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TECHNICAL MEMO #1

STATISTICAL CONSIDERATIONS IN AQUATIC ECOLOGICAL RISK CALCULATION

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CHAPTER 1

INTRODUCTION

The risk assessment process quantifies the probability that due to emission of a contaminant or contaminants target species indigenous to the receiving water body will be adversely affected. Risk, synonymous with the probability of adverse ecological effect or probability of damage to an aquatic ecosystem, is a single dimensionless probabilistic number. Alternatively, the ecological impact of pollutants in receiving waters can be evaluated using a traditional water quality approach where water concentrations are compared with established water quality standards. In the latter concept, exceedance of the criteria implies an unacceptable risk

The more accurate (and conceptually cleaner) procedure, as outlined in the WERF methodology by Parkhurst et al. (1996) and modified for stormwater discharges by Novotny and Witte (1997), removes the consideration of the water quality criteria completely. Instead, the methodology is based on a direct consideration of the joint probability of two probability functions: (1) the probability density function of the event mean concentrations (EMC) adjusted for the appropriate dilution ratio (DR) and water effect ratio (WER) effects, f(EMC) = pdf(EMC x DR/WER), and (2) the risk function g(R|EMC), which gives the value of the probability that an organism will be adversely affected by the exposure to the given stormwater EMC (as modified by DR and WER), and considering also the effects of water hardness on the LC_{50} values. The joint probability, again taking into account the probability of wet-weather events, is

$$h(R,C) = p_{ww}\,\mathrm{f(EMC)}\;\mathrm{g(R|EMC)} \qquad \textbf{(1.1)}$$

Hence, the joint probability function of Eq. 1.1 gives the probability that (1) a wet-weather event will occur, (2) a particular EMC will occur in the stormwater (given that there is a wet-weather event), and (3) an indigenous organism will be adversely impacted (given that there is a wet-weather event and given that the adjusted EMC is equal to that particular value). The integration of Eq. 1.1 over all concentrations, as summarized in Figure 1.1, will then yield the total risk that the stormwater discharges will be adverse to the indigenous aquatic life, *R*.

The paper focuses on uncertainties associated with the risk function g(R|EMC). The risk function represents the probability that an organism will be adversely affected by the exposure to the water EMC adjusted for the relevant the WER (also for DR if concentrations are given for stormwater). The risk function is represented by toxicity level of compounds for aquatic organisms established in standard toxicity bioassay tests. The test organisms include organisms from four groups: microorganisms, plants, invertebrates, and fish. The number of tested organisms varies from compound to compound However, at least eight different families of species specified by states are required for a complete test of toxic effects.

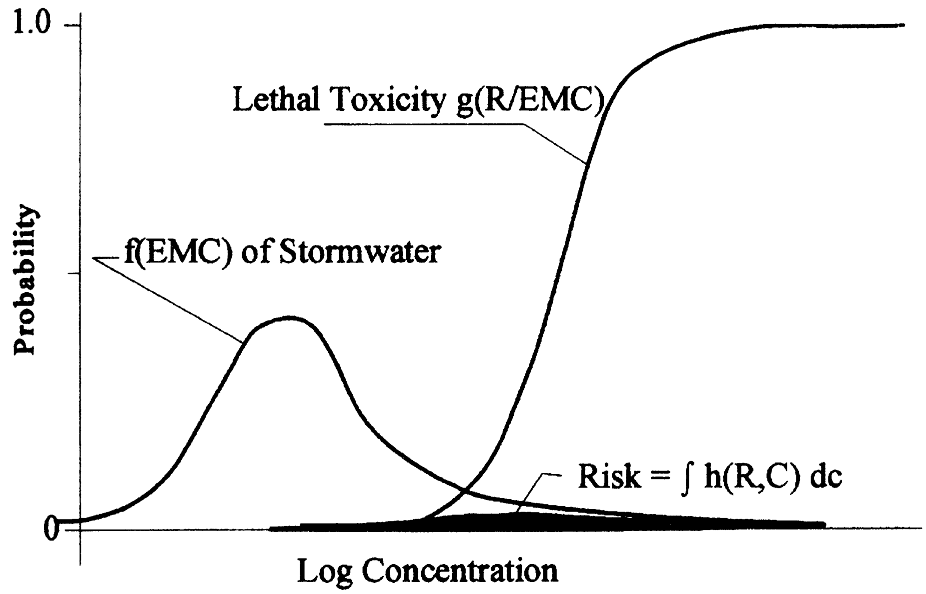


Figure 1.1. Tier-2 ecological risk assessment for stormwater impacts (from Novotny and Witte, 1997).

The most important parameter in the toxicity bioassay test used in risk calculation is the dose or concentration at which 50% of the test organisms survive or their life functions are not affected by the dose. The *lethal dose* or *concentration* (LD or LC) implies that an exposure of the test organism has resulted in death. The 50% survival dose or concentration value then represents LC_{50} or LD_{50} and it is a representative of the acute toxicity. The *effective dose* or *concentration* (ED or EC) is a term used when other effects are considered such as impact on reproduction or respiratory stresses.

LC_{50}s can be then plotted in ascending order versus percent probability of genera being affected. The values of LC_{50} can be found in the EPA documents or in data file accompanying a software developed by Parkhurst et al. (1996). For each given water body, there is a different set of indigenous or potentially indigenous species. Selecting LC_{50} for only those species leads to site or regionally specific risk function.

CHAPTER 2

DISTRIBUTION FITTING

Given that there are more than 700 species of fish in North America (Suter, 1993) and hundreds of thousands of other aquatic species, the expectation that the limited set of species that have been tested contains the most sensitive species would be quite naive. This assumption is avoided by assuming that the sensitivity of species follows some probability distribution and defining the concentration that affects the most sensitive species as the lower X-th percentile concentration. Several authors commented that the choice of distribution makes little difference (Novotny and Witte, 1997; Sutter, 1993) but the choice of protection level (percent of species), the confidence level (certainty that no more than the prescribed percentage of species will be affected), and uncertainties included in the estimation of confidence are quite important.

The distribution of concentration or toxic effects is often chosen based on statistical measures of best fit. The mathematical model is seen as a tool to efficiently describe data. However, theorizing about some underlying reality should be a part of assessing the distribution of risks. Sometimes the basic understanding of the feature of the processes that generate the variability can give rise to at least preliminary ideas about what distributions are more likely. Where data are relatively plentiful, these assumptions can be tested. In most cases, data will be too sparse.

When a large number of random variables is added together, the results follow normal distribution. The log-normal distribution describes the data when a large number of random variables is multiplied together. This is an equivalent of adding the logarithms of those numbers. The lack of memory and complete randomness characterize the exponential distribution. The generation of seasonal maxima or minima require the use of one of the extreme values distribution (Weibull, Gumbel, GEV).

The following steps have to be carefully considered when fitting a parametric distribution to data: (1) choose candidate probability distribution (e.g., based upon knowledge of processes that created the data or by inspection of the central moments of the data), (2) estimate the parameters of the distribution (probability plots, method of moments, or maximum likelihood estimates), (3) evaluate the goodness of fit of the distribution, (4) choose a significance level), and (5) interpret the results. It is possible that goodness-of-fit tests show that neither distribution can be rejected as a possible fit to the data. Then it is up to the analyst to make a final judgment.

The choice of distribution can have a profound effect on the final risk estimation, especially in the area of lower concentrations. There are two distributions involved in risk calculation: (1) distribution of concentration and (2) distribution of toxic response to given concentration. Usually, the distribution of ambient concentration is well described. It has been established by numerous studies that ambient concentration of most parameters follows log-normal distribution. Mean and standard deviation of log-concentrations provide sufficient information to fit the distribution, provided that sample size is large enough. On the other hand, the toxic response curve is defined rather poorly. Depending on specific chemical tested, sometimes only as few as 10 data points are available.

