PROCEDURE FOR REASONABLE POTENTIAL EVALUATION IN NPDES PERMIT CAG280000

Introduction

The regulatory basis for establishing water quality-based effluent limitations (WQBELs) is set forth in 40 CFR 122.44(d) of the NPDES regulations. Effluent limitations must be established for pollutants (either conventional, non-conventional, or toxic) that are, or may be discharged at levels that cause, have the reasonable potential to cause, or contribute to an excursion above any water quality standards established under the Clean Water Act. In Permit CAG28000, applicable water quality criteria are listed in Section II.B.1.a. These criteria apply after dilution at the edge of the 100-meter mixing zone. Appropriate values for pH, temperature and salinity would be used for criteria that are dependent on these factors.

The procedures described in this document for evaluating the reasonable potential for an effluent constituent to exceed an applicable water quality criterion are based on the *Technical Support Document for Water Quality-based Toxics Control* (TSD), March 1991 (EPA/505/2-90-001). EPA recommends finding that a permittee has "reasonable potential" to exceed a receiving water quality criteria if it cannot be demonstrated with a high confidence level that the predicted upper bound of the lognormal distribution of effluent concentrations is below the receiving water criteria (TSD p. 53). Once reasonable potential to exceed any criteria has been established, a WQBEL is required to be calculated for each effluent constituent exhibiting reasonable potential.

The permit requires sampling for reasonable potential and specifies that the evaluation be performed at the 99-percent confidence level and the 99-percent probability basis. The number and type of samples are specified in the permit, as is the sampling frequency. The permit also specifies that the laboratory minimum level (ML) be used to establish the concentrations at which analytical results are reported as not quantifiable.

The calculations used in this reasonable potential evaluation procedure are complex. The sequence of steps necessary to perform the evaluation is explained in detail. Each step of the procedure is referenced to the corresponding row of an example reasonable potential evaluation table (Table 1.). For example, the effluent pollutant or constituent name is found in the first row *[Seq A]* of Table 1 and the reasonable potential multiplying factor is shown in row *[Seq P]* of Table 1. Where equations and assumptions are introduced, the relevant page numbers from the TSD are cited.

A reasonable potential analysis is conducted separately for each constituent reported. To facilitate the explanation, actual discharge data for a single constituent, Nickel, from one discharge location is used as an example in this spreadsheet. The 44 nickel concentration values, as reported by the analytical laboratory, are summarized in Table 2. When results are below the laboratory ML, the laboratory ML is reported in the adjacent column of the table. This table also includes the natural logarithms of the reported concentrations (because the concentrations are assumed to be lognormally distributed) and summary statistics (mean, variance, and maximum values) required for the reasonable potential calculation.

A list of the terms and abbreviations used in the steps of this procedure are summarized in Table 3.

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Procedure for the Evaluation of Reasonable Potential

Assumptions

1. As specified in the permit, a series of produced water samples have been collected and analyzed for several constituents. The concentrations are reported either as a numeric value or as not quantifiable or not detected. Non-quantified/non-detected results are all values that cannot be quantified at the required level of confidence, which is the laboratory minimum level (ML).

2. The reported concentrations for each constituent are assumed to be statistically sampled from a population that is log-normally distributed above the laboratory ML and the measurements are independent, uncorrelated observations (TSD p. E-2).

3. If some reported concentrations cannot be quantified (i.e., are below the laboratory ML) or cannot be detected (i.e., are below the laboratory MDL), the distribution is assumed to be "delta-lognormal", in which non-quantified/non-detected values are weighted in proportion to their frequency of occurrence in the sample data set.

Procedure

The column numbers below (e.g., *[Seq B]*) refer to Table 1.

Step 1. From the data set of non-quantified/non-detected and reported concentrations for a single constituent in the discharge (Table 2.), determine:

- the number of samples, k *[Seq B]*
- the maximum measured concentration reported by the laboratory *[Seq E]*
- the maximum laboratory ML below which the parameter is detected but the concentration is not quantifiable *[Seq D]*
- the number of samples for which the concentration is not quantifiable (i.e., concentration is reported below the laboratory ML) *[Seq C]*.

Step 2. Calculate:

- the natural log (ln) of each measured value, i.e., for those concentrations greater than the laboratory ML (these values are calculated on separate worksheets within the RP spreadsheet workbook).
- the mean of the ln values *[Seq F]*.
- the variance of the ln values *[Seq G]*.

Step 3. Calculate the coefficient of variation.

The coefficient of variation is a unitless expression of variability calculated by dividing the sample standard deviation by the sample mean (TSD p. 52). However, in this case, the calculation of the coefficient of variation is complicated by two factors. The first is that the natural logarithms of the concentrations are used; the second is that the distribution of the samples can best be approximated by a special case of the lognormal distribution – the delta-lognormal distribution. The lognormal distribution models the measurements above the laboratory ML. The "delta-" applies to the non-quantified/non-detected values that are modeled with a distribution with discrete probabilities of obtaining observations at or below the laboratory ML (TSD p. E-10).

