GUIDESHEET III

CHARACTERIZATION OF WASTEWATER

An applicant is required to properly characterize the waste or wastewater to be discharged according to Rule 2220. They must determine the pollutants that may be present in the waste or wastewater in light of the process that generates it. A municipal applicant must include a list of all non-sanitary discharges into the system, including the type of wastewater discharged and substances associated with any non-sanitary discharges. This should be accomplished by evaluating any chemical additives, any chemicals or byproducts that may be released or produced from the process or process material(s), or any reaction byproducts from the process mixture or environmental media. A determination of the concentration of each substance in the wastewater is made through representative sampling and analysis [Rule 2220(3)] or mass balance estimation [Rule 2220(5)]. This information will be used to determine the type of treatment necessary to achieve the standards of Rule 2222. **These are not techniques that would be allowed to demonstrate compliance with limits established in a discharge authorization.**

Collecting representative samples, especially at facilities with seasonally variable waste streams, and calculating a statistically valid concentration can be a very complex process. Applicants are also required to provide toxicity information sufficient to develop a standard for any substances identified in the wastewater characterization. Since this information is required for an administratively complete application [Rule 2218(3)(iii) and (v)], the Michigan Department of Environmental Quality (MDEQ) strongly recommends the following to facilities applying for discharge permits:

1. Schedule a pre-application meeting with MDEQ, Water Bureau (WB), Groundwater Permits Unit (GWPU) staff and discuss the potential universe of substances that might be present in the discharge. Information on process, flow or wastewater variations should be discussed, along with timing of sample collection to ensure that sampling is representative.
2. Submit mass balance estimates for any chemical additive that would be present in the wastewater to the MDEQ, WB, GWPU prior to permit application. This may help identify substances that should be included in the sampling and analysis plan. This also allows the toxicologist to conduct a preliminary review to determine any substances that require toxicity information sufficient to develop a discharge standard required by Rule 2218(3)(v). This will help the applicant to submit an administratively complete application.
3. After meeting with staff, submit a sampling and analysis **plan** to the MDEQ, WB, GWPU for review and approval prior to conducting the characterization. The sampling and analysis work plan should include the number of samples to be collected, proposed sampling locations and timeframes for sampling, sampling technique, and the proposed list of parameters and analytical methods.

R 323.2220 Characterization of waste or wastewater to be discharged.

Rule 2220.(1) Before a permit can be issued under R 323.2218, an applicant shall properly characterize the waste or wastewater to be discharged. To properly characterize the waste or wastewater, the applicant shall determine the pollutants that may be present in the waste or wastewater in light of the process by which it is generated. The applicant shall use the methods described in this rule to make the determination.

(2) Samples of effluent collected to determine the presence of inorganic substances shall be unfiltered.

(3) For a substance for which there is an analytical method approved by the department for purposes of monitoring under this part, the waste or wastewater shall be representatively sampled using sampling procedures specified in the EPA document entitled “Test Methods for the Evaluation of Solid Waste, Physical-Chemical Methods,” SW-846, 3rd Edition, September 1986, as updated through the effective date of these rules and analyzed using analytical procedures specified in either SW-846 or the publication entitled “Guidelines Establishing Test Procedures for the Analysis of Pollutants,” 40 C.F.R. Part 136, or other methods approved by the department for purposes of monitoring under this part. SW-846 and updates and the guidelines are adopted by reference in these rules and are available for inspection at the Lansing office of the department of environmental quality, waste management division. The documents may be purchased from the United States Government Printing Office, Superintendent of Documents, P.O. Box 371954, Pittsburgh, Pennsylvania 15250-7954, or the Michigan Department of Environmental Quality, Water Bureau, P.O. Box 30458, Lansing, Michigan 48909-7773, at a cost at the time of adoption of these rules of $319.00 and $36.00, respectively, plus shipping and handling.

(4) Reporting levels shall be those approved by the department as the lowest level routinely quantifiable with acceptable precision and accuracy by standard laboratory methods. Not less than 4 discrete samples are necessary to be considered representative, unless a lesser number is approved by the department.

(5) For any other substance that may be present, an estimate of the substance concentration in the discharge shall be made with a mass balance calculation or other estimate approved by the department. The estimate shall use the annual average use rate for the substance and annual average discharge volume, except when an alternative is approved by the department.

(6) For a facility not yet operating, the discharger shall characterize the anticipated discharge using the best available information. The discharger shall identify the source of the information in the application.

(7) The department may require the characterization of sludge generated by the wastewater treatment process as it relates to the ability of the discharge to meet the standards of R 323.2222 as a condition of authorizing a discharge under these rules. The characterization shall be done according to the procedures described in subrule (3) of this rule.

(8) The department may require the characterization of other environmental media affected in the treatment of wastewater as a condition of authorizing a discharge under these rules. The characterization shall be done according to the procedures described in subrule (3) of this rule.

(9) The department may waive the requirements of this rule if the nature of the material to be characterized is sufficiently well understood to ensure that the conditions of R 323.2204(2)(a) will be met.

IDENTIFYING SUBSTANCES

Rule 2220 requires that the applicant identify the substances that are or may be present in the discharge in light of the processes that generated the wastewater. This includes consideration of the raw materials being used, chemical additives, intermediates, intentional and unintentional byproducts. Substances in the discharge must be identified and their concentrations quantified.

The applicant or their chemical supplier needs to evaluate the potential for reaction byproducts from chemical additives and the process or wastewater mixture. An evaluation of reaction byproducts must also consider possible reactions with other environmental media (e.g. soil) which may result in groundwater concentrations that exceed the Rule 2222 standards. Some examples of this would be wastewater with (1) high biological oxygen demand that may increase the leachability of native metals in the soils such as iron and manganese, or (2) residual chlorine that may react with substances in the soil and produce disinfection by products such as trihalomethanes.

Products used or incidental to the facility that may enter the wastewater must also be considered. It is recommended that an inventory of all chemical products used at the facility be reviewed to determine those that are or may enter the wastewater discharge.

Municipal applicants must list all non-sanitary sources of wastewater. Any substances from these non-sanitary sources must be identified and quantified. This may be accomplished through representative sampling and analysis and/or mass balance calculations. Sampling and analysis may be required from the owner or operator of the non-sanitary discharge into the municipal system. An industrial pretreatment program may be recommended for the municipal applicant to meet the Rule 2222 standards. The complete Ingredients of chemical products entering the discharge must be provided to the MDEQ, WB, GWPU. Chemical suppliers may list some additive ingredients as “proprietary” or “inert” on Material Safety Data Sheets. Always request the chemical supplier to provide the complete ingredient statements. Confidential ingredient information may be submitted directly to the MDEQ, WB, GWPU following the guidelines and procedures outlined in the Policy and Procedures for Submitting Confidential Information found on page 25 of this document. If the supplier wants the chemical ingredient information to remain confidential, the supplier will need to provide the mass balance calculations for the chemical products and their ingredients (see page 6).

REPRESENTATIVE SAMPLING CONSIDERATIONS

Rule 2220(3) requires substances for which there are analytical methods to be representatively sampled. A sampling strategy should consider potential variations in wastewater characteristics. These could include temporal variations (e.g., daily, weekly, seasonal), changes in processing streams, and treatment or operational variations. These considerations need to be reflected in the number of samples collected and the timing and location of sample collection. Random sampling is the general rule. A wastewater with little potential variability should have the samples collected using a random timing scheme. If there may be variability (e.g., seasonal variation from sanitary wastewater in a lagoon system, different processes at different times), two different approaches should be considered: (1) random sampling throughout the time frame variations are expected or (2) separation of the time periods into two or more sample populations with random sampling within each. If there is a lot of variability between populations, approach 1 may result in more total samples required than approach 2.