The following example illustrates how the choice of distribution for toxic response curve affects the value of risk to aquatic biota. Parkhurst et al. (1996) recommended a linearization of S-shaped curve of LC_{50}s by logit transformation to fit the toxic response curve. Other distributions will be examined and comparer, such as a normal distribution, a 3-parametric normal distribution, a Gumbel distribution, or General Extreme

Value (GEV) distribution (all in logarithmic space; i.e., the normal distribution is, in fact, log-normal). In addition, Novotny & Witte's linear approximation of lower-tail area (Novotny and Witte, 1997) is examined.

Cumulative distribution function (cdf) for the logit transformation on logarithmic space is:

$$F(x) = \frac{e^{a+bx}}{1+e^{a+bx}} \tag{2.1}$$

where x = log(EEC). The logit transformation logit (p) = ln (p / (1-p)) was originally used for linearization of the distribution. The normal distribution is fully described by mean μ and standard deviation σ. The probability density function (pdf) is defined as follows:

$$f(x)=\frac{1}{\sqrt{2\pi}\sigma}e^{-\frac{(X-\mu)^2}{2\sigma^2}} \tag{2.2}$$

where X is the logarithm of concentration. The 3-parametric normal distribution is, in fact, a transformation of normal distribution that introduces a minimal limit C_{min} for concentration. The transformed variable is X' = log (C - C_{min}) where C is the ambient concentration. The Gumbel distribution (Extreme Value Type I) originates from the theory of extremes. The cumulative density function (cdf) has the double exponential form:

$$F(X)=e^{e^{a-bX}} \tag{2.3}$$

where a is the scale parameter and b is the location parameter. They can be related to the mean and standard deviation (Bedient and Huber, 1992): $a = \mu\ b - \gamma$, where $\gamma = 0.5772$ is the Euler's constant, and $b = \pi$ / (2.4495 σ). The cdf of the GEV distribution is defined as follows:

$$F(X)=e^{-\left|1-\frac{\kappa(X-\xi)}{a}\right|^{1/\kappa}} \tag{2.4}$$

where a is the scale parameter, ξ is the location parameter, and κ is the shape parameter. The Gumbel distribution is a specific case of the GEV distribution with $\kappa = 0$.

The probability distributions were tested using the LC_{50} values for three metals: copper, zinc, and lead. The normal, Gumbel, GEV and 3-parametric normal distributions were fitted using the method of moments. The coefficients of linear approximation and of logit transformation were estimated by least square method (linear regression).

Figure 2.1 shows the fits of toxic response curve for copper for several distributions. All distributions investigated generally follow the data and can be used to estimate the empirical distribution of copper LC_{50}. The region of most interest in ecological risk assessment is the lower part of toxic response curve. This is where most of the ambient concentrations are, not in the middle or at higher concentrations. Careful examination of Figure 2.1 reveals that the normal distribution as well as the logit transformation do not capture the behavior of empirical data for LC_{50} in areas of low concentration. Gumbel distribution describes this area much better. This can be also seen from Table 2.1.

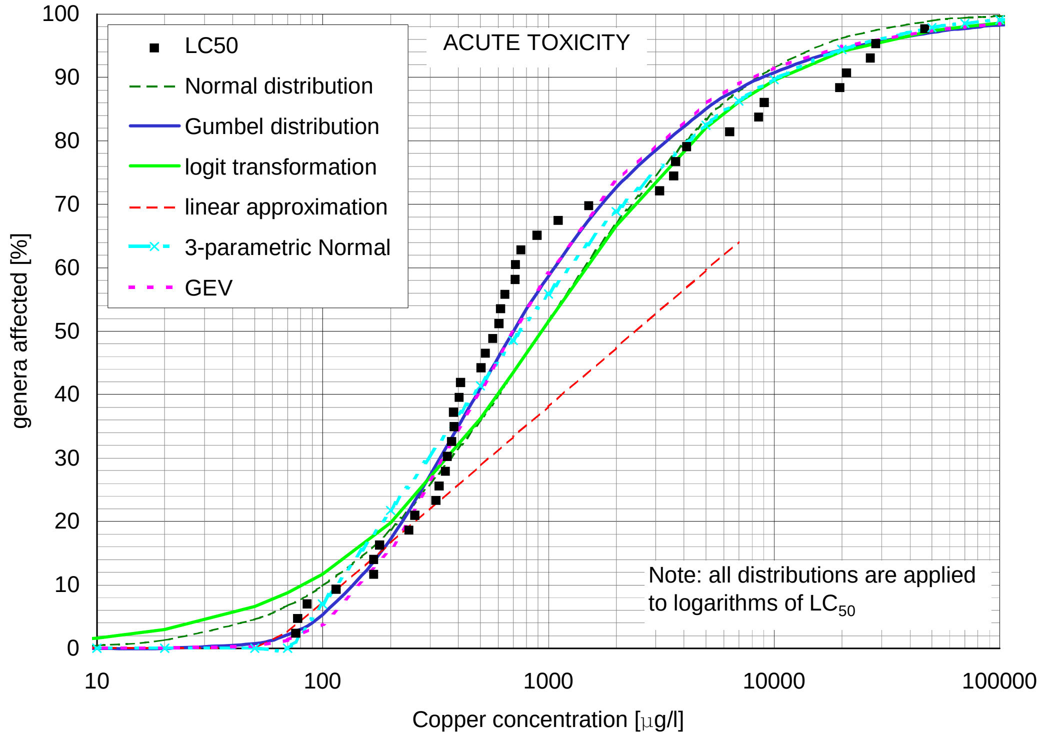


Figure 2.1. Toxic response curve for copper. Comparison of fits for different distributions. Hardness 250 mg $CaCO_3$/l.

Table 2.1. Goodness of fit for tested distributions: copper.

MODEL	Total		First 10 values	
	SSE	**R2**	**SSE**	**R2**
Normal	2,642	0.921	91	0.994
3-parametric normal	1,376	0.959	250	0.983
Gumbel	1,052	0.968	70	0.995
Logit (WERF)	2,553	0.924	191	0.987
Linear (Witte)	10,723	0.679	16	0.999
GEV	1,166	0.965	79	0.994
Total error	33,372		14,292	

Figure 2.2 shows the toxic response curve for lead and the fitted distributions. Although there is a significant difference between individual distributions and, consequently, between the ecological risks calculated for these distributions, a small number of available GMAVs does not allow for detail statistical analysis. The difference in percentage of genera affected reaches 10% throughout the whole range of concentration. In this case, the logit transformation copies the measurements in lower-tail area more closely than other investigated distributions. Only linear approximation gives comparable results.

The only problem with logit transformation is almost negligible slope of risk function for lower concentrations. For example, the average concentration of lead at site RI-23 has improved from 1.05 μg/l to 0.093 μg/l after 1987. The 99.9-percentile associated with acute toxicity has improved from 252 to 85 μg/l. Water quality criterion for acute toxicity is 545 μg Pb/l at this site. Acute toxicity should not be a problem since both values, after and before 1987, are significantly lower than the criterion. However, the acute toxicity risk values calculated using logit transformation are 7.0 x 10^{-3} and 2.4 x 10^{-3} for lead concentration before and after 1987, respectively. Water quality criterion for chronic toxicity is 21 μg Pb/l. The 99.5-percentile associated with chronic toxicity has improved from 723 to 202 μg/l. The chronic toxicity risk values calculated using logit transformation are 3.9 x 10^{-2} and 1.4 x 10^{-2} for concentration before and after 1987, respectively.

The risk values for both acute and chronic toxicity suggest a significant risk to aquatic biota. However, the acute toxicity criterion is satisfied while the chronic toxicity criterion is exceeded. The discrepancy between these two evaluations is caused by selecting distribution (logit transformation) that approaches zero very slowly. Normal distribution shows the second best fit of risk function for lead. The acute toxicity risks for the example given in the preceding paragraph are 3.0 x 10^{-4} and 2.9 x 10^{-5} for period before and after 1987, respectively. The chronic toxicity risks are then 1.2 x 10^{-2} and 1.9 x 10^{-3} for period before and after 1987, respectively. These values reflect the relationship between acute and chronic toxicity and between period before and after 1987 much closely. Thus, normal distribution is recommended for calculating ecological risk from lead.

