

TCLP Characterization of Exploration and Production Wastes in Louisiana

Final Report to Louisiana Department of Natural Resources

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March 29, 1999



Rev:4/7/99

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Summary of Results and Recommendations

A review of the toxicity characteristic leaching procedure (TCLP) analyses conducted as part of the emergency waste profiling rules of the LA Department of Natural Resources (DNR) identified the following characteristics of exploration and production (E&P) wastes in Louisiana.

C No waste type shows concentrations of the inorganic constituents (arsenic, barium, chromium, cadmium, lead, mercury, selenium and silver) in excess of the EPA TCLP standard for non-exempt waste in any but a small number of the samples. Although not directly applicable to E&P waste, the EPA standard is used here as a reference concentration level. There were a total of 669 waste batches that were statistically evaluated and each batch was analyzed for the eight aforelisted inorganic constituents giving a total of 5352 analyses used in the computations. Of these, 5,312 (99.3%) did not exceed the TCLP reference concentration for any of the eight constituents. There were only 40 instances for which the constituent concentration exceeded the TCLP reference concentration. These were distributed as follows:

Arsenic - 3 samples; Barium - 10; Cadmium - 2; Chromium - 7; Lead - 9;

Mercury - none; Selenium - 8 and Silver - 1 sample

For each element in each waste type the geometric mean and median concentrations are substantially below the TCLP reference concentration for that element. The details by waste type for these inorganic elements are given in Table 3 through Table 10 at the end of the report.

C Analyses from 1146 validated batches (out of a total of 2185) for the organic constituent, benzene, are summarized in Tables 2 and 11 at the end of the report. The probability of observing any particular benzene concentration in a waste type was well-represented by a log-normal probability distribution function. This suggests that the most likely observed concentration is the geometric mean of concentration measured in the samples of that waste type. Algebraic means and standard deviations are biased by a small number of large concentration values.

To simplify the presentation of the findings on benzene, the waste types have been divided into four classes. These are:

A - benzene concentration never or rarely in excess of 0.5 mg/L

Codes - 02, 03, 09 and 16

B - benzene concentration in excess of 0.5 mg/L in between 10 - 30% of samples

Codes - 01, 04, 05 and 11

C - benzene concentration in excess of 0.5mg/L in more than 30% of samples

Codes - 06, 07, 12, 13 and 14

D - low concentrations but insufficient samples for reliability

Codes - 08, 10, 15 and 99

Class A : Oil and water-based drilling muds (codes 02 and 03, respectively) and crude oil spill cleanup waste (code 16) exhibit most probable concentrations (medians and geometric means) that are about 10 times lower than the TCLP reference level for benzene (0.5 mg/L). These waste types constituted about 15.6% of the total E&P waste treated in commercial facilities in 1998. The occasional observations of levels in excess of 0.5mg/L for drilling muds are sufficiently rare that they are likely the result of mixing more contaminated wastes with the oil and water-based muds or inappropriate operations. Minor modifications in operating procedures or handling to insure segregation from more contaminated wastes would likely eliminate the few samples in excess of the TCLP reference concentration.

Rainwater from ring levees and pits (waste code 09) exhibited no samples that exceeded the TCLP reference concentration and the arithmetic and geometric means were both more than 2 orders of magnitude less than the reference (0.0032 and 0.0027 mg/L, respectively). Although the number of validated samples was small (7), there is no evidence that there is any significant benzene contamination in these wastes.

Class B: Waste codes 01 (produced salt water), 04 (workover/completion fluids), 05 (production pit sludge) and 11 (washout pit water) exhibited benzene concentrations in excess of 0.5 mg/L between 10 and 30% of the time. The waste types constituted about 63.2% of the total E&P wastes generated in 1998. Produced saltwater is currently deep-well injected and therefore does not pose a surface exposure risk. The median and geometric mean concentrations for waste

codes 04, 05 and 11 are substantially less than the TCLP reference concentration. A mixture of these wastes with those identified in class A would therefore be expected to contain significantly lower benzene levels than the TCLP reference concentration.

Class C: Waste codes 06 (production tank sludge), 12 (gas plant processing waste), 13 (BS and W waste) and 14 (pipeline test water) all exhibit a geometric mean or median benzene concentration in excess of the TCLP reference level. While only 4 waste code 12 samples were validated, the concentrations of benzene were sufficiently high to conclude that these wastes often contain benzene concentrations in excess of 0.5 mg/L. In addition, waste code 07 (produced sands/solids) exhibits benzene concentrations in excess of the TCLP reference level in more than 33% of the samples. The volume of waste codes 06, 07, 12, 13, and 14 was only about 3.8% of the total E&P wastes treated in commercial facilities in 1998. Pipeline water is currently deep-well injected and therefore does not pose a surface exposure risk. If a risk assessment indicates that current handling of these waste types involves potential risk, then special handling or treatment may be necessary. Steps that would need to be taken could vary from tracking the wastes to insure they are not concentrated in a single cell or land treatment facility to specific treatment of the waste.

Class D: All remaining waste categories (08 - produced fresh water, 10 - washout water, 15 - treatment facility wastes, and 99 - other wastes) exhibited no more than 1 sample having a benzene concentration greater than the TCLP reference level of 0.5 mg/L

and, except for waste code 15, both their arithmetic and geometric means were below the TCLP reference concentration. However, the number of validated samples was insufficient to demonstrate that the observed difference between the mean concentrations and the TCLP reference concentration were statistically significant. If additional samples continue the trends observed during the testing program, these waste types would be expected to contain benzene at levels and frequencies similar to those wastes identified as Class B above. These wastes constituted a total of about 9.3% of the E&P wastes generated in 1998, primarily due to washout water constituting 7.7% of the total wastes.

It should be noted that washout water (waste code 10) would normally reflect the composition of the waste being washed and therefore it is not meaningful to define its characteristics as though it were a unique waste type. Washout water should, in general, be handled in the same manner as the wastes with which it comes in contact.