In this case, the coefficient of variation becomes:

$$c\hat{v} = \frac{\left[\hat{V}(X^*)\right]^{1/2}}{\hat{E}(X^*)} \qquad \textit{[Seq K]}$$

where

$$\hat{V}(X^*) = (1-\delta)\exp(2\hat{\mu}_y + \hat{\sigma}_y^2)\left[\exp(\hat{\sigma}_y^2) - (1-\delta)\right] + \delta(1-\delta)D\left[D - 2\exp(\hat{\mu}_y + 0.5\hat{\sigma}_y^2)\right] \qquad \textit{[Seq J]}$$

$$\hat{E}(X^*) = \delta D + (1-\delta)\exp(\hat{\mu}_y + 0.5\hat{\sigma}_y^2) \qquad \textit{[Seq I]}$$

δ = the sample proportion of non-quantified and non-detected values (number of non-quantified/non-detected values divided by the total number of measurements), i.e.,

δ = r/k, where *[Seq H]*

k = total number of samples
r = number of non-quantifies/non-detected values
k-r = number of values greater than the laboratory ML
D = the highest reported laboratory ML *[Seq D]*
$\hat{\mu}_y$ = mean of the logarithmic transformed measurements greater than the laboratory ML, i.e.,

$$\hat{\mu}_y = \sum(y_i)/(k-r) \qquad r+1 \le i \le k,\ r < k \qquad \textit{[Seq F]}$$

$\hat{\sigma}_y^2$ = variance of the logarithmic transformed measurements greater than the laboratory ML, i.e.,

$$\hat{\sigma}_y^2 = \sum(y_i - \hat{\mu}_y)^2/(k-r-1) \quad r+1 \le i \le k,\ r < k \qquad \textit{[Seq G]}$$

Step 4. Calculate the reasonable potential multiplying factor.

- The coefficient of variation is used as a measure of the variability of the concentration of the constituent. This estimate is combined with a measure of the uncertainty due to a limited number of samples (i.e., a small sample size is used to represent the population) to predict a maximum concentration (TSD p. 52).

- The first step is to determine the percentile of the distribution into which the maximum measured concentration falls. This is calculated as:

$$p_n = (1 - \text{confidence level})^{1/n} \qquad \textit{[Seq L]}$$

For a 99% confidence level and 44 samples (from Table 2),

$$p_n = (1 - 0.99)^{1/44}$$

$$p_n = 90^{th} \text{ percentile}$$

That is, the largest value of 44 measurements of nickel concentrations in the produced water is greater than the 90-percentile value of the population. In other words, there is a 99 percent confidence that for every set of 44 samples collected, the maximum value of the 44 samples will be greater than 90 percent of the population of probable concentrations. USEPA Region 9 has selected a 99 percent confidence level for this permit.

- The second step is to determine the desired upper bound of the constituent concentration. Region 9 has selected the 99th percentile as the acceptable upper bound for this NPDES permit.

- The third step is to determine the ratio of the maximum measured concentration to the upper bound concentration of the distribution of nickel concentrations using the coefficient of variation and Z-score of the normal distribution values for the 99th and (in this example) the 90th percentile distributions.

Using the equations at TSD p. 52;

$$\sigma^2 = \ln\left(c\hat{v}^2 + 1\right) \qquad \textit{[Seq M]}$$

where *cv* is the value calculated in *[Seq K]* above.

The upper bound percentile at the 99-percent basis,

$$c_{99} = \exp\left(z_{99}\sigma_y - 0.5\sigma_y^2\right) = \exp\left(2.326\sigma_y - 0.5\sigma_y^2\right) \qquad \textit{[Seq N]}$$

and the calculated percentile representing the maximum reported concentration (in this example p_{44}) is

$$c_{44} = \exp\left(z_{44}^{*}\,\sigma_y - 0.5\sigma_y^2\right) = \exp\left(1.282\sigma_y - 0.5\sigma_y^2\right) \qquad \textit{[Seq O]}$$

where z* is the standard normal distribution value of the percentile of the distribution determined from the number of samples, k (k = 44 in this example and z* = 1.28155). The value of z* can be obtained from a standard normal distribution table or any statistical program, spreadsheet or calculator that can report quantiles for the standard normal distribution. The value of z* can be calculated from the following:

$$p_n = (1 - \text{confidence level})^{1/n}$$

$$z_{pn} = 4.91\left[p_n^{0.14} - (1 - p_n)^{0.14}\right] \qquad 3 < n < 50$$

- The reasonable potential multiplying factor is the ratio of the upper bound percentile (99th percentile) to the percentile represented by the maximum reported concentration in the observed data (90th percentile in this example) (TSD p. 52). That is,

$$RP_{mf} = \frac{c_{99}}{c_{44}} = 1.29 \qquad \textit{[Seq P]}$$

Step 5. Calculate the predicted concentration at the edge of the mixing zone:

- The reasonable potential multiplying factor, RP_{mf}, *[Seq P]* is multiplied by the maximum *[Seq Q]* of the highest measured concentration, C_r, *[Seq E]* or the highest reported laboratory ML, D, *[Seq D]* to determine the maximum estimated concentration, C_e, of the constituent (in this example, nickel) in the discharge before dilution in the mixing zone *[Seq Q]*.