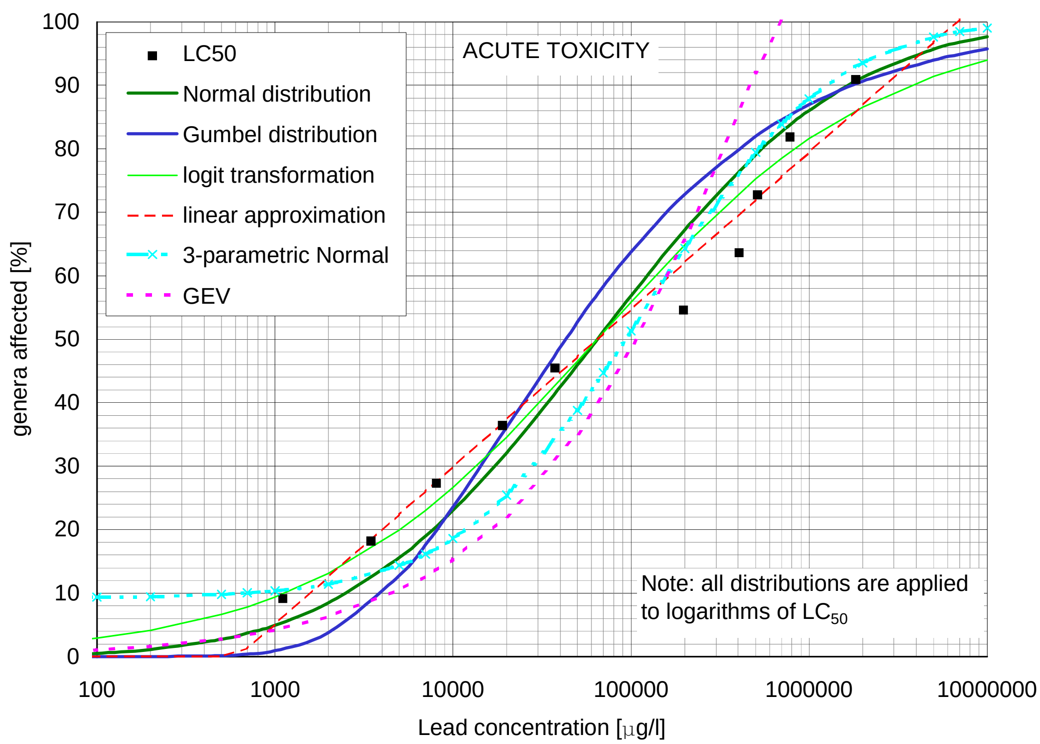


Figure 2.2. Toxic response curve for lead. Comparison of fits for different distributions. Hardness 250 mg $CaCO_3$/l.

Table 2.2. Goodness of fit for tested distributions: lead.

MODEL	Total		First 5 values	
	SSE	R2	SSE	R2
Normal	506	0.926	135	0.960
3-parametric normal	714	0.895	398	0.883
Gumbel	922	0.865	219	0.936
Logit (WERF)	254	0.963	25	0.993
Linear (Witte)	153	0.678	11	0.997
GEV	2,171	0.682	746	0.781
Total error	6,818		3,409	

Figure 2.3 shows the toxic response curve for zinc and the fitted distributions. In this case, the transition between low and high percentage of genera affected is quite abrupt. Also the lower-tail area is much more gradual for zinc comparing with copper (note the slope of linear approximation). This resulted in underestimating the cdf values by all investigated distributions except for linear approximation. Linear approximation would be the best choice when mean ambient concentration falls between 0.4 and 8 mg Zn/l. However, the highest mean concentration in investigated sites reaches 8 μg Zn/l, orders of magnitude smaller and way below the minimal concentrations for linear approximation as well as for 3-parametric normal distribution. For lower concentration, both normal distribution and logit transformation can be recommended. It should be noted that using logit transformation will result in values of ecological risk higher than when using normal distribution (see the example given in discussion about risk function for lead, page 6).

Table 2.3. Goodness of fit for tested distributions: zinc.

MODEL	Total		First 5 values	
	SSE	R2	SSE	R2
Normal	695	0.975	81	0.991
3-parametric normal	560	0.980	55	0.994
Gumbel	2,076	0.925	196	0.978
Logit (WERF)	707	0.974	47	0.995
Linear (Witte)	34,603	-0.256	8	0.999
GEV	535	0.981	64	0.993
Total error	27,546		8,758	

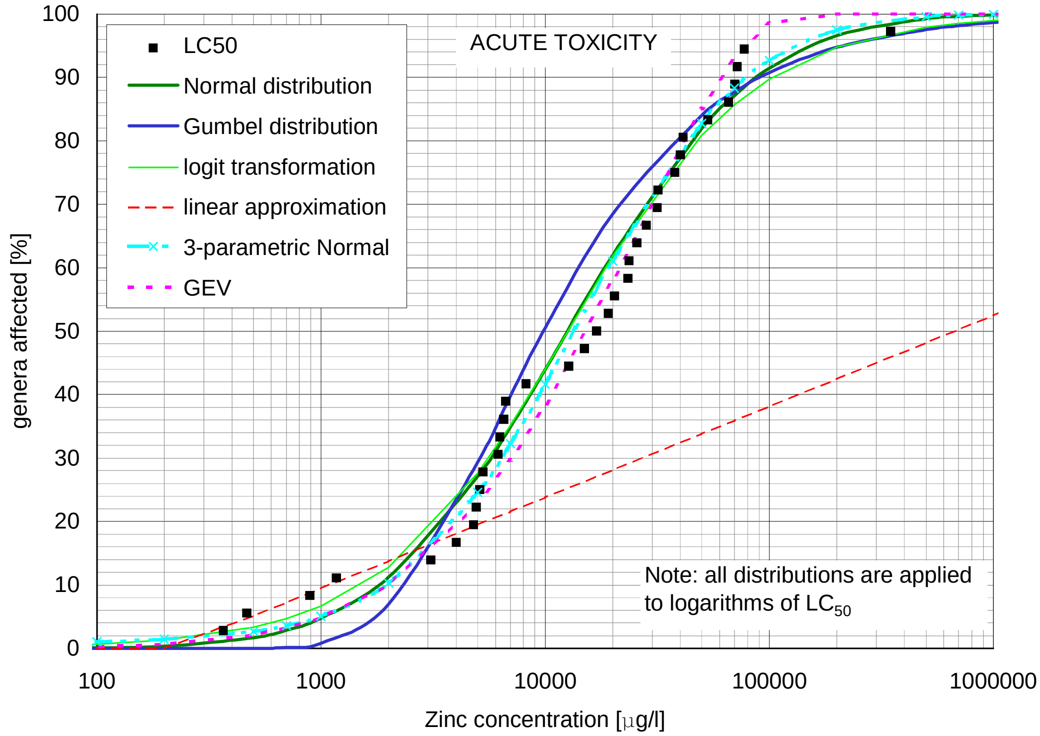


Figure 2.3. Toxic response curve for zinc. Comparison of fits for different distributions. Hardness 250 mg $CaCO_3$/l.

Table 2.4 shows the ecological risk calculated for different distributions fitting the toxic response curve. The ambient concentration of copper at site RI-23 follows log-normal distribution with mean of 0.309 and standard deviation of 0.358. This corresponds to the average concentration of 2.04 µg Cu/l. The average concentration of lead and zinc is given in Table 2.4. The average water hardness of 444 mg $CaCO_3$/l was assumed.