C A volume averaged benzene concentration was calculated to attempt to define the characteristics of a representative mixed waste. The most probable benzene concentration for each waste type (the geometric mean) was weighted with the volume of that waste type treated in commercial facilities during 1998. This calculates the geometric mean of the volume weighted concentrations. The volume weighted benzene concentration calculated in this manner for all classes of wastes was 0.299 mg/L. More than half of the benzene in this estimate of the volume weighted geometric mean comes from the single

waste code 12, which is based upon a small number of samples and therefore subject to significant uncertainty. A volume weighted mixture of Class A, B and D wastes (excluding all of Class C and the currently injected waste 01), would exhibit a geometric mean benzene concentration of 0.062 mg/L, approximately 8 times lower than the TCLP reference level. The volume weighted geometric mean of just waste codes 02, 03, 04, 05, 09 and 11 (i.e. Class A and B wastes) is 0.039 mg/L, almost 13 times lower than the TCLP reference.

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1.0. Introduction/Objectives :

The exploration and production (E & P) of oil and gas is integral to the development and economic well-being of the State of Louisiana. The technical aspects of extracting oil and gas from the subsurface environment necessarily leads to the production of large quantities of waste by-products. These wastes fall into three broad categories: produced water, drilling fluids and cuttings, and associated wastes. In 1986, the United States Environmental Protection Agency classified these wastes as non-hazardous and certified them to be exempt from the Resource Conservation and Recovery Act (RCRA) provisions. Therefore the regulation and disposal of the E&P waste was placed under the jurisdiction of the responsible States.

In Louisiana, the Department of Natural Resources (DNR) manages and oversees the disposal of E&P waste. Under the Louisiana Administrative Code Title 43 Part XIX, Statewide Order No. 29B set forth the rules and regulations to be followed in treating E&P wastes in Louisiana. Statewide Order No. 29B was last modified in December 1990. In 1998, the Commissioner of Conservation promulgated an Emergency Rule that required a waste profile analysis of E&P waste prior to shipment to a commercial facility and waste verification testing upon receipt by a commercial facility. This Emergency Rule was adopted to further protect the public health, safety and welfare of the people of the State of Louisiana. The Louisiana State University (LSU) was contracted by DNR to advise on appropriate methodologies of testing, validate the experimental data collected during the Emergency Rule period, conduct statistical analysis of the data , and to suggest possible treatment alternatives.

This report summarizes the efforts undertaken by LSU to validate the experimental data and statistically evaluate the concentrations of various constituents within each waste category

identified by DNR. It is expected that this information will be used by DNR and other contractors to determine the potential hazards associated with the E&P wastes and the need for and the nature of any revisions to existing E&P waste handling rules.

The analyses required of E&P wastes under the emergency rule included toxicity characteristic leaching procedure (TCLP) analyses for a variety of metals and the organic compound, benzene, and volatile screening analyses for detecting benzene and total volatile organic compounds. The current report will summarize only the results of the TCLP testing. The screening for volatiles will require detailed further analysis before recommendations can be made on the quality and effectiveness of such screening.

TCLP analyses are commonly used to indicate whether certain wastes should be handled as hazardous wastes. As indicated above, E&P wastes are specifically excluded from these hazardous waste rules but the constituent concentration levels that identify hazardous wastes can be used as a reference to compare to the levels of these constituents in the E&P wastes. Throughout this report, TCLP regulatory limits are used as such a reference but it should be recognized that these are not applicable to E&P waste nor do they provide a direct indication of the risks posed by E&P wastes. At best, the TCLP provides some indication of the mobility of the specific contaminants for leaching into groundwater and it is not possible to directly infer concentrations in the air or other media that might result from treatment of these wastes.

2.0 E&P Waste Testing and Reporting:

2.1. Categories of E&P Waste:

The various types of wastes generated during E&P activities and disposed of at offsite facilities were classified by DNR into specific categories as shown below with their fraction of the total volume generated during 1998:

<u>Waste</u>	<u>Waste Type/ Description</u>	<u>Volume Fraction(1998)</u>
01	Salt water (produced brine)	59.8%
02	Oil base mud / cuttings	3.7%
03	Water base mud / cuttings	11.8%
04	Workover / completion fluids	1.8%
05	Production pit sludge	1.0%
06	Production tank sludge	0.9%
07	Produced sand / solids	0.6%
08	Produced formation fresh water	0.1%
09	Rainwater - ring levees / pits	7.4%
10	Washout water	7.7%
11	Washout pit water	0.6%
12	Gas plant processing waste	0.5%
13	BS&W waste - commercial salvage oil operators	0.2%
14	Pipeline test water / Pipeline pig water	1.6%
15	E& P waste generated by commercial facilities	1.7%
16	Crude oil spill clean-up waste	0.1%
99	UIC - 23 approved waste (other)	0.2%
TOTAL VOLUME - 1998		19,251,893 Barrels

Note that there were insufficient samples to fully characterize some of these waste types as outlined later in this report. In addition, waste code 10 is wash water whose characteristics would be defined by the material being washed. A similar concern could be raised for waste codes 11 and 14. Characterization information is most useful for waste codes 01-07 which are clearly defined and identifiable and for which a large number of samples exist.

2.2 E&P Waste Testing Requirements:

The Emergency Rule specified testing procedures for each of the above classes of E&P waste. These included general tests such as pH, conductivity, chloride, oil and grease, total sulfide and reactive sulfides. In addition the Rule also required that each waste must be analyzed by the Toxicity Characteristic Leaching Procedure (TCLP) for the following volatiles: benzene, toluene, ethyl benzene and xylene. In addition, TCLP tests were also required for the following metals: arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver. TCLP samples were to be analyzed for organics and metals according to approved standard methods (EPA Test Methods for Evaluating Solid Waste, SW 846, Third Edition, Revised 12/96 or latest revision). A waste profile (Form UIC-28) was to accompany each E&P waste shipping unit to a commercial facility. The UIC-28 along with the summary information for an entire batch, the UIC-35, were to accompany the laboratory reports to be submitted to the Office of Conservation (OC) by the generator or commercial facility operator.

2.3. Data Collection and Reporting:

All data were transmitted to DNR by the generators or commercial facility operators, and then copied to LSU. Forms UIC - 35, UIC - 28 , chain-of-custody, laboratory results and quality assurance/quality control (QA/QC) documents were provided to LSU. The validation of the data, the statistical analysis and the generation of this report were completed within 90 days from receipt of the last of the laboratory data packages.