WHERE TO COLLECT SAMPLES

The following provides guidance where to collect samples.

Sanitary Wastewater

Characterization of sanitary wastewater shall be carried out by obtaining at least four sets of discrete samples that are representative of the wastewater quality to be discharged. In order to be considered representative, the sample shall be obtained from the following locations for the specific treatment and disposal method.

1. Lagoons

   Sanitary wastewater from a lagoon treatment system shall be sampled from a location where the wastewater is sufficiently mixed. An appropriate location to obtain a mixed wastewater sample is from a pump house or sampling port following lagoon storage and as close as possible to the end-of-pipe discharge location.

   Seasonal variations in lagoon treatment and discharge mixing should be considered in the sampling strategy. Consideration should also be given to the timeframe when the lagoon will actually be discharging. If there is not a winter discharge, then sampling at this time may not provide accurate discharge information.

   If there is no sampling location as described above the samples shall be obtained directly from the final lagoon at close proximity and at a similar depth as the discharge pipe. The samples should be obtained while an active discharge is occurring from the lagoon.

2. Mechanical plants

   Samples shall be obtained from the pump house or sampling port following treatment and prior to the end-of-pipe discharge location.

Process or Industrial Wastewater

1. Septic Tank / Tile Field

   At least four sets of discrete samples shall be obtained to characterize the wastewater. Samples shall be obtained from the final septic tank or a sampling port located between the septic tank and the discharge location.

2. Others

   We strongly recommend that facilities take advantage of pre-application meetings with GWPU staff, and after meeting with staff, submit a sampling and analysis plan to the GWPU, WB for review and approval prior to conducting the characterization. The sampling and analysis work plan should include the number of samples to be collected, proposed sampling locations and timeframes for sampling, sampling technique, and the proposed list of parameters and analytical methods. Information on process, flow, or wastewater variations should also be included with the timing of the sample collection to demonstrate the sampling strategy is representative.

Number of Samples to be Collected

It is necessary to have a sufficient number of waste or wastewater samples to adequately represent the quality or characteristics. In general, the minimum number of samples for a fairly homogeneous waste stream is four discrete samples. If there are variations in the process that will effect the characteristics of the waste stream, the number of samples and collection timing must reflect those variations to adequately represent those variable characteristics.

A determination will need to be made if the sample population (number of samples) is sufficient to represent the waste or wastewater quality. This may be accomplished by following the guidance found on page 8 of this Guidesheet, titled “Statistical Evaluation: Wastewater Characterization Sampling” or other methodology approved by the MDEQ, WB, GWPU. For most parameters it is more efficient and economical to collect more than the minimum number of samples needed during the initial sampling process. If these samples are maintained under proper laboratory protocol, they can be accessed and evaluated without having to reconvene a field sampling crew.

Analytical Methods

Samples shall be analyzed by the analytical procedures specified in “Test Methods for the Evaluation of Solid Waste, Physical-Chemical Methods,” SW-846, 3rd Edition, September 1986 as updated through August 26, 1999 or “Guidelines Establishing Test Procedures for the Analysis of Pollutants,” 40 CFR Part 136. Other analytical procedures may be approved by the DEQ on a case-by-case basis.

Reporting Levels

See page 18 of this Guidesheet for analytical reporting limits acceptable to the MDEQ, WB, GWPU for wastewater characterization. The MDEQ, WB, GWPU may approve alternate limits with appropriate justification. Pursuant to Rule 2222(6)(b) the applicant may be required by the MDEQ, WB, GWPU to characterize the discharge in an alternate manner (e.g., sampling and analysis of a specific process wastewater upstream from the discharge point or a mass balance calculation). This may be required for a substance whose Rule 2222(5) standard is below the detection limit and there is knowledge that the substance may be present in the discharge above the standard.

Mass Balance Calculations

The discharge concentration must be estimated for substances present in the wastewater that do not have a readily available analytical method or with a detection level above the Rule 2222(5) standard. These could range from substances added to the wastewater to those entering the wastewater incidentally such as cleaning agents. A mass balance estimate is acceptable to the MDEQ, WB, GWPU pursuant to Rule 2220(5). Guidance for calculating mass balance concentrations is found on page 26 of this Guidesheet. Mass balance calculations must be completed for all chemical products including all ingredients of those products, and substances known to form through reaction or breakdown the ingredients. The chemical supplier may prefer to complete the mass balance calculations to maintain the confidentiality of their proprietary products (see Policy and Procedures for Submitting Confidential Information found on page 25 of this document.) The MDEQ, WB, GWPU may approve alternate methods to characterize the waste or wastewater for these substances on a case-by-case basis.

It cannot be emphasized enough that mass balance estimates should be submitted prior to submitting a permit application. This will help the applicant for the following reasons:

1. Additional substances may need to be included in the sampling and analysis. Mass balance estimates of additives may indicate that a substance's calculated discharge concentration will exceed the standard for that substance. If the substance can be analyzed from a wastewater sample, the MDEQ, WB, GWPU will recommend that the applicant include it in the parameter list for the sampling and analysis plan. If additional substances are identified prior to implementation of the sampling and analysis plan, samples for all parameters can be collected at the same time. Otherwise, additional sampling may be necessary.
2. Some substances may require toxicity information to be submitted as part of the permit application. Rule 2218(3)(a)(v) states that the applicant must provide the necessary information to determine a standard if the MDEQ has not already developed the standard. MDEQ toxicologists will review the preliminary submittal and inform the applicant which substances already meet standards, any substance that does not meet the standard, and any substance that requires additional toxicity information to develop a standard. Without the required toxicity information, an application will be returned as administratively incomplete.

The permit will include additive use limitations based on the mass balance calculations. It is highly recommended that the applicant consider this in specifying use rates in the application and mass balance calculations. If these use rates may increase (e.g., a new process line is planned) during the permit authorization period (usually five years), it will benefit the applicant to estimate the use rates for the end of the authorization period.

Characterization - New Facilities

New facilities are required to characterize the anticipated discharge based on best available information. This best available information could include published or site specific information on the wastewater characteristics of a similar facility with similar processes and treatment and/or mass balance estimated concentrations of anticipated additives.

Sludge Characterization

The MDEQ, WB, GWPU has the authority to require sludge or wastewater treatment residuals to be characterized if those materials may impact the ability to meet the required standards under Rule 2222. Sludge characterization methodology that is acceptable to the MDEQ, WB, GWPU is available in Guidesheet VI. The MDEQ, WB, GWPU on a case-by-case basis, may approve alternate methods.

STATISTICAL EVALUATION
WASTEWATER CHARACTERIZATION SAMPLES

The following is a step by step description of the approach used to calculate **confidence limits** based on the analytical data derived from the preliminary samples.

1. Calculate a preliminary estimate of the mean, $\bar{X}$

$$\bar{X} = (X_1 + X_2 + X_3 + ... X_n) / n$$

where:

n = number of discrete measurements (samples)
Xi = individual measurements

2. Calculate a preliminary estimate of the variance (S^2) and the standard deviation (S). Standard deviation is a function of both sampling variability and measurement variability.

$$S^2 = [(X_1-\bar{X})^2+(X_2-\bar{X})^2+...(X_n-\bar{X})^2] / n-1$$

$$S = (S^2)^{1/2}$$

3. Calculate the standard error of the mean (Sx). Standard error is inversely proportional to the square root of the number of samples (increasing n from 4 to 16 reduces Sx by 50 percent).

$$Sx = S / (n)^{1/2}$$

4. Since the concern is generally only whether the upper limit of a confidence interval is below or above the standard, the lower confidence limit (LCL) need not be considered. If pH is a parameter of concern, however, both the LCL and the upper confidence limit (UCL) must be evaluated. The UCL can be calculated using the one-tailed (one-sided) t values with n-1 degrees of freedom derived from a table of the Student's t distribution. Where only small sized statistical samples are involved (n<30), the normal or Gaussian distribution is not accurate, and the t distribution must be used.