  That is,

$$C_e = [\text{Maximum}(Cr_{max}, D)] \times RP_{mf}$$

- The background seawater concentration (if any), C_s, *[Seq T]* is added. Five metals, arsenic, copper, mercury, silver, and zinc, have been determined to have seawater background concentrations high enough to be considered in this evaluation. These background concentrations are specified in Table 1 of Appendix A to the Permit. For the remaining constituents, $C_s = 0$.

- The receiving water concentration at the edge of the mixing zone, C_o, for a single constituent is determined from the following equation from Appendix A of the Permit:

$$Co = \frac{Ce + (Dq \times Cs)}{(Dq + 1)}$$

where,

C_o = the predicted concentration at the edge of the mixing zone *[Seq R]*,
C_e = the estimated maximum end-of-pipe discharge concentration *[Seq Q]*,
C_s = the background seawater concentration (if any, from Table 1 of Appendix A to the Permit) *[Seq T]*, and
D_q = the quarterly dilution value expressed in parts seawater per part wastewater.

Step 6. Compare the predicted concentration at the edge of the mixing zone, C_o, with the appropriate water quality criteria (WQC) listed in the Permit to determine if reasonable potential exists:

- If C_o *[Seq R]* is greater than the WQC *[Seq S]*, the upper bound concentration in the effluent is greater than the WQC after dilution at the edge of the mixing zone (at the 99th percent confidence level).

The results of this comparison appear in *[Seq U]*.

- A "YES" indicates the maximum concentration of the parameter is predicted to exceed the WQC (i.e., $C_o >$ WQC) at the given dilution ratio and reasonable potential has been determined to exist.
- A "n/c" indicates that insufficient measurements were reported to make a statistically valid determination of reasonable potential to exceed the WQC. The number of samples, k, must be equal to or greater than 3 to calculate a statistically valid result.
- A "NO" in this column indicates that the predicted maximum concentration will not exceed the WQC at a 99 percent confidence level and reasonable potential has been determined not to exist.

Step 7. Calculate the minimum dilution necessary to maintain a condition of no reasonable potential to exceed a WQC. This limiting dilution is termed the minimum dilution limit, D_{min}.

- To ensure reasonable potential does not occur, the predicted concentration at the edge of the 100-m mixing zone, C_o, must be less than or equal to the WQC.

That is, the predicted C_o, based on the quarterly dilution value:

$$C_o = \frac{C_e + (D_q \times C_s)}{(D_q + 1)} \qquad \textit{[Seq R]}$$

where,

Ce	=	the estimated maximum end-of-pipe discharge concentration *[Seq Q]*,	
D_q	=	quarterly dilution value	
WQC	=	permitted water quality criterion	*[Seq S]*
C_s	=	ambient or receiving water background concentration.	*[Seq T]*

- Calculate the minimum dilution limit, D_{min}, by substituting the WQC for the predicted C_o and D_{min} for D_q and rearranging the terms,

$$D_{min} = \frac{C_e - WQC}{WQC - C_s} \qquad \textit{[Seq W]}$$

- Using this equation, reasonable potential to exceed a WQC can be determined from a comparison of the quarterly averaged dilution, D_q, with D_{min}. Any time D_q (actual dilution) falls below D_{min}, (i.e., when $D_q < D_{min}$) reasonable potential to exceed the WQC will exist.

Note: the minimum dilution limit is related to the percent reasonable , %RP, by the following equation:

$$\%RP = \frac{C_o}{WQC} \times \frac{100}{1} = \frac{D_{min}}{D_q} \qquad \textit{[Seq V]}$$

where the predicted C_o is calculated in *[Seq R]* and includes adjustments for background concentration.