3.0. Data Validation and Statistical Analysis:

3.1. Data Validation:

In order to ascertain the validity of the data that was collected and reported, LSU performed a detailed data validation. This entailed answering the following questions for the data generated for each test batch:

- (a) Are laboratory results reported? Samples are not counted as validated for a particular constituent unless an analysis was conducted and results reported for that constituent.
- (b) Does a UIC-35 or UIC-28 form accompany laboratory results?
- (c) Is there agreement between the batch number on the generator's UIC -35 or UIC-28 form and that on the laboratory results data sheet or is there another means of tying the laboratory data sheet to that waste batch?
- (d) Is there agreement between the sample waste category as defined on the forms accompanying the sample (UIC 35 or UIC-28 and the Chain-of-Custody form, if available)? Errors or indications of multiple waste types were occasionally observed in the UIC-35, UIC-28 or in the chain of custody. If the UIC-28 reflecting the particular load that was sampled for TCLP showed a single or majority of a single waste code with wash or rinse water (typically waste code 10), the waste was assumed to reflect the predominant waste code. If mixed with a waste code other than wash water or with a volume of wash water that exceeded the primary waste volume, the waste was treated as a mixed waste and ruled invalid.

- (e) Does the sample holding time (between the sampling time and date of analysis) conform to EPA standard methods? This is 14 days for benzene and other volatiles.
- (f) Does the method specified agree with the standard method in 29-B?
- (g) Is the matrix spike recovery criteria as specified by EPA standard methods?
- (h) Is a method blank specified and does it meet expected criteria?
- (i) Is the minimum detection limit at or below the TCLP standards for benzene and metals for hazardous wastes?

If the answers to all of the above questions were “yes”, the data for that batch was considered “valid”. All other data were termed “invalid”. Note that validation is largely defined by benzene criteria in that holding times and detection limits are generally limited by that constituent. Additional valid samples could be used in the characterization for metals and inorganic constituents but it was felt that validation on the basis of individual constituents was unnecessary. As will be seen, very few inorganic constituents were ever present at levels approaching or exceeding TCLP reference limits.

Of a total of 2185 unique batches in the LSU database, 1146 or 52.4% were validated for benzene. It must be remembered that the expected use of the data was to define the statistical characteristics of a particular waste type and not to identify particular problem waste batches. The listed criteria means that some of the data might be identified as valid even though certain errors may be present in the supporting paperwork. For example, errors in the UIC-35 may be disregarded if there were sufficient contrary information in the chain of custody or UIC-28 paperwork to define the waste type and sample handling sufficiently. The criteria were selected to

ensure that the waste type and sample handling procedures were valid based upon the preponderance of the evidence presented.

As indicated previously, only about half of the samples met data validation requirements.

This low validation rate was due to a combination of factors including:

1. The significant change in requirements of this program relative to previous E&P testing required improved operator/analyst sample handling and training which took time to implement.

2. Changes in the data documentation requirements midway through the emergency rule testing program resulting in insufficient validation information on many early data packages

3. The large number of samples, extensive documentation, and the transmission through various offices led to some recording errors, delays and lost documentation

4. Inadequate segregation of various waste types led to invalidation of some waste batches. Segregation of E&P waste types is not normally required but needed for this program in order to characterize specific waste types.

5. Analysis for certain constituents was not required of all waste types. Since these were handled as missing data in the database, they artificially increase the fraction of invalidated data for these constituents.

6. No attempt was made to validate metal and inorganic sample analyses if the benzene analysis was invalidated. This was because sufficient inorganic analyses were available without the additional effort of validation on a constituent by constituent basis.

7. Conflicting waste codes or other batch information were sometimes unresolved leaving no clear identification for a particular sample result.

8. The remainder of the samples were invalidated on purely technical grounds including over the 14 day holding time required for benzene analysis or failure to meet matrix recovery criteria.

No differences were noted in the general trends exhibited by validated versus invalidated data. In addition, no samples from a particular generator or treatment facility was invalidated at a particular high rate. Samples analyzed by one laboratory were invalidated at a relatively high rate because their standard data package does not include the date of analysis making it impossible to determine if sample holding time criteria were met. Approximately 5% of the total number of samples were invalidated as a result of this problem. The wash water waste code (10) was also invalidated at an artificially high rate because this waste is normally mixed with other waste types and reflect the constituents of those waste types. The data for these mixtures is included in the analysis of the waste type being washed but invalidated in waste code 10, causing the artificially high invalidation rate in that waste code.

3.2. Statistical Analysis of Data:

Data that qualified as having being validated were used in the subsequent statistical analysis. Two separate statistical analyses were employed. In the first, the maximum, arithmetic mean, standard deviation, geometric mean, and median of the concentrations observed in the validated data sets were evaluated for each waste type and constituent. For this analysis, all validated samples in which a particular constituent was reported as below detection limits were assumed to contain a level of one-half the reported detection limit. This approach associates below detection limit samples with a concentration equal to their expected average value.

In the second analysis, all measured concentration levels were fit to a log-normal probability distribution. In this analysis, non-detected concentrations are not explicitly considered except to reduce the probability of observing detectable concentrations. The fitted log-normal probability distribution can be used to predict the probability of observing any particular constituent concentration in that waste type.

In all cases described herein, the volumes of the various waste types were not considered in the characterization of a particular waste type. In particular, the concentrations associated with a small waste batch were treated identically to concentrations measured as part of a large waste batch. It may be useful to evaluate the statistics on a volume-weighted basis to provide a clearer picture of the true characteristics of a particular waste type. For the purposes of the current data, however, it must be remembered that the TCLP measurements reflect only the first load in a batch and that sometimes subsequent loads involved different waste types, different wastes or similar wastes but generated weeks and sometimes months after the first load. It is unclear whether the concentrations measured via the TCLP in that first load would appropriately represent these subsequent loads. The observed characteristics of the waste types, however, can be used with historical generation rates for that waste type to define volume-weighted loadings of mixtures.