5. The 95 percent UCL is calculated by using the following formula and substituting the values determined above plus the appropriate t value obtained from the t table.

$$UCL = \bar{X} + [t_{0.95},(n-1)] \ast Sx$$

The term in brackets indicates a one-tailed t-test at n-1 degrees of freedom. See the t-distribution table on page 16 of this Guidesheet, Cumulative t Distribution. To find the appropriate t value look at the first row (one-tailed) and find the column for 0.950, this is the column of t-values for a 95 percent confidence limit. Now find the appropriate row based on the n-1 degrees of freedom (e.g., if you have four samples n=4 and n-1=3 so, look in the row with 3 in the first column). The appropriate t-value is the number in the one-tailed 0.950 column and the n-1 degrees of freedom row.

The UCL number resulting from this formula will indicate with a 95 percent probability that the wastewater is either above or below the standard developed for the substance being subjected to the test.

If the preliminary data indicates that the sample population has a sufficient variability that results in the UCL exceeding the standard although most or all of the individual samples and the mean of samples are below the standard, more samples may be necessary. To determine how many more samples may be necessary, the Lambda relationship should be used. A step by step approach to calculating the appropriate sample size follows:

1. Based on the preliminary sample set, the appropriate number of samples to be collected can be estimated by use of the Lambda relationship and then consulting a table of values (see page 17 of this Guidesheet, NUMBER OF OBSERVATIONS FOR t TEST OF MEAN) and their corresponding sample size number.

   $$Lambda = (standard - \bar{X}) / S$$

   The lower the calculated value, the more samples are required to maintain a certain level of confidence. Also, as the $\bar{X}$ approaches the standard, Lambda becomes smaller, and therefore a greater sample size is indicated for a certain level of confidence.

2. To obtain the appropriate sample size from the table of values (see page 17 of this Guidesheet, NUMBER OF OBSERVATIONS FOR t TEST OF MEAN) use the single sided value for alpha (A) and beta (B) to test at the desired significance level (for 5 percent, = 0.05). Generally, use the column corresponding to single sided A = 0.05 and B = 0.05. Use the lambda value calculated from the equation in 1. above to determine the appropriate row. The appropriate number of samples is the value in the column single sided A = 0.05 and B = 0.05 and the row Lambda. This estimates the total number of samples (adequacy of the sample population) to determine if the wastewater will meet the standard based on the variability of the preliminary samples. The number of additional samples necessary is the value from the table minus the number of preliminary samples.

3. Randomly collect any additional samples that may be needed using the same approach and random numbers sequence as the first sampling. All field and laboratory procedures should be kept as consistent as possible to lower the amount of variability in the data.

4. Use all data values to calculate new $\bar{X}$, S, Sx, and S^2.

5. If the new $\bar{X} \geq$ standard, then the substance is present at an unacceptable concentration and the study would be complete.

6. If $\bar{X}$ < standard and $\bar{X}$ > ***S²***, calculate ***C*** (the criterion for determining if a substance is present above the standard). If $\bar{X}$ **= *S²*** or $\bar{X}$ **< *S²*,** the data must be transformed prior to calculating ***C***. The data must be transformed, most likely with a log or log normal transformation, to fit a normal distribution. Using the new data, ***C*** is calculated by the formula:

$$C = (standard - \bar{X}) / Sx$$

7. Compare the calculated ***C*** value to the two-tailed t value for the 95 percent level of confidence. The two-tailed t-value is used because both the possibility that ***C*** is > t or that ***C*** is < t must be checked. Use $t_{0.95}$ and df (degrees of freedom) = n-1.

8. If ***C* >** t value, the substance is present at unacceptable concentrations and the study would be over. If ***C*** < t value, reestimate the total number of additional samples to be collected by deriving a new Lambda. Use the newly calculated values of $\bar{X}$ and ***S*.**

9. If this new number of samples is not more than 20 percent greater than the last set collected, it is unlikely that additional samples would decrease ***Sx***. Therefore, additional samples would be unnecessary, the wastewater will likely meet the standard and the study would be complete.

CALCULATION OF CONFIDENCE LIMITS AND LAMDA CALCULATION

STATISTICAL SAMPLING – Example Problem

A food-canning factory is discharging process wastewater. From April to November the wastewater enters a small holding tank and is then discharged through spray irrigation. From November to April the wastewater is discharged directly to a seepage bed. From July through October the factory processes and cans several locally grown fruits and vegetables. In the off season (November through June), the factory processes and cans pork and beans. The discharge contains nutrients from processing the food, additives, cleaners and chlorine for disinfection. One cleaning system is used during production of the fresh fruits and vegetables, but another cleaning system is necessary during production of the pork and beans. The substances of concern for this example are total inorganic nitrogen (ammonia-N, nitrate-N and nitrite-N), chloride, and total trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane and bromoform). The following sampling data was collected to meet the minimum requirements for wastewater characterization:

	Sample date				
Parameter/units	5/14	8/17	12/19	3/10	Standard
Total Inorganic Nitrogen (mg/l)	5.5	2.5	5.2	5.8	5
Chloride (mg/l)	234	132	228	230	250
Total Trihalomethanes (μg/l)	10	2	9	8	20

1. Based on the Total Inorganic Nitrogen (TIN), Chloride and Total Trihalomethanes (THMs) data supplied:

   Calculate S^2, S, Sx

   Calculate the 95 percent UCL

With what degree of confidence can it be stated that each of these substance concentrations does not exceed the appropriate standard [TIN = 5 mg/l per R 222(2)(a), chloride = 250 mg/l per R 2222(3)(b), and total THMs = 20 μg/l per R 2222(4)]?

2. If more samples are deemed necessary, determine how many.

   Calculate the Lambda value for substance(s) that need more samples.

   Calculate the appropriate number of additional samples using A = 0.05 and B = 0.05.

Total Inorganic Nitrogen

STATISTICAL SAMPLING ANSWER SHEET
Given four samples with TIN concentrations of 5.5, 2.5, 5.2 and 5.8 mg/l and

$$\bar{X} = 4.75 \text{ mg/l}$$

(1a) Calculate S^2

$$S^2 = [(X_1 - \bar{X})^2 + (X_2 - \bar{X})^2 + \ldots (X_n - \bar{X})^2] / n-1$$

$$=[(5.5 - 4.75)^2 + (2.5 - 4.75)^2 + (5.2 - 4.75)^2 + (5.8 - 4.75)^2] /3$$

$$= 2.31$$

Calculate S

$$S = (S^2)^{½} = (2.31)^{½} = 1.52$$

Calculate Sx

$$Sx = S/(n)^{½} = 1.52 /(4)^{½} = 0.76$$

(1b) Calculate the 95 percent UCL

$$\textbf{95 percent UCL} = \bar{X} + [t_{0.95,(n-1)}]*Sx$$

To find the appropriate t value from the Cumulative t Distribution table on page 16 of this Guidesheet, look at the first row (one-tailed) and find the column for 0.950, this is the column of t-values for a 95 percent confidence limit. Now find the appropriate row based on the n-1 degrees of freedom (there are four samples, so n=4 and n-1=3). The appropriate t-value is 2.353 from the one-tailed 0.950 column and the 3 degrees of freedom row.

$$= 4.75 + (2.353)*(0.76)$$

$$= 6.54$$

(1c)

$$\textbf{90 percent UCL} = \bar{X} + [t_{0.90,(n-1)}]*Sx$$

To find the appropriate t value, go to the Cumulative t Distribution table on page 16 of this Guidesheet, look at the first row (one-tailed) and find the column for 0.900, this is the column of t-values for a 90 percent confidence limit. Again use the row for 3 degrees of freedom (n-1). The appropriate t-value is 1.638 from the one-tailed 0.900 column and the 3 degrees of freedom row.

$$= 4.75 + (1.638)*(0.76)$$

$$= 5.99$$

$$\textbf{80 percent UCL} = \bar{X} + [t_{0.80,(n-1)}]*Sx$$

To find the appropriate t value from the Cumulative t Distribution table on page 16 of this Guidesheet, look at the first row (one-tailed) and find the column for 0.800, this is the column of t-values for a 80 percent confidence limit. Find the row for 3 degrees of freedom. The appropriate t-value is 0.978 from the one-tailed 0.800 column and the 3 degrees of freedom row.

$$= 4.75 + (0.978)*(0.76)$$

$$= 5.49$$

The preceding calculations indicate that even with only 80 percent confidence that the TIN concentration exceeds the standard. Therefore, it is a low probability that additional samples would provide data that would pass. Therefore the lambda test is not necessary. Consideration should be given for either treating the effluent prior to discharge or discharging in a manner to meet the alternate TIN standard in R 2222(2)(b).