Table 2.4. Comparison of acute ecological risks at site RI-23 calculated for different distributions.

Distribution	**Copper**	**Lead**	**Zinc**
mean dissolved concentration [µg/l]	*2.04*	*1.24*[1)]	*4.72*
Normal	2.5 E-04	2.9 E-05	3.1 E-06
3-parametric normal	9.9 E-09	9.2 E-02	7.5 E-03
Gumbel	1.9 E-07	5.1 E-09	1.3 E-09
logit transformation	3.1 E-03	2.4 E-03	2.9 E-04
linear approximation	2.6 E-08	7.9 E-09	3.8 E-07
GEV	5.4 E-08	5.3 E-04	2.8 E-05

[1)] period after 1987

This example illustrates how the selection of theoretical distribution can introduce a difference of 4-5 orders of magnitude into the risk calculation. Using logit transformation as recommended by WERF results in relatively high value of risk to aquatic biota. The difference becomes less significant when ambient concentration increases and the integration range comes closer to the range covered by toxicity values (GMAV) where fitted distributions do not differ as much as in low concentration area.

The linear approximation approach differs from traditional distribution fit approach in that it assumes the existence of some minimal concentration C_{min} below which there is no risk to aquatic biota. This assumption is also employed in the 3-parametric normal distribution. The minimal copper concentration for the above mentioned example is C_{min} = 57.7 μg/l for linear approximation and C_{min} = 70.5 μg/l for the 3-parametric normal distribution. Theoretical probabilistic distributions approach minus infinity on logarithmic scale as the percentage of genera affected approaches zero, i.e. the minimal concentration is C_{min} = 0.0 μg/l. Using the unbounded distributions is more conservative than the assumption of no minimal concentration.

The question is whether the minimal concentration exists. The values defining the toxic response curve are based on LC_{50}s and represent the genera mean acute values (GMAV). The probabilistic approach is based on the assumption that all GMAVs come from the same distribution regardless the genera. Imposing the minimal concentration on distribution would mean that we *know* there is no genus that would exhibit 50% mortality rate below this limiting concentration. However, there is a minimal concentration for every organism, species, or genus. This would correspond to *no observed effect concentration* (NOEC) as detected during chronic toxicity tests. Thus, the minimum concentration has the probability distribution of its own rather than being a single value.

Up to now, only limited number of species has been tested for toxic response. This makes the task of distribution fitting extremely difficult. There is 42 observations of GMAVs for copper, 35 for zinc, and 10 for lead. The lower the number of observations, the wider the confidence limits for parameter estimation. The Gumbel distribution has been recommended to fit the toxic response curve for copper in ecological risk calculation. The normal distribution has been recommended to fit the toxic response for zinc and lead. The most difficult problem encountered in selecting proper distribution is the lack of information on effects in the area of existing ambient concentrations.

CHAPTER 3

EFFECT OF HARDNESS

The risk in the previous section has been calculated for a constant (average) hardness of 444 mg $CaCO_3$/l. However, hardness is not constant in any receiving water body. The background hardness is determined by aquifer geology. Rainfall/runoff water is typically soft water that dilutes the base flow, especially in dolomite rich area around Milwaukee, WI.

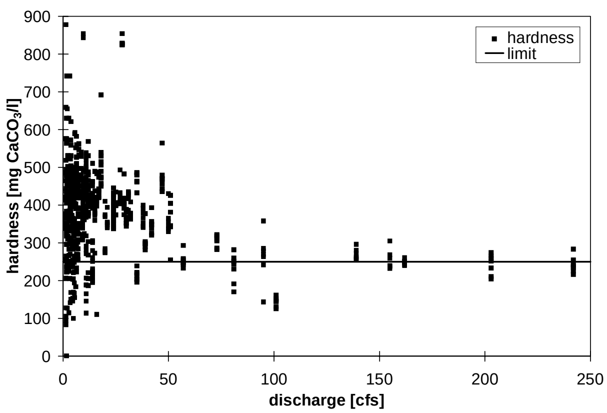


Figure 3.1. Hardness versus discharge. Site RI-23, Oak Creek watershed.

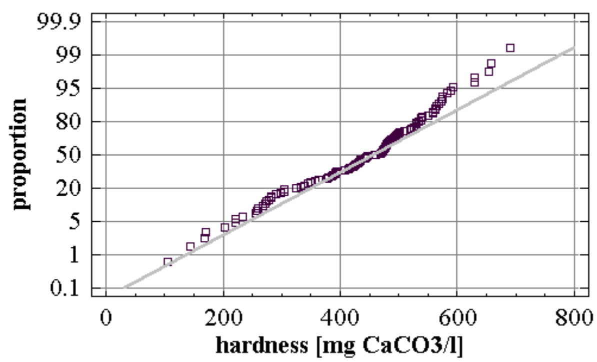


Figure 3.2. Normal probability plot of hardness. Site RI-23, Oak Creek watershed.

Figure 3.1 shows the effect of flow on hardness in monitoring site RI-23 in the Oak Creek watershed. High flows are associated with relatively constant hardness of 250 mg $CaCO_3$/l. The variability of hardness is quite large, especially for flows smaller then 25 cfs. Figure 3.2 shows that hardness approximately follows normal probability distribution. The average hardness is 444 mg $CaCO_3$/l and standard deviation is 143 mg $CaCO_3$/l.

The toxicity relationship for metals were determined from the laboratory tests with standard water hardness of 50 mg $CaCO_3$/l. Novotny and Witte suggested using the formula provided in the criteria document (US EPA, 1992) to correct LC_{50} values for other values of hardness:

$$\chi = \frac{LC_{50}(H)}{LC_{50}(50\text{mg}/\text{l})} = \left| \frac{H}{50} \right|^{\alpha} \qquad \textbf{(3.1)}$$

where H is the hardness [mg $CaCO_3$/l], and α is the parameter specific for given toxic pollutant. For example, for copper α = 0.9422.

Since the Gumbel distribution is fitted to LC_{50}s in logarithmic space, let us establish a new variable that will be used in arithmetic space: x = log (LC_{50}). In the previous section, the Gumbel distribution has been selected as the most appropriate for copper risk function. Copper is selected for the following analysis since the number of available LC_{50} values enable us to fit the risk function properly. The parameters of distribution (Eq. 2.3) can be related to mean μ and standard deviation σ of x for test hardness of 50 mg $CaCO_3$/l:

$$a = \mu\, b - 0.5772$$
$$b = \pi / (2.4495\, \sigma)$$

The standard deviation and mean of x_H adjusted for hardness can be related to those of x for test hardness:

$$\sigma_H = \sigma, \text{ and } \mu_H = \mu + \log \chi$$

With this, cdf of the risk function can be rewritten as:

$$F(x) = e^{-e^{a_H - b_H\, x}} = e^{-e^{a + b \log \chi - b\, x}} \qquad \textbf{(3.2)}$$

where a_H and b_H are the parameters of the distribution for hardness *H*, and *a* and *b* are the parameters of the distribution for test hardness of 50 mg $CaCO_3$/l. Using the LC_{50}s for copper, the method of moments will yield the following parameters:

$$a = 3.3686$$
$$b = 1.7071$$

The risk function thus becomes a family of individual functions defined by distribution of hardness. The risk function integrated over both hardness and heavy metal concentration will yield the total risk that incorporates the effect of hardness. Figures 3.3 and 3.4 show that hardness and copper concentration are uncorrelated. Site RI-23 is shown separately since hardness from that site comes from different distribution (statistical significance level $\alpha = 0.05$). Bivariate normal distribution can be used to describe variables.

