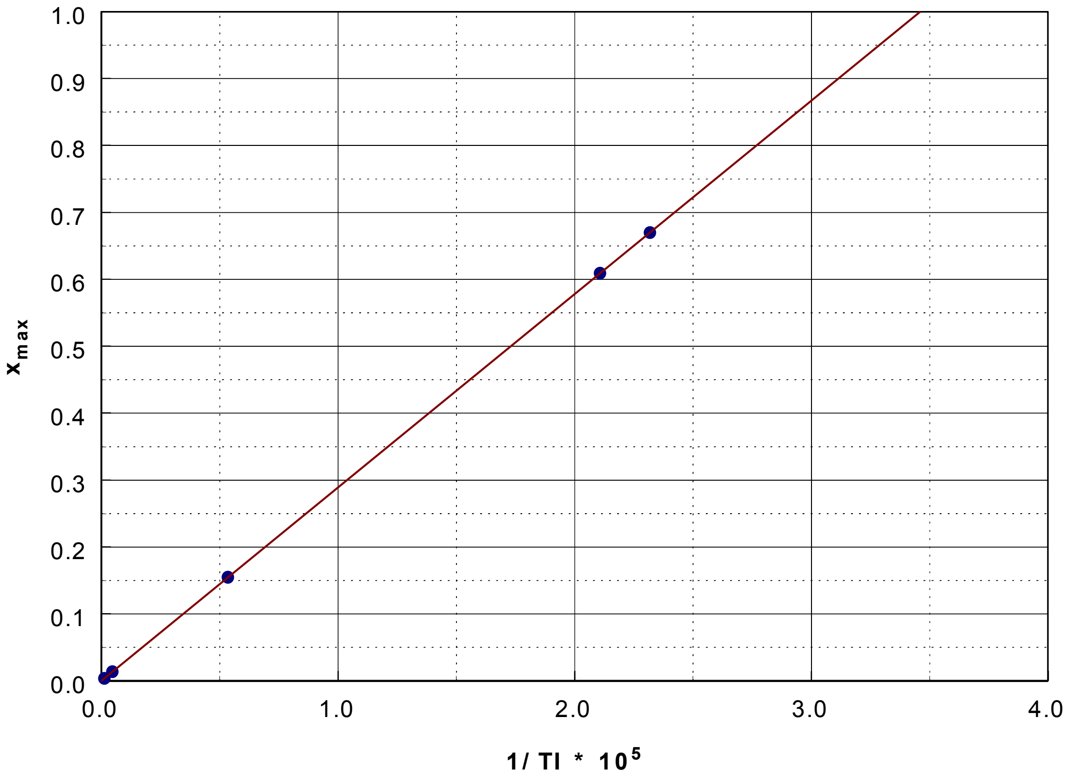

Figure 2
Toxic Index versus x_{max}

Using an area source Gaussian dispersion model, local air quality guidelines, and the Stiver and Mackay evaporation algorithm, the value of *LOVRS* can be found utilizing only two chemicals. This is done by plotting the Toxic Index versus the downwind distance to the air quality guideline concentration. A vertical line representing the distance from the facility to the nearest population center will intersect the line defined by the two chemical points at the *LOVRS* value. Figure 3 shows this methodology using the chemicals hydrazine and warfarin.

The *LOVRS* value found is applicable for use in computing maximum allowable concentrations for other chemicals that may be stored at the facility.

CONCLUSIONS

A method for using readily available material properties, combined with local air quality guidelines, to determine the maximum allowable storage concentration of a wide range of low volatility chemicals has been developed. This method requires the use of only two chemicals to determine the value of the LOw Volatility Ranking System index. The value of *LOVRS* thus determined can be used to screen other chemicals to determine the highest concentration that they can be stored at the facility.

This technique is simple to use and uses readily available models and chemical properties. It is suitable for use by both facility operators and regulators.

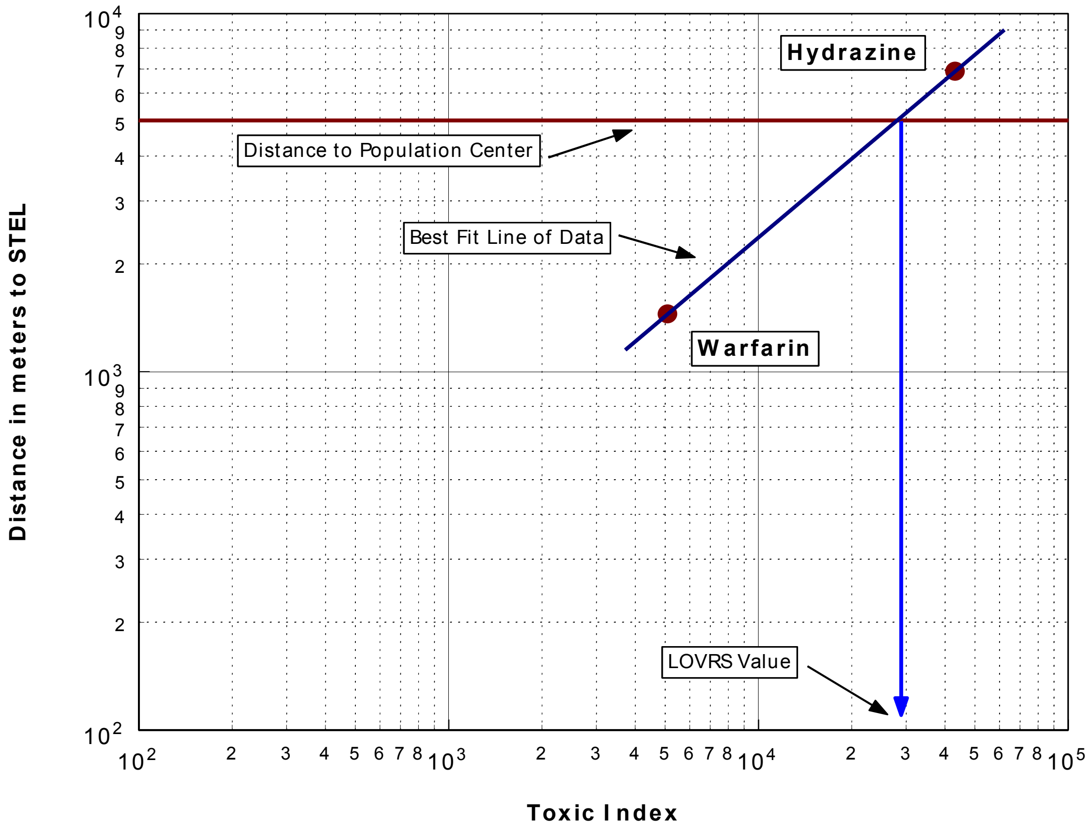

Figure 3
Calculation of *LOVRS* Index

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