The statistical measures generated from the raw (or non-volume-weighted) TCLP data are summarized below with brief explanations of the same:

(a) Maximum, Arithmetic Mean and Standard Deviation: This information provides an indication of the range of concentrations. The mean and standard deviation are of limited usefulness, however, because it is significantly skewed by small numbers of large concentration samples. If

the maximum value is more than 2 standard deviations larger than the average, it is an indication that the data are skewed and the calculated average is not useful.

(b) Geometric Mean: The geometric mean of a set of n positive numbers is the nth root of the product of the numbers. If the data are well-described by a log-normal distribution, as is often the case, the geometric mean represents the concentration most likely to be observed in a waste load.

(c) Median: The median is the middle value of the set of data. That is, one-half of the values exceed the median and one-half are less than the median. If a given data set follows a log normal probability distribution, the geometric mean and median will be identical. The median is superior to the arithmetic mean as a measure of the central tendency when the data are skewed.

In addition to the above measures of the data distribution, we have also provided the number and percentage of validated data points, and the number and percentage of the validated data that exceeded the TCLP reference concentration for each compound within each waste type. As indicated earlier, it should be remembered that the TCLP regulatory levels do not currently apply to E&P wastes and, in any event, these levels do not directly indicate levels that pose significant human and ecological risks. The translation of the observed statistical levels to risks is part of a separate evaluation being undertaken by the LA DNR.

4.0 Results and Discussion

Table 1 represents the TCLP regulatory levels set by the U.S. EPA for the compounds benzene, arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver for which TCLP data were collected as required by the Emergency Rule 29B. This table should serve as the reference for subsequent data presented in Tables 2-10.

Tables 2-10 represent all the relevant statistical information that we generated for each compound within each waste type. As suggested earlier, the geometric mean and median are the most useful in interpreting results. In addition the percentage of samples that exceeded the TCLP hazardous waste regulatory limit can be used as a reference to characterize waste types.

As shown by Tables 3-10, very few analyses of any waste type exhibited inorganic constituent concentrations that exceeded their respective TCLP reference levels. There was a total of only 40 individual samples (0.7%) out of 5352 individual inorganic constituent analyses in the validated samples that exceeded their respective reference limits. Further analysis is required to determine if even these occasional exceedances can be eliminated by changes in the manner that the waste is generated or managed. Based upon the low exceedance rate of the TCLP reference concentration, it is highly unlikely that any mixture of E&P wastes applied to a waste treatment cell would yield an average concentration in excess of TCLP limits.

Significantly more E&P waste samples exhibited benzene concentrations exceeding the TCLP reference level of 0.5 mg/L. Oil and water-based drilling muds (waste code 02 and 03), however, exhibit a geometric mean and median sample concentration that is about 10 times lower than the TCLP reference limit. Of 366 total validated samples in these two waste codes, only 16 (4%) indicated benzene concentrations in excess of the TCLP reference limit. As a result, it is unlikely that any mixture of a significant number of batches of oil and water based drilling muds would exceed TCLP reference concentrations. Further study is underway of the individual batches that exceeded the TCLP reference concentration. Given the rare nature of these occurrences it is likely that the exceedances represent non-representative batches that may involve undocumented mixing with other types of waste or may be correctable with avoidance of certain

operating procedures. It is hoped that the additional analyses will identify approaches to eliminating all exceedances of the TCLP reference concentration in these waste types.

Crude oil spill clean up wastes (Code 16) also exhibited a geometric mean approximately 10 times smaller than the TCLP reference concentration and only 1 (7.1% of the validated samples) exceeded the reference. Although the number of samples is small, there is no reason on the basis of the available data to treat waste code 16 in a manner other than oil and water based drilling muds.

Only a small number (7) of validated samples of waste code 09 (rainwater from ring levees and pits) were included in the study. None of the samples showed a benzene concentration more than 0.005 mg/L (i.e. 100 times less than the TCLP reference level), however, suggesting that this waste code is not significantly contaminated with benzene. Note, however, that one invalidated test batch was a mixture of waste codes 06 and 09 and contained benzene at a TCLP concentration of 250 mg/L. This example illustrates the need to segregate waste types if different treatment and/or disposal methods are envisioned as a result of the characterization provided by this study.

Certain waste types exhibit mean concentrations that exceed the TCLP reference limit of 0.5 mg/L for benzene. The arithmetic mean shows very large values for many waste types due to the bias introduced by one or two large values among a large number of small or non-detectable values. The geometric mean represents the most likely observed concentration for log-normally distributed data and the median represents the concentration for which half of the samples are higher and half are lower. Because these measures provide a better indication of the central tendency of the data, we will focus on them.

Waste codes 06 (production tank sludge), 07 (produced sands/solids), 12 (gas plant processing waste), 13 (BS&W waste) and 14 (pipeline test water) all exhibit exceedance of the TCLP reference limit of 0.5 mg/L in more than 1/3 of the samples or have a geometric mean or median in excess of the limit. This conclusion, however, is based on only 4 validated samples for waste code 12, which is insufficient to fully characterize the waste type. The concentration and percentage of batches that exceed 0.5 mg/L benzene suggests that these waste types may require segregation and alternative treatment, should it be determined that the benzene concentrations result in unacceptable risks to human and ecological health. As noted previously, the TCLP does not directly indicate the extent of these risks nor suggest that the waste types exhibiting higher benzene concentrations pose a risk. The level of risk associated with the particular waste types is to be assessed separately by LA DNR using the characterization data provided herein.

The geometric mean and median for the remaining waste types are less than the TCLP reference concentration and the percentage of failures of this standard are less than 1/3 of the samples or there are too few samples to reliably characterize the waste type. In addition, waste code 10, washout water, is essentially impossible to characterize since it is generally associated with other waste types and reflects the composition of those wastes. If wash water is reused, however, it is important to recognize that it may be as contaminated as the most contaminated of the wastes with which it comes in contact.

Two of the waste codes that have moderate benzene levels, waste codes 01 (produced saltwater) and 14 (pipeline test water), are transported in sealed systems and injected underground. Therefore the benzene levels that these wastes contain do not contribute to any surface environmental concerns.