Chloride

STATISTICAL SAMPLING ANSWER SHEET
Given four samples with chloride concentrations of 234, 132, 228 and 230 mg/l and

$$\bar{X} = 206 \text{ mg/l}$$

(1a) Calculate S^2

$$S^2 = [(X_1-\bar{X})^2+(X_2-\bar{X})^2+...(X_n-\bar{X})^2] / n-1$$
$$=[(234 - 206)^2 + (132 - 206)^2 + (228 - 206)^2 + (230 - 206)^2] /3$$
$$= 2440$$

Calculate S

$$S = (S^2)^{1/2} = (2440)^{1/2} = 49.4$$

Calculate Sx

$$Sx = S/(n)^{1/2} = 49.4/(4)^{1/2} = 24.7$$

(1b) Calculate the 95 percent UCL

$$\textbf{95 percent UCL} = \bar{X} + [t_{0.95,(n-1)}]*Sx$$
$$= 206 + (2.353)*(24.7)$$
$$= 264$$

(1c)

$$\textbf{90 percent UCL} = \bar{X} + [t_{0.90,(n-1)}]*Sx$$
$$= 206 + (1.638)*(24.7)$$
$$= 246$$

The preceding calculations indicate that it can be stated with somewhere between 90 percent and 95 percent confidence that the chloride concentration does not exceed the standard. A 95 percent level of confidence is recommended. This indicates more samples may need to be taken. A lower confidence interval may be chosen, but it increases the risk that permit limits will be exceeded with the wastewater variability.

2a. Calculate the Lambda value for chloride

$$\textbf{Lambda} = (\text{standard} - \bar{X}) / S$$
$$= (250 - 206) / 49.4 = 0.89$$

2b. Calculate the number of additional samples

From the table Number of Observations for t Test of Mean, page 17 of this Guidesheet, using a single-sided test with A = 0.05 and B = 0.05, and a lambda value of 0.89 (use row 0.90) from the above calculation, the table indicates approximately 15 total samples need to be collected. Therefore, based on the four preliminary samples that were collected (15 – 4 = 11), an additional 11 samples need to be taken.

Total Trihalomethanes

STATISTICAL SAMPLING ANSWER SHEET

Given four samples with total trihalomethanes (THM) concentrations of 10, 2, 9 and 8 μg/l and

$$\bar{X} = 7.25\ \mu g/l$$

(1a) Calculate S^2

$$S^2 = [(X_1 - \bar{X})^2 + (X_2 - \bar{X})^2 + \ldots (X_n - \bar{X})^2] / n-1$$
$$= [(10 - 7.25)^2 + (2 - 7.25)^2 + (9 - 7.25)^2 + (9 - 7.25)^2] / 3$$
$$= 12.92$$

Calculate S

$$S = (S^2)^{1/2} = (12.92)^{1/2} = 3.59$$

Calculate Sx

$$Sx = S/(n)^{1/2} = 3.59 / (4)^{1/2} = 1.80$$

(1b) Calculate the 95 percent UCL

$$\text{95 percent UCL} = \bar{X} + [t_{0.95,(n-1)}]*Sx$$
$$= 7.25 + (2.353)*(1.80)$$
$$= 11.48$$

The preceding calculations indicate that it can be stated with 95 percent confidence that the total THM concentration does not exceed the standard. Additional samples are not necessary to characterize the wastewater for total THM.

CONCLUSION:

This data indicate that there are two separate populations. The May 14, December 19 and March 10 samples appear similar, with the August 17 sample looking somewhat different. It is clear from these sampling events that there are different wastewater characteristics during the different types of processing (pork and beans versus fresh fruits and vegetables). It is necessary to treat different processes with different wastewater characteristics as separate effluents. The best approach for determining the number of necessary samples would be to treat these as two different wastewater effluents with four samples from each process. This should decrease the variability in the statistical analysis and allow the 95 percent UCL of the chloride concentration to meet the standard with less samples necessary (eight samples as two separate populations vs. 15 samples for a single population). In this example, the separate sample population issue only impacts the number of samples necessary for chloride. In most cases, all substances should be evaluated as separate populations. However, if there are multiple sources of different substances in the wastewater, each substance or set or substances may need to be evaluated individually. If the facility had sanitary wastewater mixed with wastewater from multiple processes, the substances in the sanitary wastewater component should not vary as much as that from the process wastewater components. Again, a preapplication meeting would help the applicant to identify the different considerations necessary for representative wastewater characterization, especially with multiple wastewater sources.

Cumulative t Distribution

one-tailed	0.550	0.750	0.080	0.900	0.950	0.975	0.990	0.995
two-tailed	0.100	0.500	0.600	0.800	0.900	0.950	0.980	0.990
1	0.158	1.000	1.376	3.078	6.314	12.706	31.821	63.657
2	0.142	0.816	1.061	1.886	2.920	4.303	6.925	9.925
3	0.137	0.765	0.978	1.638	2.353	3.182	4.541	5.841
4	0.134	0.741	0.941	1.533	2.132	2.776	3.747	4.604
5	0.132	0.727	0.920	1.476	2.015	2.571	3.365	4.032
6	0.131	0.718	0.906	1.440	1.943	2.447	3.143	3.707
7	0.130	0.711	0.896	1.415	1.895	2.365	2.998	3.499
8	0.130	0.706	0.889	1.397	1.860	2.306	2.896	3.355
9	0.129	0.703	0.883	1.383	1.833	2.262	2.821	3.250
10	0.129	0.700	0.879	1.372	1.812	2.228	2.764	3.169
11	0.129	0.697	0.876	1.363	1.796	2.201	2.718	3.106
12	0.128	0.695	0.873	1.356	1.782	2.179	2.681	3.055
13	0.128	0.694	0.870	1.350	1.771	2.160	2.650	3.012
14	0.128	0.692	0.868	1.345	1.761	2.145	2.624	2.977
15	0.128	0.691	0.866	1.341	1.753	2.131	2.602	2.947
16	0.128	0.690	0.865	1.337	1.746	2.120	2.583	2.921
17	0.128	0.689	0.863	1.333	1.740	2.110	2.567	2.898
18	0.127	0.688	0.862	1.330	1.734	2.101	2.552	2.878
19	0.127	0.688	0.861	1.328	1.729	2.093	2.539	2.861
20	0.127	0.687	0.860	1.325	1.725	2.086	2.528	2.845
21	0.127	0.686	0.859	1.323	1.721	2.080	2.518	2.831
22	0.127	0.686	0.858	1.321	1.717	2.074	2.508	2.819
23	0.127	0.685	0.858	1.319	1.714	2.069	2.500	2.807
24	0.127	0.685	0.857	1.318	1.711	2.064	2.492	2.797
25	0.127	0.684	0.856	1.316	1.708	2.060	2.485	2.787
26	0.127	0.684	0.856	1.315	1.706	2.056	2.479	2.779
27	0.127	0.684	0.855	1.314	1.703	2.052	2.473	2.771
28	0.127	0.683	0.855	1.313	1.701	2.048	2.467	2.763
29	0.127	0.683	0.854	1.311	1.699	2.045	2.462	2.756
30	0.127	0.683	0.854	1.310	1.697	2.042	2.457	2.750
40	0.126	0.681	0.851	1.303	1.684	2.021	2.423	2.704
60	0.126	0.679	0.848	1.296	1.671	2.000	2.390	2.660
120	0.126	0.677	0.845	1.289	1.658	1.980	2.358	2.617
	0.126	0.674	0.842	1.282	1.645	1.960	2.326	2.576