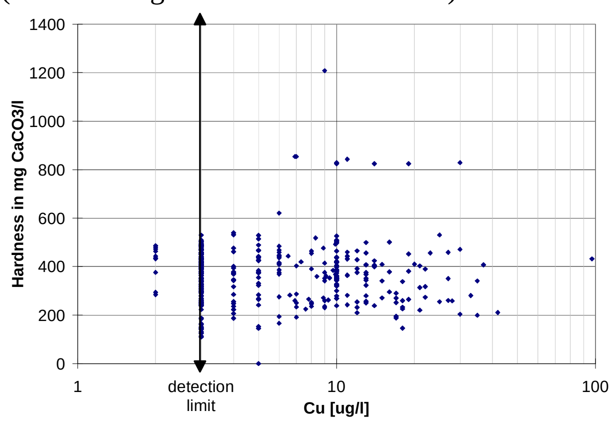


Figure 3.3. Distribution of hardness [mg $CaCO_3$/l] and copper [μg/l]. Oak Creek watershed, all sites except RI-23.

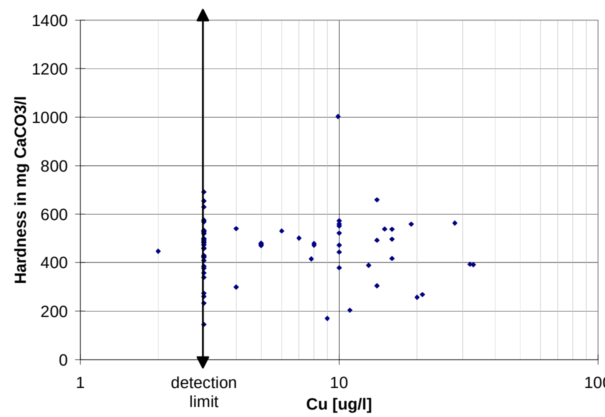


Figure 3.4. Distribution of hardness [mg $CaCO_3$/l] and copper [μg/l]. Oak Creek watershed, site RI-23

Two approaches were taken to investigate the effect of hardness on resulting risk: (1) Monte Carlo simulation; and (2) direct integration over two variables. During Monte Carlo simulation, the variable space was sampled for hardness 5,000 times. For each sampling, the risk function was first adjusted for selected hardness (Eq. 3.2) and then integrated over copper concentration. This approach allows us to investigate distribution of the risk as it changes with hardness. The second approach results in one value of the risk. The direct integration over hardness compacts the family of risk functions into one risk function that already includes the probability distribution of hardness. Further analysis will help us to determine what percentile from hardness distribution should be selected for simple evaluation (integration only over the metal concentration).

Hardness recommended for adjusting risk function

Another series of calculations was performed to investigate if there is one single hardness expressed as a percentile of normal distribution that can be recommended for adjusting risk function, thus eliminating need for double integration. The risk function for copper was integrated over hardness and the resulting function was analyzed. Since the relationship between the function parameters and hardness distribution (mean, standard deviation) is known, the representative hardness that would result in the same distribution can be calculated (Eqs. 3.1, 3.2).

The following hardness distributions were considered in this analysis (all with normal distribution): mean 300 mg $CaCO_3$/l (st. dev. of 10, 25, 50, 75, and 99), mean 150 mg $CaCO_3$/l (st. dev. of 5, 10, 25, 35, 49), and mean 60 mg $CaCO_3$/l (st. dev. of 5, 10, 15 and 19). The representative (recommended) hardness percentile for all scenarios is shown in Figure 3.5. The recommended percentile in all scenarios varies from 44% to 60% and is decreasing with increasing standard deviation. When standard deviation is normalized by average hardness, the percentiles for all scenarios follow the same function (Figure 3.6).

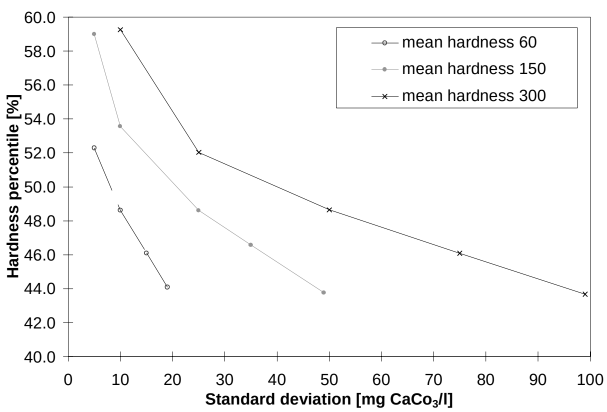


Figure 3.5. Relationship between recommended hardness and hardness distribution (mean and standard deviation). Copper.

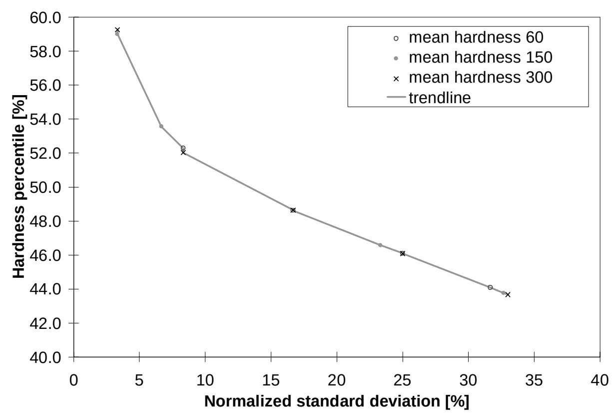


Figure 3.6. Relationship between recommended hardness percentile and hardness distribution (mean and standard deviation). Standard deviation is normalized by mean hardness. Copper.

Tables 3.1, 3.2, and 3.3 show numeric values of both representative hardness and ecological risk associated with a particular hardness distribution for site RI-23 in Oak Creek watershed. Although the risk increases with standard deviation (and representative hardness), the maximal increase is only 30% and can be considered negligible with respect to uncertainty in parameter estimates. The change effects only second significant digit with the order of magnitude remaining constant. Thus, the average hardness is recommended for the use in ecological risk calculation. The parameters of distribution for copper as in Eq. 3.2 can be calculated using values of *a* and *b* for hardness of 50 mg $CaCO_3$/l (see page 11) as follows:

$$a_H = a + b \log \chi = a + b\, \alpha \log(H/50) = 0.63595 + 1.6084 \log(H)$$

$$b_H = 1.7071 \qquad (= constant)$$

However, if precise calculation is required, Figure 3.6 may be used to estimate recommended percentile for representative hardness from know hardness distribution by simply dividing standard deviation by average hardness and finding corresponding percentile, if desired. This may be advisable when the distribution of hardness is flat, i.e. standard deviation is relatively large.

Table 3.1. Comparison of risks calculated for hardness ~N(300, σ) in site RI-23

Standard deviation σ	**Gumbel Parameter a_H**	**Risk**	**Representative hardness**
10	4.6256518	1.085E-06	302.3
25	4.6231769	1.102E-06	301.3
50	4.6162397	1.150E-06	298.3
75	4.602857	1.250E-06	292.6
99	4.5825091	1.418E-06	284.2
		1.124E-06	300

Table 3.2. Comparison of risks calculated for hardness ~N(150, σ) in site RI-23

Standard deviation σ	**Gumbel Parameter a_H**	**Risk**	**Representative hardness**
5	4.141308	1.800E-05	151.1
10	4.140169	1.811E-05	150.9
25	4.131933	1.892E-05	149.1
35	4.121868	1.997E-05	147.0
49	4.099201	2.252E-05	142.3
		1.851E-05	150

Table 3.3. Comparison of risks calculated for hardness ~N(60, σ) in site RI-23

Standard deviation σ	**Gumbel Parameter a_H**	**Risk**	**Representative hardness**
5	3.4992975	3.944E-04	60.29
10	3.4919220	4.070E-04	59.65
15	3.4786547	4.306E-04	58.53
19	3.4622838	4.615E-04	57.17
		3.997E-04	60

The similar series of calculation was carried out for normal distribution (zinc and lead). The relationship between recommended hardness percentile and normalized standard deviation is shown in Figure 3.7. The relationships are very similar, regardless of original distribution used to fit the risk function or heavy metal (copper, lead, or zinc).