Certain of the waste types (e.g. 6, 7, 12, and 13) are low volume wastes that may pose potential problems if disposed along with other low volume waste types. During our validation exercise we observed that in some instances wastes could not be attributed to a specific category since they were mixed and contained significant fractions of two or more waste types. As indicated previously, waste mixing should be avoided if particular waste types require segregation and alternative treatment. Note, however, that if a large volume of an innocuous waste (for example, water-based drilling mud) is mixed with a small volume of a waste type containing a higher level of benzene, the mixture is likely to meet the TCLP reference concentration. The acceptance of this as an initial dilution prior to treatment should be based upon protection of the human and ecological health. It may, however, prove viable to define relative cell loadings of various waste types such that the mixture within a cell is unlikely to exceed any arbitrary standard such as the TCLP reference concentrations.

Potentially more useful than the statistical parameters generated in Tables 3-10 is the concentration probability distributions generated for benzene in each waste type. These distributions represent fits to the log-normal probability distribution and give the probability of any particular benzene concentration for any waste type. Table 11 summarizes the statistics of the best fit log-normal distribution line. Included in the statistics is the correlation coefficient which indicates the percent of the variance described by the best-fit curve and the probability that a sample of each waste type will be greater than the TCLP reference value. Note that this probability will generally be different from the corresponding value presented in Table 2. This value represents a best-fit to the detectable benzene concentrations as opposed to simply the number of samples observed to fail this criteria as presented in Table 2.

Plots indicating this log normal fit were generated for each waste type and are included following Table 11. The plots were limited to the constituent benzene because it is only this constituent that provides any significant number of concentrations that are high relative to the TCLP reference level. The concentration of benzene is plotted on the horizontal axis of each plot and the probability of any particular sample having a concentration equal to or below that concentration is presented on the vertical axis. For reference the TCLP reference concentration of 0.5 mg/L is shown on each plot as a fine vertical line. The intersection of that reference line with the fitted log-normal distribution curve (solid line passing through the data) is the probability of any particular sample having a concentration equal to or less than the TCLP reference level. The 95% confidence limits for predicting probability given a concentration are shown as short dashed lines surrounding the best-fit curve. Note the fitted log-normal distribution plots as a straight line in the coordinates shown in the figures (logarithmic axis of concentrations and a normal probability axis in the vertical). All validated data for that waste type are also shown on the figure indicating the number of data points available to generate the best-fit line. The degree of scatter about the best-fit line also indicates the adequacy of a log-normal distribution fit as does the 95% confidence limits.

Although certain waste types were identified above as exhibiting higher benzene concentrations, it should be recognized that these waste types often represent only a small proportion of the total E&P waste generated. The majority of E&P wastes (~60%) is produced saltwater, which is deep-well injected, and a significant fraction of the remainder is oil and water based drilling muds which generally contain low levels of benzene. The typical waste that is treated at commercial waste treating facilities is a mixture of these with the low volume wastes

that may contain higher benzene levels. A volume averaged benzene concentration was calculated to attempt to define the characteristics of a representative mixed waste. The most probable benzene concentration for each waste type (the geometric mean) was weighted with the volume of that waste type treated in commercial facilities during 1998. This calculates the geometric mean of the volume weighted concentrations. The volume weighted benzene concentration calculated in this manner for all classes of wastes was 0.299 mg/L. More than half of the benzene in this estimate of the volume weighted geometric mean comes from the single waste code 12, which is based upon a small number of samples and therefore subject to significant uncertainty. The volume weighted geometric mean benzene concentration may therefore not be representative of the overall waste mixture. A volume weighted mixture of Class A, B and D wastes (excluding all of Class C, including waste code 12, and the currently injected waste, 01), would exhibit a geometric mean benzene concentration of 0.062 mg/L, approximately 8 times lower than the TCLP reference level. The volume weighted geometric mean of just waste codes 02, 03, 04, 05, 09 and 11 (i.e. Class A and B wastes) is 0.039 mg/L, almost 13 times lower than the TCLP reference.

Table 1. TCLP Characteristics and Regulatory Levels.

Compound	Regulatory Reference Level (mg/L in TCLP extract)
Benzene	0.5
Arsenic	5
Barium	100
Cadmium	1
Chromium	5
Lead	5
Mercury	0.2
Selenium	1
Silver	5

Table 2. Statistics for E & P Waste (TCLP data).**Compound : Benzene**

Waste Code	Total number of samples	Number validated (%)	Mean mg/L	Standard deviation mg/L	Maximum mg/L	Geometric mean mg/L	Median mg/L	Number of TCLP failures (%)	Remarks
01	112	61(54.5%)	2.83	12.64	90	0.16	0.13	18(29.5%)	
02	230	148(64.8%)	0.62	5.26	63.6	0.05	0.05	9(6.1%)	
03	392	218(55.6%)	5.5	74.6	1,100	0.04	0.05	7(3.2%)	
04	464	276(59.5%)	8.0	75.3	907	0.10	0.05	40(14.5%)	
05	39	20(51.3%)	0.67	1.69	7.3	0.12	0.05	5(25%)	
06	294	162(55.1%)	206	1,308	15,000	0.77	0.48	79(48.7%)	
07	278	150(53.9%)	33.2	235	2,500	0.27	0.19	55(36.7%)	
08	6	4(66.7%)	0.31	0.25	0.63	0.22	0.28	1(25%)	
09	22	7(31.8%)	0.0032	0.0017	0.005	0.0027	0.004	0(0%)	
10	242	5(2.1%)	0.20	0.28	0.7	0.087	0.118	1(20%)	
11	75	44(58.7%)	0.96	4.31	28.3	0.07	0.05	6(13.6%)	
12	9	4(44.4%)	684	1,317	2,660	31	37	3(75%)	
13	29	12(41.4%)	10.8	25.1	88.8	1.1	1.5	8(66.7%)	
14	18	11(61.1%)	4.4	5.7	16.6	0.9	2.0	8(72.7%)	
15	3	2(66.7%)	1.3	1.8	2.6	0.3	1.3	1(50%)	
16	19	14(73.7%)	0.12	0.20	0.75	0.03	0.04	1(7.1%)	
99	41	8(19.5%)	0.22	0.20	0.53	0.12	0.17	1(12.5%)	