NOTE: For one-tailed distributions a/2 = 1-p
For two-tailed distributions a = 1-p

NUMBER OF OBSERVATIONS FOR t TEST OF MEAN

Level for t Test

Single-sided A=0.005 A=0.01 A=0.025 A=0.05

Double-sided A=0.01 A=0.02 A=0.05 A=0.1

	Single-sided A=0.005 / Double-sided A=0.01					Single-sided A=0.01 / Double-sided A=0.02					Single-sided A=0.025 / Double-sided A=0.05					Single-sided A=0.05 / Double-sided A=0.1				
LAMBDA	B=0.01	0.05	0.1	0.2	0.5	0.01	0.05	0.1	0.2	0.5	0.01	0.05	0.1	0.2	0.5	0.01	0.05	0.1	0.2	0.5
0.15																				122
0.20										139					99					70
0.25					110					90				128	64			139	101	45
0.30				134	78				115	63			119	90	45		122	97	71	32
0.35			125	99	58			109	85	47		109	88	67	34		90	72	52	24
0.40		115	97	77	45		101	85	66	37	117	84	68	51	26	101	70	55	40	19
0.45		92	77	62	37	110	81	68	53	30	93	67	54	41	21	80	55	44	33	15
0.50	100	75	63	51	30	90	66	55	43	25	76	54	44	34	18	65	45	36	27	13
0.55	83	63	53	42	26	75	55	46	36	21	63	45	37	28	15	54	38	30	22	11
0.60	71	53	45	36	22	63	47	39	31	18	53	38	32	24	13	46	32	26	19	9
0.65	61	46	39	31	20	55	41	34	27	16	46	33	27	21	12	39	28	22	17	8
0.70	53	40	34	28	17	47	35	30	24	14	40	29	24	19	10	34	24	19	15	8
0.75	47	36	30	25	16	42	31	27	21	13	35	26	21	16	9	30	21	17	13	7
0.80	41	32	27	22	14	37	28	24	19	12	31	22	19	15	9	27	19	15	12	6
0.85	37	29	24	20	13	33	25	21	17	11	28	21	17	13	8	24	17	14	11	6
0.90	34	26	22	18	12	29	23	19	16	10	25	19	16	12	7	21	15	13	10	5
0.95	31	24	20	17	11	27	21	18	14	9	23	17	14	11	7	19	14	11	9	5
1.00	28	22	19	16	10	25	19	16	13	9	21	16	13	10	6	18	13	11	8	5
1.1	24	19	16	14	9	21	16	14	12	8	18	13	11	9	6	15	11	9	7	
1.2	21	16	14	12	8	18	14	12	10	7	15	12	10	8	5	13	10	8	6	
1.3	18	15	13	11	8	16	13	11	9	6	14	10	9	7		11	8	7	6	
1.4	16	13	12	10	8	14	11	10	9	6	12	9	8	7		10	8	7	5	
1.5	15	12	11	9	7	13	10	9	8	6	11	8	7	6		9	7	6		
1.6	13	11	10	8	6	12	10	9	7	5	10	8	7	6		8	6	6		
1.7	12	10	9	8	6	11	9	8	7		9	7	6	5		8	6	5		
1.8	12	10	9	8	6	10	8	7	7		8	7	6			7	6			
1.9	11	9	8	7	6	10	8	7	6		8	6	6			7	5			
2.0	10	8	8	7	5	9	7	7	6		7	6	5			6				
2.1	10	8	7	7		8	7	6	6		7	6				6				
2.2	9	8	7	6		8	7	6	5		7	6				6				
2.3	9	7	7	6		8	6	6			6	5				5				
2.4	8	7	7	6		7	6	6			6									
2.5	8	7	6	6		7	6	6			6									
3.0	7	6	6	5		6	5	5			5									
3.5	6	5	5			5														

4.0 6

99% confidence 95% confidence

WASTEWATER CHARACTERIZATON

DETECTION LIMITS

VOLATILE ORGANICS 624/8260 PLUS	GROUNDWATER MDEQ Lab Reported Detection Limits (ug/l)	SEDIMENT/ SOILS MDEQ Lab Reported Detection Limits (ug/kg)	EPA ANALYTICAL METHOD SW-846	MDEQ TECHNIQUE
Acrylonitrile	5	250.0	624/8260	8260 +
Benzene	1	50.0	624/8260	8260 +
Bromochloromethane	1	100.0	624/8260	8260 +
Bromodichloromethane	1	100.0	624/8260	8260 +
Bromoform	1	100.0	624/8260	8260 +
Bromomethane	5	250.0	624/8260	8260 +
2-Butanone (MEK)	(5)	250.00	624/8260	8260 +
Carbon Disulfide	5	250.0	624/8260	8260 +
Carbon Tetrachloride	1	50.0	624/8260	8260 +
Chlorobenzene	1	50.0	624/8260	8260 +
Chloroethane	5	250.0	624/8260	8260 +
Chloroform	1	50.0	624/8260	8260 +
Chloromethane	5	250.0	624/8260	8260 +
Dibromochloromethane	1	100.0	624/8260	8260 +
1,2-Dibromo-3-chloropropane	5	250.0	624/8260	8260 +
Dibromomethane	1	100.0	624/8260	8260 +
1,2-Dibromoethane	1	50.0	624/8260	8260 +
1,2-Dichlorobenzene	1	100.0	624/8260	8260 +
1,3-Dichlorobenzene	1	100.0	624/8260	8260 +
1,4-Dichlorobenzene	1	100.0	624/8260	8260 +
1,4-Dichloro-2 butene (trans)	1	100.0	624/8260	8260 +
Dichlorodifluoromethane	5	250.0	624/8260	8260 +
1,1-Dichloroethane	1	50.0	624/8260	8260 +
1,2-Dichloroethane	1	50.0	624/8260	8260 +
1,1-Dichloroethene	1	50.0	624/8260	8260 +
1,2-Dichloroethene (cis)	1	50.0	624/8260	8260 +
1,2-Dichloroethene (trans)	1	50.0	624/8260	8260 +
1,2-Dichloropropane	1	50.0	624/8260	8260 +
1,3-Dichloropropene (cis)	1	50.0	624/8260	8260 +
1,3-Dichloropropene (trans)	1	50.0	624/8260	8260 +
Diethyl ether	10	250.0	624/8260	8260 +
Ethylbenzene	1	50.0	624/8260	8260 +
Hexachloroethane	1	100.0	624/8260	8260 +
2-Hexanone	5	250.0	624/8260	8260 +
Isopropylbenzene	1	100.0	624/8260	8260 +
Methylene Chloride	(5)	250.0	624/8260	8260 +
Methyl iodide	1	100.0	624/8260	8260 +
2-Methylnaphthalene	5	250.0	624/8260	8260 +
4-Methyl-2-Pentanone (MIBK)	5	250.0	624/8260	8260 +
Methyl Tertiary Butyl Ether (MTBE)	5	250.0	624/8260	8260 +
Naphthalene	5	250.0	624/8260	8260 +
2-Propanone (acetone)	25	750.0	624/8260	8260 +
n-Propylbenzene	1	100.0	624/8260	8260 +
Styrene	1	50.0	624/8260	8260 +