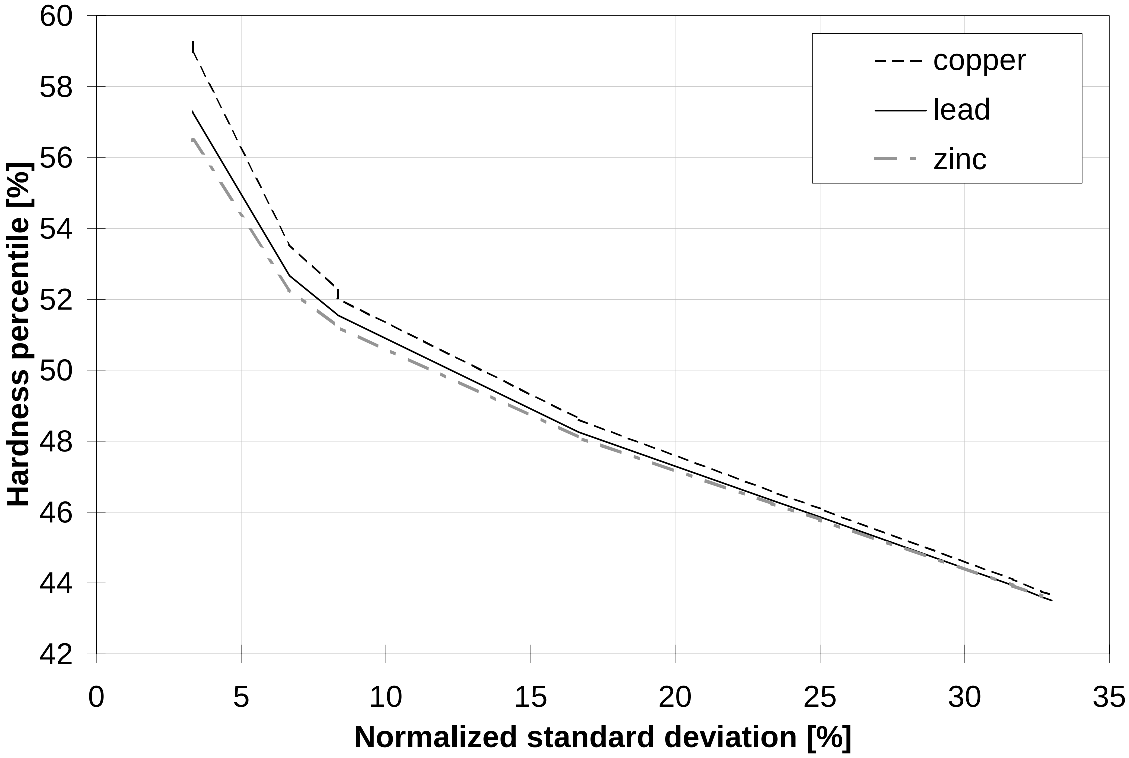


Figure 3.7. Relationship between recommended hardness percentile and hardness distribution (mean and standard deviation). Standard deviation is normalized by mean hardness. Copper, lead, zinc.

Monte Carlo simulation

Monte Carlo simulation was carried out 5,000 times to estimate the distribution of ecological risk in monitoring site RI-23 (Oak Creek watershed). Hardness was randomly generated. The risk function was first adjusted for simulated hardness, then adjusted function was integrated over metal concentration. The hardness at this site follows normal distribution with mean of 444 mg $CaCO_3$/l and standard deviation of 143 mg $CaCO_3$/l. The normal distribution is not bounded by zero, which means that some simulated values can be negative. These values were eliminated from analyses (only one case occurred in simulation). The copper concentration at site RI-23 follows log-normal distribution with log-mean of μ_{Cu} = 0.309 and log-standard deviation of σ_{Cu} = 0.358.

Let's now look into parameters describing the distribution of risk. The range of risk values from 1.81 x 10^{-8} to 1.28 x 10^{-5} represents 95% cases. The mean value of risk is 3.335 x 10^{-5},two orders of magnitude higher than the risk calculated with average hardness (1.892 x 10^{-7}). However, the distribution is highly skewed (skewness = 58.6), even after logarithmic transformation (skewness = -1.21, see Figures 3.8 and 3.9). The median 1.950×10^{-7} is much closer to the risk based on single hardness value. Transformed variable $y = risk^{-0.16}$ can be fit a normal distribution with a mean of 11.78 and standard deviation of 2.888 (see Figures 3.10 and 3.11). The mean corresponds to the risk of 2.020×10^{-7} and is comparable to the median of risk as well as to the risk based on single hardness value. These analysis confirm the use of average hardness for recalculating LC_{50}s in risk estimation.

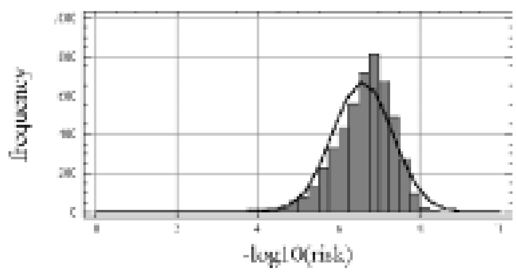


Figure 3.8. Probability distribution: -log(risk). Monte Carlo simulation for site RI-23, Oak Creek watershed.

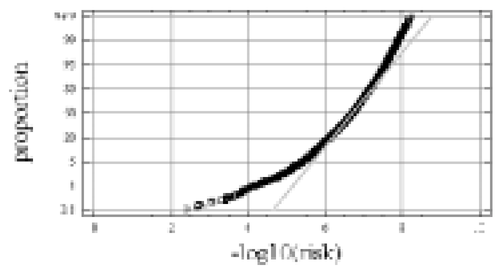


Figure 3.9. Normal probability plot: -log(risk). Monte Carlo simulation for site RI-23, Oak Creek watershed.

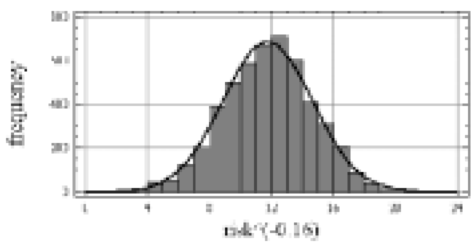


Figure 3.10. Probability distribution: $risk^{-0.16}$. Monte Carlo simulation for site RI-23, Oak Creek watershed.

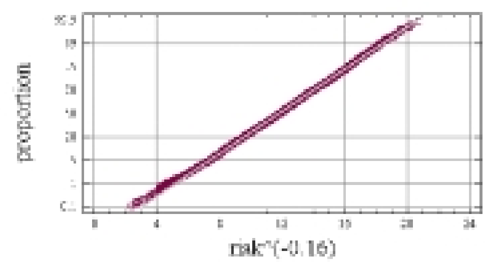


Figure 3.11. Normal probability plot: $risk^{-0.16}$. Monte Carlo simulation for site RI-23, Oak Creek watershed.

CHAPTER 4

DEVELOPED SOFTWARE

Calculations of risk in previous chapter was carried out in Excel. Individual spreadsheets have been set up for each investigated metal. The information on LC_{50}s is used to estimate parameters of several probability distributions for risk function. The ambient concentration is assumed to follow log-normal distribution. After all required input data are entered, user runs custom macro that allows further specification of calculation methods.

Data required

Toxicity assay data. The acute toxicity values LC_{50} for reference hardness of 50 mg $CaCO_3$/l are entered into 'LC50' worksheet. The values are recalculated based on user specified hardness and parameter α (see Eq. 3.1). The LC_{50} for chronic toxicity are recalculated from acute values using Acute-To-Chronic ratio.

Water quality data are organized in 'WQ' worksheet. Database of investigated monitoring sites contains site identification and parameters of log-normal distribution in logarithmic space. Both total and dissolved concentrations can be entered into the database, although only dissolved concentrations are presently used in risk calculation.