Table 3. Statistics for E & P Waste (TCLP data).**Compound : Arsenic**

Waste Code	Total number of samples	Number validated (%)	Mean mg/L	Standard deviation mg/L	Maximum mg/L	Geometric mean mg/L	Median mg/L	Number of TCLP failures (%)	Remarks
01	112	60(53.6%)	0.10	0.19	1.22	0.03	0.02	0(0%)	
02	230	147(63.9%)	0.10	0.55	6.5	0.03	0.02	1(0.7%)	
03	392	30(7.6%)	0.11	0.45	2.5	0.02	0.03	0(0%)	
04	464	24(5.2%)	0.20	0.39	1.5	0.02	0.04	0(0%)	
05	39	20(51.3%)	0.11	0.33	1.5	0.02	0.02	0(0%)	
06	294	162(55.1%)	0.08	0.14	0.65	0.02	0.02	0(0%)	
07	278	148(53.2%)	0.16	0.89	9.9	0.02	0.02	1(0.7%)	
08	6	4(66.7%)	0.11	0.19	0.4	0.017	0.02	0(0%)	
09	22	7(31.8%)	0.006	0.007	0.02	0.003	0.005	0(0%)	
10	242	4(1.7%)	0.128	0.254	0.51	0.004	0.001	0(0%)	
11	75	20(26.7%)	0.132	0.121	0.25	0.038	0.142	0(0%)	
12	9	4(44.4%)	0.125	0.154	0.35	0.031	0.075	0(0%)	
13	29	12(41.4%)	1.173	3.728	13	0.017	0.005	1(8.3%)	
14	18	11(61.1%)	0.085	0.097	0.25	0.019	0.08	0(0%)	
15	3	2(66.7%)	0.007	0.009	0.013	0.003	0.007	0(0%)	
16	19	6(31.6%)	0.009	0.012	0.025	0.002	0.0005	0(0%)	
99	41	8(19.5%)	0.114	0.190	0.445	0.019	0.02	0(0%)	

Table 4. Statistics for E & P Waste (TCLP data).**Compound : Barium**

Waste Code	Total number of samples	Number validated (%)	Mean mg/L	Standard deviation mg/L	Maximum mg/L	Geometric mean mg/L	Median mg/L	Number of TCLP failures (%)	Remarks
01	112	60(53.6%)	25.9	63.6	372	4.3	4.0	4(6.6%)	
02	230	147(63.9%)	4.38	9.92	101	1.97	2.30	1(0.7%)	
03	392	30(7.6%)	5.08	11.81	66	2.18	1.99	0(0%)	
04	464	24(5.2%)	4.31	6.15	22	1.22	0.86	0(0%)	
05	39	20(51.3%)	1.61	1.59	5	0.96	1.15	0(0%)	
06	294	162(55.1%)	10.2	62.8	790	1.91	2.08	1(0.15%)	
07	278	148(53.2%)	6.0	18.4	191	1.67	1.75	1(0.67%)	
08	6	4(66.7%)	318.5	263.8	646	44.7	314.0	3(75%)	
09	22	7(31.8%)	0.93	0.75	2.5	0.74	0.77	0(0%)	
10	242	4(1.7%)	8.13	10.98	24.1	3.35	3.81	0(0%)	
11	75	20(26.7%)	3.72	3.90	14.7	1.77	2.62	0(0%)	
12	9	4(44.4%)	2.32	4.09	8.5	0.66	0.3	0(0%)	
13	29	12(41.4%)	8.99	8.83	26.6	4.72	4.83	0(0%)	
14	18	11(61.1%)	4.58	6.31	21.6	1.73	2.57	0(0%)	
15	3	2(66.7%)	3.31	1.38	4.29	3.17	3.31	0(0%)	
16	19	6(31.6%)	1.30	1.24	3.71	0.98	0.74	0(0%)	
99	41	8(19.5%)	2.36	1.77	5.55	1.68	2.2	0(0%)	

Table 5. Statistics for E & P Waste (TCLP data).**Compound : Cadmium**

Waste Code	Total number of samples	Number validated (%)	Mean mg/L	Standard deviation mg/L	Maximum mg/L	Geometric mean mg/L	Median mg/L	Number of TCLP failures (%)	Remarks
01	112	60(53.6%)	0.05	0.09	0.5	0.02	0.01	0(0%)	
02	230	147(63.9%)	0.02	0.05	0.25	0.01	0.01	0(0%)	
03	392	30(7.6%)	0.04	0.10	0.5	0.01	0.01	0(0%)	
04	464	24(5.2%)	0.18	0.40	1.5	0.02	0.005	2(0.7%)	
05	39	20(51.3%)	0.015	0.016	0.05	0.01	0.01	0(0%)	
06	294	162(55.1%)	0.04	0.08	0.5	0.01	0.01	0(0%)	
07	278	148(53.2%)	0.03	0.05	0.35	0.01	0.01	0(0%)	
08	6	4(66.7%)	0.098	0.080	0.2	0.055	0.095	0(0%)	
09	22	7(31.8%)	0.005	0	0.005	0.005	0.005	0(0%)	
10	242	4(1.7%)	0.006	0.003	0.01	0.006	0.005	0(0%)	
11	75	20(26.7%)	0.030	0.002	0.05	0.019	0.047	0(0%)	
12	9	4(44.4%)	0.09	0.173	0.35	0.010	0.004	0(0%)	
13	29	12(41.4%)	0.056	0.086	0.25	0.144	0.008	0(0%)	
14	18	11(61.1%)	0.017	0.021	0.05	0.009	0.005	0(0%)	
15	3	2(66.7%)	0.005	0	0.005	0.005	0.005	0(0%)	
16	19	6(31.6%)	0.008	0.008	0.025	0.006	0.005	0(0%)	
99	41	8(19.5%)	0.003	0.075	0.22	0.009	0.01	0(0%)	