VOLATILE ORGANICS 624/8260 PLUS (cont.)	GROUNDWATER MDEQ Lab Reported Detection Limits (ug/l)	SEDIMENT/ SOILS MDEQ Lab Reported Detection Limits (ug/kg)	EPA ANALYTICAL METHOD SW-846	MDEQ TECHNIQUE
1,1,1,2 - Tetrachloroethane	1	100.0	624/8260	8260 +
1,1,2,2-Tetrachloroethane	1	100.0	624/8260	8260 +
Tetrachloroethene	1	50.0	624/8260	8260 +
Toluene	1	50.0	624/8260	8260 +
1,1,1-Trichloroethane	1	50.0	624/8260	8260 +
1,2,4-Trichlorobenzene	5	250.0	624/8260	8260 +
1,1,2-Trichloroethane	1	50.0	624/8260	8260 +
Trichloroethene	1	50.0	624/8260	8260 +
Trichlorofluoromethane	5	250.0	624/8260	8260 +
1,2,3-Trichloropropane	1	100.0	624/8260	8260 +
1,2,4-Trimethylbenzene	1	100.0	624/8260	8260 +
1,3,5-Trimethylbenzene	1	100.0	624/8260	8260 +
Vinyl Chloride	5	100.0	624/8260	8260 +
o-Xylene	1	50.0	624/8260	8260 +
m & p-Xylene	2	100.0	624/8260	8260 +

* Indicates semiquantitative analysis   ( ) = Detection limit dependent upon laboratory background level

PHENOLS SCAN 8	GROUNDWATER MDEQ Lab Reported Detection Limits (ug/l)	SEDIMENT/ SOILS MDEQ Lab Reported Detection Limits (ug/kg)	EPA ANALYTICAL METHOD SW-846	MDEQ TECHNIQUE
2-Chlorophenol	10		625/8270	Scan 8
4-Chloro-3-methylphenol	10		625/8270	Scan 8
M-Cresol & P-Cresol	20		625/8270	Scan 8
O-Cresol	10		625/8270	Scan 8
2,4-Dichlorophenol	10		625/8270	Scan 8
2,4-Dimethylphenol	10		625/8270	Scan 8
2,4-Dinitrophenol	50		625/8270	Scan 8
2-Methyl-4,6-dinitrophenol	50		625/8270	Scan 8
2-Nitrophenol	10		625/8270	Scan 8
4-Nitrophenol	50		625/8270	Scan 8
Pentachlorophenol	50		625/8270	Scan 8
Phenol	10		625/8270	Scan 8
2,4,5-Trichlorophenol	10		625/8270	Scan 8
2,4,6-Trichlorophenol	10		625/8270	Scan 8

CHLORINATED HYDROCARBONS SCAN 3/BASE NEUTRAL	GROUNDWATER MDEQ Lab Reported Detection Limits (ug/l)	SEDIMENT/ SOILS MDEQ Lab Reported Detection Limits (ug/kg)	EPA ANALYTICAL METHOD SW-846	MDEQ TECHNIQUE
2-Chloronaphthalene		200	625/8270	B/N
	0.2		612/8121	Scan 3
1,2-Dichlorobenzene	1.0	100	625/8270	B/N
	1.0	100	8260	8260
1,3-Dichlorobenzene	1.0	100	625/8270	B/N
	1.0	100	8260	8260
1,4-Dichlorobenzene	1.0	100	625/8270	B/N
	1.0	100	8260	8260
Hexachlorobenzene	0.02	50	612/8121	Scan 3
Hexachlorobutadiene	0.02	50	612/8121	Scan 3
Hexachlorocyclopentadiene		2000	625/8270	B/N
	0.02		612/8121	Scan 3
Hexachloroethane	0.02	50	612/8121	Scan 3
1,2,4-Trichlorobenzene		200	625/8270	B/N
	0.02		612/8121	Scan 3

HALOETHERS BASE/NEUTRAL	GROUNDWATER MDEQ Lab Reported Detection Limits (ug/l)	SEDIMENT/ SOILS MDEQ Lab Reported Detection Limits (ug/kg)	EPA ANALYTICAL METHOD SW-846	MDEQ TECHNIQUE
Bis(2-chloroethyl)ether	1.0	100	625/8270	B/N
Bis(2-chloroethoxy) methane	2.0	200	625/8270	B/N
Bis(2-chloroisopropyl) ether	1.0	100	625/8270	B/N
4-Bromodiphenylether	2.0	200	625/8270	B/N
4-Chlorodiphenylether	1.0	100	625/8270	B/N

NITROSAMINES BASE/NEUTRAL	GROUNDWATER MDEQ Lab Reported Detection Limits (ug/l)	SEDIMENT/ SOILS MDEQ Lab Reported Detection Limits (ug/kg)	EPA ANALYTICAL METHOD SW-846	MDEQ TECHNIQUE
N-Nitrosodiphenylamine	2.0	200	625/8270	B/N
N-Nitroso-di-n-propylamine	2.0	200	625/8270	B/N
1,2-Diphenylhydrazine	2.0	200	625/8270	B/N
2,4-Dinitrotoluene	5.0	500	625/8270	B/N
2,6-Dinitrotoluene	5.0	500	625/8270	B/N
Isophorone	1.0	100	625/8270	B/N
Nitrobenzene	2.0	200	625/8270	B/N

PHTHALATES BASE/NEUTRAL	GROUNDWATER MDEQ Lab Reported Detection Limits (ug/l)	SEDIMENT/ SOILS MDEQ Lab Reported Detection Limits (ug/kg)	EPA ANALYTICAL METHOD SW-846	MDEQ TECHNIQUE
Bis(2-ethylhexyl) phthalate	2.0	200	625/8270	B/N
Butyl benzyl phthalate	1.0	100	625/8270	B/N
Di-n-butyl phthalate	1.0	100	625/8270	B/N
Diethyl phthalate	1.0	100	625/8270	B/N
Dimethyl phthalate	2.0	200	625/8270	B/N
Di-n-octyl phthalate	2.0	200	625/8270	B/N

POLYNUCLEAR AROMATIC HYDROCARBONS BASE/NEUTRAL	GROUNDWATER MDEQ Lab Reported Detection Limits (ug/l)	SEDIMENT/ SOILS MDEQ Lab Reported Detection Limits (ug/kg)	EPA ANALYTICAL METHOD SW-846	MDEQ TECHNIQUE
Acenaphthene	1.0	100	625/8270	B/N
Acenaphthylene	1.0	100	625/8270	B/N
Anthracene	1.0	100	625/8270	B/N
Benzo(a)anthracene	1.0	100	625/8270	B/N
Benzo(b)fluoranthene	2.0	200	625/8270	B/N
Benzo(k)fluoranthene	2.0	200	625/8270	B/N
Benzo(a)pyrene	2.0	200	625/8270	B/N
Benzo(g,h,i)perylene	2.0	200	625/8270	B/N
Chrysene	1.0	100	625/8270	B/N
Dibenzo(a,h)anthracene	1.0	200	625/8270	B/N
Fluoranthene	1.0	100	625/8270	B/N
Fluorene	1.0	100	625/8270	B/N
Indeno(1,2,3-c,d)pyrene	1.0	200	625/8270	B/N
Naphthalene	1.0	100	625/8270	B/N
Phenanthrene	1.0	100	625/8270	B/N
Pyrene	1.0	100	625/8270	B/N