Integration parameters. The user has an option to specify starting point of integration X_0, a metal concentration. Similarly, the integration step is defined as a change in concentration in logarithmic space. As default, there are 100 integration steps. The number of integration steps can be changed after some modifications of the spreadsheet (not recommended without thorough knowledge of the way the spreadsheet is set up). The user can then consult chart 'gf_integr' that shows log-normal distribution of ambient concentration, selected distribution of the risk function, joint risk function, and cumulative of joint risk function (i.e., integration along the integration interval). Figure 4.1 shows an example of this chart.

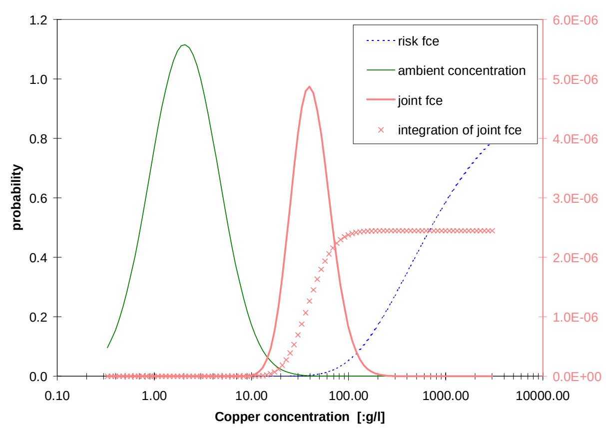


Figure 4.1. Example of 'gf_integration' chart.

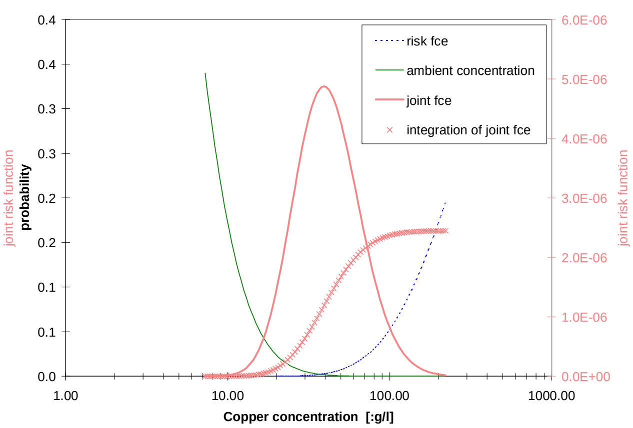


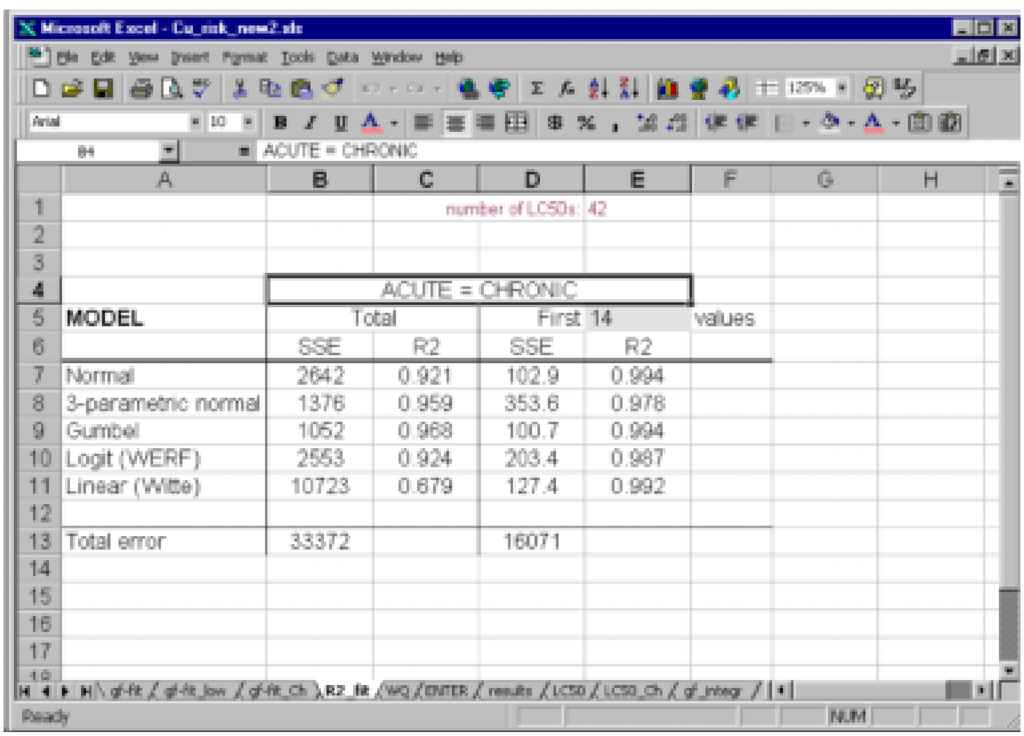
Figure 4.2. Example of correct selection of integration interval.

The goal is to focus the integration over the interval where peak of the joint function occurs (Figure 4.2). However, as long as the peak is included in integration interval, the difference in resulting risk value is usually not significant. The total values of risk for the above given examples differ in 5th significant digit.

Selection of distribution

The following distributions are included in the spreadsheet (all in logarithmic space): normal, 3-parametric normal, Gumbel, General Extreme Value (GEV), logistic transformation (Parkhurst et al., 1996), and linear approximation (Novotny and Witte, 1997). The parameters of distribution are estimated using either method of moments (normal, 3-parametric normal, Gumbel and GEV distributions) or linear regression (logistic transformation and linear approximation). Only for linear approximation, users can select the number of points *N* included in parameter estimation. Then, only the first *N* values of LC_{50} are used in regression.

Several charts are created as a part of the spreadsheet. The charts show the LC_{50} values together with all fitted distributions for both acute and chronic toxicity data. One chart shows the area of lower concentration in detail. Another way to decide on distribution is to compare sum of squared errors (SSE) or coefficient of determination (R^2). The smaller the SSE, the better the fit. For the ideal fit, SSE is equal to zero and $R^2 = 1$. The values of SSE and R^2 for each fitted distribution can be found in worksheet 'R2_fit'. One set of values shows the goodness of fit for all LC_{50}s available, another set of values shows the goodness of fit for specified number of LC_{50}s. The second set of statistics can help us to compare the fit in area of low concentrations and also a fit of the linear approximation. Since only first *N* values are used to estimate parameters of linear regression, the goodness of fit statistics for all LC_{50}s indicate a worse fit than when partial statistics.


number of LC50s: 42

ACUTE = CHRONIC

MODEL	Total		First 14 values	
	SSE	R2	SSE	R2
Normal	2642	0.921	102.9	0.994
3-parametric normal	1376	0.959	353.6	0.978
Gumbel	1052	0.968	100.7	0.994
Logit (WERF)	2553	0.924	203.4	0.987
Linear (Witte)	10723	0.679	127.4	0.992
Total error	33372		16071	

Figure 4.3. Goodness of fit statistics for copper, hardness of 250 mg $CaCO_3$/l. Worksheet 'R2_fit'.

Risk calculation

After the spreadsheet is modified for a specific metal and water quality data for all monitoring sites are added into the database, the user can start calculate the risk. Worksheet 'ENTER' (Figure 4.4) is the home base for all calculations. Users can enter desired integration parameters and select a water quality site by its identification number. The water quality parameters are automatically brought from the database into this worksheet. Hardness has to be entered separately, but this can be changed, if desired.