Table 6. Statistics for E & P Waste (TCLP data).**Compound : Chromium**

Waste Code	Total number of samples	Number validated (%)	Mean mg/L	Standard deviation mg/L	Maximum mg/L	Geometric mean mg/L	Median mg/L	Number of TCLP failures (%)	Remarks
01	112	60(53.6%)	0.24	0.95	7.3	0.03	0.01	1(1.6%)	
02	230	147(63.9%)	0.15	0.43	4.0	0.03	0.01	0(0%)	
03	392	30(7.6%)	0.35	0.78	4.2	0.07	0.12	0(0%)	
04	464	24(5.2%)	11.1	46.6	227	0.05	0.02	2(0.7%)	
05	39	20(51.3%)	0.10	0.21	0.9	0.02	0.01	0(0%)	
06	294	162(55.1%)	0.69	6.25	78.7	0.03	0.01	3(0.45%)	
07	278	148(53.2%)	0.09	0.49	5.9	0.02	0.01	1(0.67%)	
08	6	4(66.7%)	0.05	0.09	0.2	0.02	0.07	0(0%)	
09	22	7(31.8%)	0.009	0.008	0.025	0.007	0.005	0(0%)	
10	242	4(1.7%)	0.011	0.009	0.025	0.009	0.008	0(0%)	
11	75	20(26.7%)	0.364	0.463	1.29	0.071	0.139	0(0%)	
12	9	4(44.4%)	0.099	0.167	0.35	0.024	0.022	0(0%)	
13	29	12(41.4%)	0.110	0.189	0.5	0.026	0.012	0(0%)	
14	18	11(61.1%)	0.079	0.110	0.25	0.025	0.011	0(0%)	
15	3	2(66.7%)	0.43	0.27	0.62	0.38	0.43	0(0%)	
16	19	6(31.6%)	0.058	0.077	0.18	0.020	0.015	0(0%)	
99	41	8(19.5%)	0.075	0.104	0.26	0.031	0.02	0(0%)	

Table 7. Statistics for E & P Waste (TCLP data).**Compound : Lead**

Waste Code	Total number of samples	Number validated (%)	Mean mg/L	Standard deviation mg/L	Maximum mg/L	Geometric mean mg/L	Median mg/L	Number of TCLP failures (%)	Remarks
01	112	60(53.6%)	0.94	2.95	14.4	0.09	0.07	3(4.9%)	
02	230	147(63.9%)	0.46	1.26	12.6	0.14	0.16	2(1.4%)	
03	392	30(7.6%)	0.53	0.85	4.2	0.17	0.19	0(0%)	
04	464	24(5.2%)	0.94	3.06	15	0.07	0.03	1(0.4%)	
05	39	20(51.3%)	0.12	0.18	0.81	0.05	0.03	0(0%)	
06	294	162(55.1%)	0.26	1.07	11.8	0.05	0.04	2(0.3%)	
07	278	148(53.2%)	0.18	0.50	4.38	0.049	0.02	0(0%)	
08	6	4(66.7%)	1.35	1.41	2.85	0.54	1.25	0(0%)	
09	22	7(31.8%)	0.07	0.023	0.11	0.06	0.06	0(0%)	
10	242	4(1.7%)	0.05	0.04	0.10	0.04	0.04	0(0%)	
11	75	20(26.7%)	0.21	0.31	1.46	0.09	0.19	0(0%)	
12	9	4(44.4%)	0.11	0.16	0.35	0.05	0.03	0(0%)	
13	29	12(41.4%)	0.82	1.88	6.4	0.08	0.07	1(8.3%)	
14	18	11(61.1%)	0.10	0.15	0.52	0.06	0.05	0(0%)	
15	3	2(66.7%)	0.48	0.24	0.64	0.45	0.48	0(0%)	
16	19	6(31.6%)	0.04	0.02	0.09	0.04	0.04	0(0%)	
99	41	8(19.5%)	0.43	0.68	2.07	0.14	0.22	0(0%)	

Table 8. Statistics for E & P Waste (TCLP data).**Compound : Mercury**

Waste Code	Total number of samples	Number validated (%)	Mean mg/L	Standard deviation mg/L	Maximum mg/L	Geometric mean mg/L	Median mg/L	Number of TCLP failures (%)	Remarks
01	112	60(53.6%)	0.006	0.016	0.103	0.001	0.0005	0(0%)	
02	230	147(63.9%)	0.002	0.007	0.05	0	0.0005	0(0%)	
03	392	30(7.6%)	0.006	0.094	0.5	0.012	0.025	0(0%)	
04	464	24(5.2%)	0.019	0.045	0.2	0.001	0.0004	0(0%)	
05	39	20(51.3%)	0.002	0.004	0.015	0.0008	0.0005	0(0%)	
06	294	162(55.1%)	0.005	0.014	0.1	0	0.0005	0(0%)	
07	278	148(53.2%)	0.002	0.0087	0.08	0.00076	0.0005	0(0%)	
08	6	4(66.7%)	0.0005	0.0003	0.001	0.0005	0.0005	0(0%)	
09	22	7(31.8%)	0.012	0.017	0.05	0.006	0.005	0(0%)	
10	242	4(1.7%)	0.010	0.019	0.04	0.001	0.0006	0(0%)	
11	75	20(26.7%)	0.008	0.006	0.025	0.004	0.01	0(0%)	
12	9	4(44.4%)	0.0008	0.001	0.0025	0.0004	0.0004	0(0%)	
13	29	12(41.4%)	0.006	0.009	0.03	0.001	0.0005	0(0%)	
14	18	11(61.1%)	0.013	0.026	0.08	0.002	0.001	0(0%)	
15	3	2(66.7%)	0.003	0.003	0.005	0.001	0.003	0(0%)	
16	19	6(31.6%)	0.002	0.004	0.01	0.0004	0.0003	0(0%)	
99	41	8(19.5%)	0.0008	0.0007	0.003	0.0006	0.0005	0(0%)	