PCB's PESTICIDES SCAN 3		GROUNDWATER MDEQ Lab Reported Detection Limits (ug/l)	SEDIMENT/ SOILS MDEQ Lab Reported Detection Limits (ug/kg)	EPA ANALYTICAL METHOD SW-846	MDEQ TECHNIQUE
Aldrin		0.02	50	608/8081	Scan 3
a-BHC		0.02		608/8081	Scan 3
b-BHC		0.02		608/8081	Scan 3
d-BHC		0.02		608/8081	Scan 3
g-BHC (Lindane)		0.02	50	608/8081	Scan 3
BP-6 (PBB)		0.1	250	608/8081	Scan 3
a-Chlordane		0.02	50	608/8081	Scan 3
g-Chlordane		0.02	50	608/8081	Scan 3
4,4'-DDD		0.1	50	608/8081	Scan 3
4,4'-DDE		0.02	50	608/8081	Scan 3
4,4'-DDT		0.02	50	608/8081	Scan 3
Dieldrin		0.02		608/8081	Scan 3
Endosulfan I		0.02		608/8081	Scan 3
Endrin		0.02		608/8081	Scan 3
Heptachlor		0.02	50	608/8081	Scan 3
Heptachlor epoxide		0.02	50	608/8081	Scan 3
Hexabromobenzene		0.02	100	608/8081	Scan 3
Methoxychlor		0.1		608/8081	Scan 3
Mirex		0.2	50	608/8081	Scan 3
PCB 1016	*	0.2	500	608/8081	Scan 3
PCB 1221	*	0.2	500	608/8081	Scan 3
PCB 1232	*	0.2	500	608/8081	Scan 3
PCB 1242		0.2	500	608/8081	Scan 3
PCB 1248	*	0.2	500	608/8081	Scan 3
PCB 1254		0.2	500	608/8081	Scan 3
PCB 1260		0.2	500	608/8081	Scan 3
PCB 1262	*	0.2	500	608/8081	Scan 3
PCB 1268	*	0.2	500	608/8081	Scan 3
Pentachlorobenzene		0.02		612/8121	Scan 3
Pentachloronitrobenzene		0.02	50	612/8121	Scan 3
Toxaphene	*	0.1	500	608/8081	Scan 3
1,2,3-Trichlorobenzene		0.02		8121	Scan 3
1,3,5-Trichlorobenzene		0.02		8121	Scan 3
1,2,3,4-Tetrachloro benzene		0.02		8121	Scan 3
1,2,4,5-Tetrachloro benzene		0.02		8121	Scan 3

* Estimated RDL

Volatile 624/8260: Purge and Trap with high resolution capillary gas chromatography with mass spectrometry detection
Scan 3: Dual column high resolution capillary gas chromatography with dual electron capture detectors
Scan 8: High resolution capillary gas chromatography with mass spectrometry detection
B/N: High resolution capillary gas chromatography with mass spectrometry detection

METALS	GROUNDWATER MDEQ Lab Reported Detection Limits (ug/l)	SEDIMENT/ SOILS MDEQ Lab Reported Detection Limits (ug/kg)	EPA ANALYTICAL METHOD SW-846	MDEQ TECHNIQUE
Aluminum	50.0	5000.0	200.7/6010	ICP
Antimony	1		204.1/7040	Hydride
Arsenic		500.0	206.3/7061	Hydride
Arsenic	1		206.2/7060	Furnace
Barium	5.0	1000.0	200.7/6010	ICP
Beryllium	1	200.0	200.7/6010	ICP
Boron	20.0		200.7/6010	ICP
Cadmium		500.0	200.7/6010	ICP
Cadmium	0.2+		213.2	Furnace
Calcium	1000.0	50000.0	215.1/7140	At. Abs.
Chromium		2000.0	200.7/6010	ICP
Chromium	1		218.2	Furnace
Chromium VI	5.0		7196	DPC
Cobalt	2.0		219.2	Furnace
Cobalt		5000.0	200.7/6010	ICP
Copper		1000.0	200.7/6010	ICP
Copper	1		220.2	Furnace
Iron	20.0	2500.0	200.7/6010	ICP
Lead	1		239.2	Furnace
Lithium		2000.0	317 B *	Furnace
Lithium	8.0			ICP
Magnesium	1000.0	50000.0	242.1/7450	At. Abs.
Manganese	5.0	1000.0	200.7/6010	ICP
Mercury	0.2	100.0	245.1/7470, 7471	At. Abs.
Molybdenum	25.0	5000.0	200.7/6010	ICP
Nickel		5000.0	200.7/6010	ICP
Nickel	2.0		249.2	Furnace
Potassium	100.0	5000.0	258.1/7610	At. Em.
Selenium	1	500.0	270.3/7740	Hydride
Silver	0.5+	250	272.2	Furnace
Sodium	1000.0	50000.0	273.1/7770	At. Abs.
Titanium	10.0	1000.0	200.7/6010	ICP
Thallium	2		272.2	Furnace
Vanadium	10.0	1000.0	200.7/6010	ICP
Zinc	4.0	1000.0	200.7/6010	ICP

* Standard Methods For the Examination of Water and Wastewater
At. Abs. = Atomic Absorption Spectroscopy
At. Em. = Atomic Emission Spectroscopy
ICP = Argon Plasma Emission Spectroscopy
DPC = Diphenylcarbazide
\+ = Matrix Dependent
@ = Cold Vapor

NON-METALS	GROUNDWATER MDEQ Lab Reported Detection Limits (ug/l)	EPA ANALYTICAL METHOD OR SW-846	MDEQ TECHNIQUE
Alkalinity	20000.0	310.1	Auto Analyzer
Alkalinity, Bicarbonate	10000	Calculate	
Alkalinity, Carbonate	10000.0	Calculate	
Ammonia	10.0	350.1	Auto Phenolate
BOD-Carb.	2000.0	405.1	5 Day-DO Probe
BOD-Total	2000.0	405.1	5 Day-DO Probe
Chloride	1000.0	325	Auto Analyzer
COD (High Level)	10000.0	410	Titrimetric
COD (low level)	5000.0	410	Colorimetric Bridge
Cyanide	5.0	335.2/9010	Man Dist, Man PBA Color
Dissolved Oxygen	100.0	360.2	Manual Titration
Hardness (Ca2CO3)	5000.0	130.2	Calculate
Nitrate + Nitrite	10.0	353.2	Auto CD Reduction
Nitrite	10.0	353.2	Auto Diazotization
Nitrogen, Kjeldahl	100.0	351.2	BD, Auto Salicylate
OrthoP	10.0	365	Auto Ascorbic Acid Reduction
Phenolics	1.0	420.2	Auto Dist., Auto 4AAP
Phenolics	10.0	420.2/9066	Manual Dist., Auto 4AAP
Phosphorous, Total	10.0	365.4	BD, Auto Ascorbic Acid Reduction
Residue	20000.0	160.1	Total Filt-TDS 180C
Residue	4000.0	160.2	Non Filt-Susp. Sol. 105C
Silicates	50.0	370.1	Auto Ascorbic Acid Reduction
Sulfate	2000.0	375.4	AutoAnalyzer
TOC	500.0	415.1	UV/Persulfate (DC-80)
Turbidity	0.40 #	180.1	Turbidimeter

* = umhos/cm
\# = NTU

4AAP	= 4 Amino Antipyrene		
Bridge	= Conductivity meter	BOD	= Biochemical Oxygen Demand
DO Probe	= Dissolved Oxygen (YSI) Probe	COD	= Chemical Oxygen Demand
CD Reduc.	= Cadmium Reduction	TOC	= Total Organic Carbon
BD	= Block Digester	TDS	= Total Dissolved Solids
Man. Dist.	= Manual Distillation	Auto Dist.	= Automated Distillation
Calculate	= Value is calculated from existing data		

POLICY AND PROCEDURES FOR SUBMITTING CONFIDENTIAL INFORMATION

Michigan Department of Environmental Quality
Water Bureau – Permits Section
Groundwater Permits Unit

A request for confidential handling of material must be accompanied with a demonstration that the information qualifies for exemption from public disclosure in accordance with Section 13 of 1976 PA 442 and Part 31 Section 11 of 1994 PA 451, as amended. The specific language from these statutes is provided below.