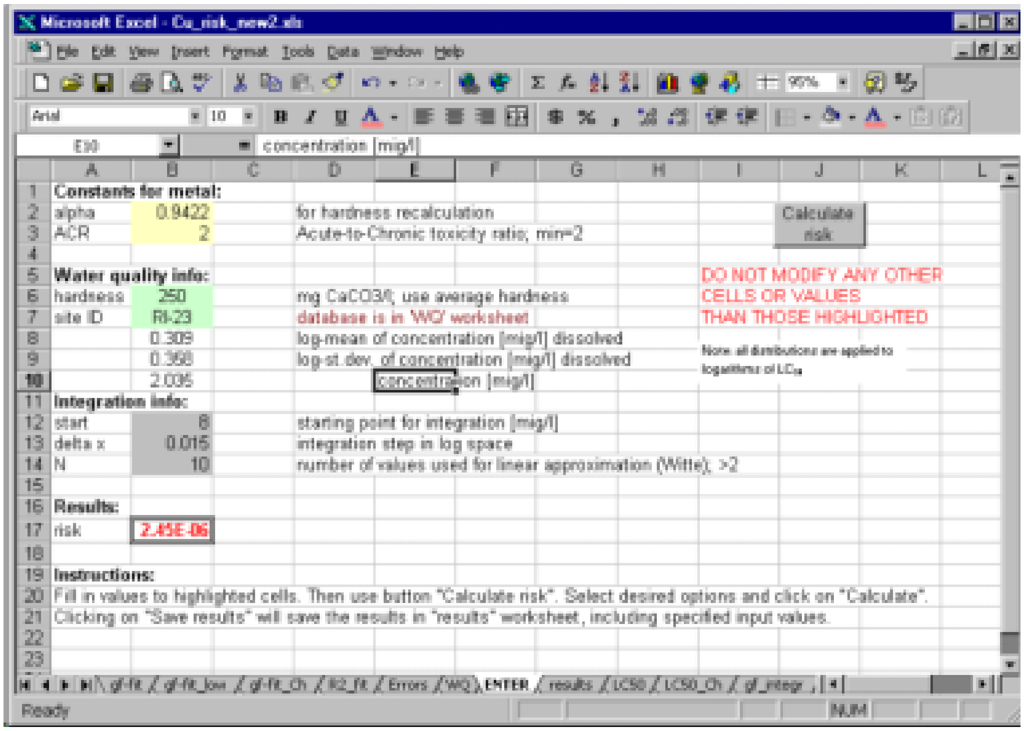


Figure 4.4. The main worksheet of the spreadsheet used in risk calculations. 'ENTER'

Clicking on button 'Calculate risk' will bring up a dialog (Figure 4.5) where users can select distribution for the risk function and decide whether acute or chronic toxicity risk should be evaluated. Clicking on 'Calculate' button will calculate the risk based on specified parameters and update the value in 'ENTER' worksheet.

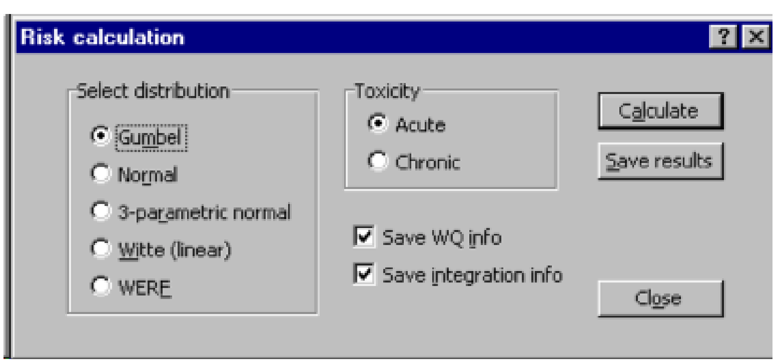


Figure 4.5. Risk calculation dialog. Select distribution and toxicity for calculations.

Users also have an option to save the results of their calculation in separate worksheet ‘results’. This can be done by clicking on ‘Save results’ button in risk calculation dialog. The information on monitoring site (its identification), distribution selected for risk function, toxicity (acute or chronic), and final value of risk are saved always when pressing this button. In addition, water quality data and integration parameters can be also saved when specified by checking off the appropriate box on the dialog. Figure 4.6 shows an example of ‘results’ worksheet with few calculations completed and saved, including all additional information.

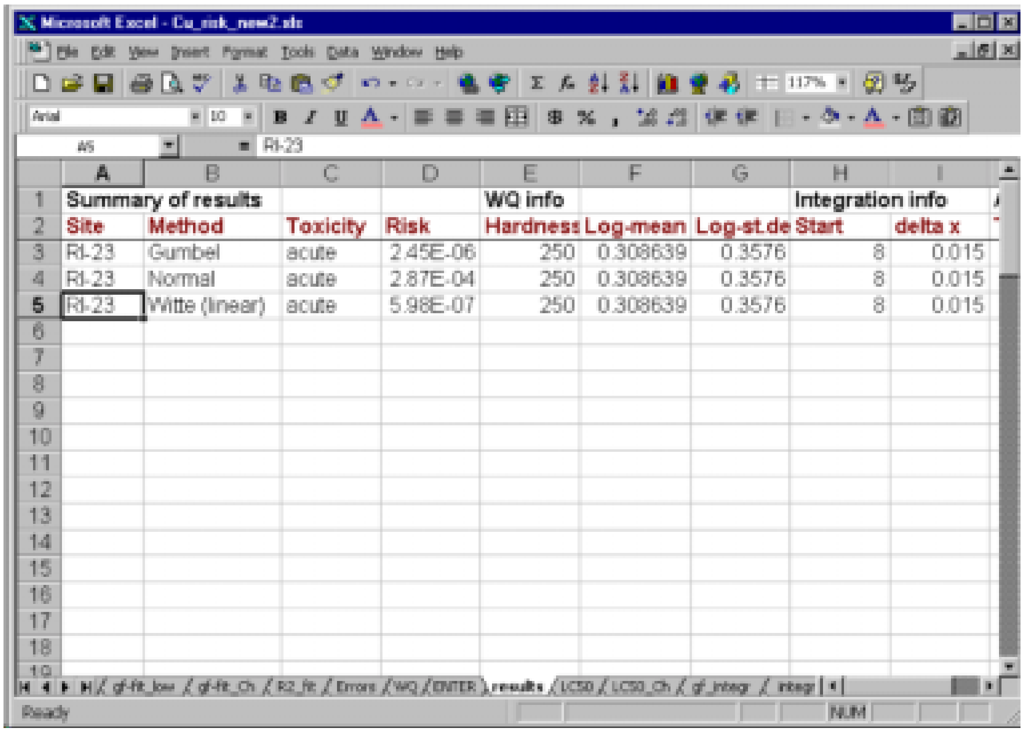


Figure 4.6. Example of ‘results’ worksheet.

The values in the worksheets and charts are updated automatically with any change in referenced cells. The only exceptions is with chart showing the integration interval ‘gf_integr”. The values are partially updated with change in integration parameters. However, the full update is carried out with risk calculation, using the ‘Calculate’ button in risk calculation dialog.

CHAPTER 5

CONCLUSIONS

This report has focused on practical aspects of ecological risk calculation. A simple Excel-based software package has been developed to facilitate calculation of ecological risk. The package gives users a choice for distribution of risk function, enables users to create water quality database, and control integration parameters. First, several probabilistic distributions of risk function were compared and effect of selecting one distribution has been described. Although the parameters of goodness-of-fit for individual distributions may be similar, the distributions differ significantly in low-tail area. Unfortunately, this is where ambient concentrations are usually found. The choice of distribution can then result in orders of magnitude discrepancies.

Gumbel distribution has been recommended to fit toxic response curve for copper. Normal distribution has been recommended to fit toxic response for zinc and lead. The use of logit transformation has been discouraged because of high value of resulting ecological risk and low sensitivity in areas of low ambient concentration.

The effect of hardness distribution on calculation has been investigated. With increasing standard deviation, the ecological risk increases. However, the increase is not significant. Using the 50-percentile of hardness (average) if normal distribution is assumed for risk calculation has been recommended.

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