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TABLE 1. Example Reasonable Potential Evaluation and Predicted Receiving Water Concentrations of Produced Water Discharge for NPDES Permit CAG280000

Sequence no.	Variable	Value
A	Chemical name	Nickel
B	No. of samples, k	44
C	No. of nondetects, r	15
D	Max reported ML (mg/L)	0.08
E	Max reported concentration (mg/L)	0.14
F	LNMEAN, μ_y	-2.43
G	LNVAR, σ_y^2	0.08
H	δ, the proportion of nonquantified and nodetected values	0.34
I	E(X)	0.088
J	V(X)	0.0005
K	cv(X)	0.247
L	$P_n@_{.99}$	0.901
M	σ^2	0.059
N	C_{99}	1.71
O	C_P	1.33
P	Reasonable potential multiplying factor	1.29
Q	Max of reported effluent conc'n & ML (mg/L)	0.14
R	Predicted max RWC (mg/L) at dilution of 1000	0.00018
S	Water Quality Criteria (mg/L)	0.008
T	Background value (mg/L)	0
U	Exceeds Water Quality Criterion?	no
V	Predicted RWC as % of WQC	2
W	Minimum dilution required to meet criteria	22

Note: The data set of 44 reported concentrations for nickel is shown in Table 2.
The abbreviations and terms used in this table are described in Table 3.

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TABLE 2. Example laboratory results for the analysis of nickel in produced water

Sample No.	Measured (ug/L) x_i	ML (ug/L)	Natural Logarithm of Reported Values, y_i	
1	Below ML	0.05		
2	Below ML	0.05		
3	Below ML	0.05		
4	Below ML	0.05		
5	0.13		-2.040	
6	0.07		-2.659	
7	Below ML	0.05		
8	0.05		-2.996	
9	0.08		-2.526	
10	0.12		-2.120	
11	0.09		-2.408	
12	0.14		-1.966	
13	0.09		-2.408	
14	0.06		-2.813	
15	Below ML	0.05		
16	Below ML	0.05		
17	0.06		-2.813	
18	0.07		-2.659	
19	0.07		-2.659	
20	0.09		-2.408	
21	0.06		-2.813	
22	Below ML	0.05		
23	0.07		-2.659	
24	0.1		-2.303	
25	0.08		-2.526	
26	0.14		-1.966	
27	0.13		-2.040	
28	0.11		-2.207	
29	0.09		-2.408	
30	Below ML	0.08		
31	0.087		-2.442	
32	Below ML	0.02		
33	0.14		-1.966	
34	0.09		-2.408	
35	0.081		-2.513	
36	Below ML	0.08		
37	Below ML	0.08		
38	Below ML	0.08		
39	Below ML	0.08		
40	Below ML	0.08		
41	0.087		-2.442	
42	0.099		-2.313	
43	0.088		-2.430	
44	0.08		-2.526	
	15	No. of non-detects (< ML)	-2.429	Mean value, μ
	44	Total no. of samples, k	0.076	Variance, σ^2
	0.14	Max. measured concentration		

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TABLE 3. List of Symbols and Abbreviations

δ	The proportion of nonquantified and nodetected values in the sample data set
μ_y	Sample mean of the distribution of the natural log of the concentrations greater than the ML
σ_y^2	Sample variance of the distribution of the natural log of the concentrations greater than the ML
c_{99}	Upper bound at the 99-percent basis of the normal distribution of the reported concententrations of the analyte
C_e	Estimated maximum end-of-pipe discharge concentration $C_e = [Max(C_r, D)] \times RP_{mf}$
c_n	Calculated percentile of the distribution representing the maximum reported concentration
C_o	Predicted concentration at the edge of the mixing zone
C_r	Highest reported concentration
C_s	Background concentration in seawater
cv(X)	Estimate of the coefficient of variation of the delta-lognormal distribution
D	Maximum of the laboratoy MLs for a single analyte
D_{min}	Minimum dilution necessary to maintain a condition of no reasonable potential
D_q	Quarterly dilution value expressed in parts seawater per part wastewater
E(X)	Estimate of the mean of the delta-lognormal distribution
ML	Laboratory minumum limit: the minimum concentration at which the laboratory can report a quantifiable result for an analyte at a high level of confidence
k	Number of values reported by the laboratory for a single analyte
k-r	Number of reported concentrations greater than the ML
p_n	Percentile of the distribution into which the maximum measured concentration falls
r	Number of samples of a single analyte for which the concentrations are not quantifiable, i.e., the number of concentrations reported below the ML
RWC	Receiving water concentration
RP_{mf}	Reasonable potential multipling factor
TSD	Technical Support Document for Water Quality-based Toxics Control. USEPA/505/2-90-001. US Environmental Protection Agency, Office of Water, March 1991
V(X)	Estimate of the variance of the delta-lognormal distribution
WQC	Applicable water quality criterion as defined in the Permit
x_i	Data set of concentrations reported by the laboratory for a single analyte
y_i	Natural logarithm of the reported concentrations, $y_i = \ln(x_i)$
z^*	Standard normal distribution value of the percentile of the distribution determined from the number of samples. z^* can be obtained from a standard normal distribution table or any statistical program, spreadsheet or calculator that can report quantiles for the standard normal distribution

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