Pursuant to Section 13 of 1976 PA 442, the Freedom of Information Act, "(1) A public body may exempt from disclosure as a public record under this Act:

(d) Records or information specifically described and exempted from disclosure by statute.

Part 31 Section 11 of 1994 PA 451, as amended, also indicates that, "The department shall provide proper and adequate facilities and procedures to safeguard the confidentiality of manufacturing proprietary processes except that confidentiality shall not extend to waste products discharged to the waters of the state."

Material received that is marked “Confidential - Attention Chief of the Groundwater Permits Unit” will be transmitted unopened to the Groundwater Permits Unit Chief. If it is determined that confidentiality be granted, the documents will be stamped "CONFIDENTIAL" in bold red letters. A letter that acknowledges receipt of the information and confidentiality will be transmitted to the sender. The existence of this material will be noted in a nonconfidential file using a tracking sheet and the restricted information then be placed in a locked file cabinet. Access to this file is through the Groundwater Permits Unit Secretary. All confidential information will be returned by certified mail 60 days following completion of the evaluation or final action on the permit application. If confidentiality cannot be granted, the material will be returned to the sender.

Form for Estimating Discharge Concentrations for Chemical Additives by Mass Balance – **Required pursuant to Rule 2220(4)**

MASS BALANCE CALCULATIONS

THE MASS BALANCE ESTIMATES MAY BE SENT DIRECTLY FROM THE PRODUCT SUPPLIER AS CONFIDENTIAL INFORMATION TO:

MICHIGAN DEPARTMENT OF ENVIRONMENTAL QUALITY
WATER BUREAU – PERMITS SECTION
GROUNDWATER PERMITS UNIT
PO BOX 30458
LANSING, MI 48909-7773
ATTENTION: GROUNDWATER PERMITS UNIT CHIEF

PLEASE INCLUDE THE NAME AND PHONE NUMBER OF THE CONTACT PERSON WHO COMPLETED THE MASS BALANCE ESTIMATES.

PRODUCT (One form per product)

Product Specific Gravity (PSG): Property of the liquid product, can usually be found on MSDS sheet (sp. gr. or d.). May also be determined by weight per volume of the product and dividing by the weight per volume for water (8.34 pounds/gallon or 3.785 kilograms/gallon).

Product Annual Use Rate: **The amount of product used per year, either in gallons per year for liquids or pounds per year for solids, and kilograms per year for solids and liquids.**

Product Annual Use Rate – Metric Conversion: To calculate kilograms per year for solids, multiply the pounds per year by 0.4536. To calculate kilograms per year for liquids, multiply gallons per year times specific gravity times 3.785 kilograms per gallon (Gal/year x PSG x 3.785).

Product Mass Balance Concentration:

The calculated concentration of a product, or its ingredients, present in a discharge of a given volume. First, calculate the product **mass balance concentration. Mass balance concentration is calculated by dividing Kilograms per year by the annual volume of the discharge, in millions of liters. (kilograms per year / Million liters per year).**

INGREDIENTS (one or more within each product)

CAS #: The Chemical Abstract Service Registry number must be provided as a unique identifier of the chemical.

Fractional Content by Weight (FCW): Percent of ingredient present divided by 100. If Ingredient #1 is 5 percent of the product mixture, then the FCW is 5/100 = 0.05

Ingredient Mass Balance

Concentration: To calculate the ingredient mass balance concentration, multiply the product mass balance concentration by the fractional content by weight. (Product Mass Balance Concentration x Fractional Content by Weight)

NOTE: If the same ingredient is found in more than one product that is included in the discharge, the Mass Balance Concentration should be summed for each occurrence of the ingredient, and listed as the total Mass Balance Concentration for that ingredient. The best identifier for a chemical ingredient is the CAS #.

Form for Estimating Discharge Concentrations for Chemical Additives by Mass Balance – **Required pursuant to Rule 2220(4)**

EXAMPLE CALCULATIONS ***(equation used – see page 24 for explanation)***

Facility Name: XYZ Company **Facility ID #: GW0000050** **Date: 12/12/98**
Contact Person: Joe Chemiste, ChemCorp **Phone #: 1-800-888-8888**

Average Annual Discharge Volume: 10 Million Gallons Per Year
37.85 Million Liters Per Year

Product Name		**Product Specific Gravity (PSG) (Liquids only)**	**Product Annual Use Rate Liquid (gal/year) Solid (lbs/year)**	**Product Annual Use Rate Metric Conversion (kgs/year)**	**Product Mass Balance Concentration (PMBC, mg/l)**
SOLID **Product 1 – A B Additive**			**100 lbs/year**	**45.36** ***(100 x .4536)***	**1.20** ***(45.36/37.85)***
Ingredient Name	**CAS #**	**Fractional Content by Weight (FCW)**			**Ingredient Mass Balance Concentration (IMBC, mg/l)**
Ingredient 1a	**0000-00-1**	**0.5**			**0.60** ***(.5 x 1.2)***
Ingredient 1b	**0000-00-2**	**0.3**			**0.36** ***(.3 x 1.2)***
Ingredient 1c	**0000-00-3**	**0.2**			**0.24** ***(.2 x 1.2)***

Product Name		**Product Specific Gravity (PSG) (Liquids only)**	**Product Annual Use Rate Liquid (gal/year) Solid (lbs/year)**	**Product Annual Use Rate Metric Conversion (kgs/year)**	**Product Mass Balance Concentration (PMBC, mg/l)**
LIQUID **Product 2 – 1234 Cleaning Product**		**1.1**	**100**	**416.35** ***(1.1 X 100 X3.785)***	**11.00** **(*416.35 / 37.85)***
Ingredient Name	**CAS #**	**Fractional Content by Weight (FCW)**			**Ingredient Mass Balance Concentration (IMBC, mg/l)**
Water	**7732-18-5**	**0.5**			**5.50** ***(.5 x 11)***
Ingredient 2a	**0000-00-2**	**0.25**			**2.75** ***(.25 X 11)***
Ingredient 2b	**0000-00-4**	**0.15**			**1.65** ***(.15 X 11)***

Total for Ingredient 1b and 2a	**0000-00-2**				3.11 TOTAL (.36 + 2.75 = 3.11)

Form for Estimating Discharge Concentrations for Chemical Additives by Mass Balance - **Required pursuant to Rule 2220(4)**

Use one form for each product.

Facility Name:	**Facility ID #:**	**Date:**
Contact Person:	**Phone #:**	
Average Annual Wastewater Volume (million gallons **per year):**	**Million Gallons Per Year**	
Average Annual Wastewater Volume (million liters **per year):**	**(Million Gallons Per Year x 3.785 liters per gallon)**	

Product Name		**Product Specific Gravity (PSG) (Liquids only)**	**Product Annual Use Rate Liquid (gal/year) Solid (lbs/year)**	**Product Annual Use Rate Metric Conversion (kgs/year)**	**Product Mass Balance Concentration (PMBC, mg/l)**
Ingredient Name	**CAS #**	**Fractional Content by Weight (FCW)**			**Ingredient Mass Balance Concentration (IMBC, mg/l)**

Add as many rows/columns as necessary to provide data for all additives.

Note: Specific gravity is only required for **liquid products.**