Table 9. Statistics for E & P Waste (TCLP data).**Compound : Selenium**

Waste Code	Total number of samples	Number validated (%)	Mean mg/L	Standard deviation mg/L	Maximum mg/L	Geometric mean mg/L	Median mg/L	Number of TCLP failures (%)	Remarks
01	112	60(53.6%)	0.08	0.12	0.4	0.04	0.02	0(0%)	
02	230	147(63.9%)	0.05	0.07	0.4	0.03	0.02	0(0%)	
03	392	30(7.6%)	0.05	0.09	0.5	0.01	0.02	0(0%)	
04	464	24(5.2%)	0.13	0.22	1	0.02	0.03	0(0%)	
05	39	20(51.3%)	0.019	0.016	0.05	0.009	0.02	0(0%)	
06	294	162(55.1%)	0.175	0.688	6.34	0.029	0.02	5(0.75%)	
07	278	148(53.2%)	0.073	0.215	2.07	0.025	0.02	2(1.33%)	
08	6	4(66.7%)	0.11	0.19	0.4	0.017	0.02	0(0%)	
09	22	7(31.8%)	0.0005	0	0.0005	0.0005	0.0005	0(0%)	
10	242	4(1.7%)	0.006	0.009	0.02	0.001	0.002	0(0%)	
11	75	20(26.7%)	0.029	0.023	0.05	0.011	0.035	0(0%)	
12	9	4(44.4%)	0.150	0.146	0.35	0.041	0.125	0(0%)	
13	29	12(41.4%)	0.063	0.113	0.4	0.013	0.021	0(0%)	
14	18	11(61.1%)	0.035	0.034	0.1	0.012	0.023	0(0%)	
15	3	2(66.7%)	0.0005	0	0.0005	0.0005	0.0005	0(0%)	
16	19	6(31.6%)	0.005	0.010	0.025	0.009	0.0005	0(0%)	
99	41	8(19.5%)	0.541	1.26	3.63	0.05	0.03	1(12.5%)	

Table 10. Statistics for E & P Waste (TCLP data).**Compound : Silver**

Waste Code	Total number of samples	Number validated (%)	Mean mg/L	Standard deviation mg/L	Maximum mg/L	Geometric mean mg/L	Median mg/L	Number of TCLP failures (%)	Remarks
01	112	60(53.6%)	0.15	0.35	2.5	0.03	0.01	0(0%)	
02	230	147(63.9%)	0.06	0.18	1.5	0.02	0.01	0(0%)	
03	392	30(7.6%)	0.03	0.09	0.5	0.01	0.01	0(0%)	
04	464	24(5.2%)	0.12	0.29	1	0.02	0.005	0(0%)	
05	39	20(51.3%)	0.05	0.09	0.25	0.015	0.01	0(0%)	
06	294	162(55.1%)	0.12	0.49	5.6	0.018	0.01	1(0.15%)	
07	278	148(53.2%)	0.05	0.11	0.5	0.014	0.01	0(0%)	
08	6	4(66.7%)	0.16	0.14	0.33	0.08	0.16	0(0%)	
09	22	7(31.8%)	0.005	0	0.005	0.005	0.005	0(0%)	
10	242	4(1.7%)	0.06	0.10	0.2	0.02	0.01	0(0%)	
11	75	20(26.7%)	0.13	0.12	0.25	0.04	0.13	0(0%)	
12	9	4(44.4%)	0.09	0.17	0.35	0.014	0.005	0(0%)	
13	29	12(41.4%)	0.10	0.17	0.5	0.02	0.01	0(0%)	
14	18	11(61.1%)	0.07	0.11	0.25	0.01	0.005	0(0%)	
15	3	2(66.7%)	0.005	0	0.005	0.005	0.005	0(0%)	
16	19	6(31.6%)	0.008	0.008	0.025	0.007	0.005	0(0%)	
99	41	8(19.5%)	0.066	0.093	0.22	0.018	0.01	0(0%)	

**Table 11. Statistics for Fitted Log-Normal Probability Distributions.
Compound : Benzene**

Waste C ode	a (Note 1)	b (Note 1)	r² (Note 2)	Probability of exceeding 0.5mg/L (TCLP Reference)
01	0.857	0.658	0.88	26%
02	1.87	0.342	0.93	4%
03	1.89	0.337	0.96	4%
04	1.31	0.485	0.93	12%
05	1.08	0.629	0.81	19%
06	0.224	0.536	0.97	48%
07	0.653	0.657	0.92	32%
08	1.64	2.78	0.98	21%
09	8.97	3.52	0.66	0%
10	1.25	0.928	0.89	17%
11	1.30	0.529	0.95	13%
12	-0.915	0.611	0.98	86%
13	-0.0061	0.819	0.97	60%
14	0.0841	0.689	0.768	55%
15	0.393	0.666	1.0	43%
16	1.359	0.598	0.79	11%
99	2.16	3.17	0.85	11%

Notes for Table 11

Note 1

a and b are parameters in the equation which defines the fitted log-normal probability distribution for concentration of benzene in each of the waste codes. The probability of a batch exhibiting a benzene TCLP concentration equal to or lower than C is given by

$$P(\text{Concentration} \leq C) = 0.5 + 0.5 * \operatorname{erf} \left[\frac{a + b * \log(C)}{\sqrt{2}} \right]$$

Where

P - Probability of TCLP benzene concentration equal to or lower than C

erf - Standard error function

a,b - From Table 11 for each waste type

log(C) - Logarithm (base 10) of concentration defining upper bound for calculation of probability

The probability of exceeding the TCLP reference concentration for benzene (0.5 mg/L)

$$P(\text{Concentration} > 0.5 \text{ mg/L}) = 1 - P(\text{Concentration} \leq 0.5 \text{ mg/L})$$

It is this number which is shown in the last column of Table 11. This number may differ slightly from that presented in Table 2 since this result is based on the best fit probability distribution whereas Table 2 is the actual percentage of samples among the test batches that did not meet the TCLP reference concentration.

The geometric mean of the distribution, its most probable value, is given by $C_{gm} = 10^{-a/b}$ where a and b are again given in Table 11 and C_{gm} is in units of mg/L. Note that the fitted geometric mean is generally different from that calculated in Tables 2-10 since those calculations involve the arbitrary assignment of a value to the below detection limit concentrations.

Note 2

r^2 is the correlation coefficient. A value close to 1 suggests that the linearized form of the log-normal probability distribution is closely approximated by a straight line. The linearized forms are shown on the attached figures. The correlation coefficient defines directly the fraction of the variance in the linearized data that is described by the straight line. That is a correlation coefficient of 0.88 for waste code 01 suggests that the fitted log-

normal probability distribution describes 88% of the variance in the sample data. The remaining 12% is due to factors not described by the log-normal probability distribution.

Appendix

Log-Normal Probability Distribution Plots for Benzene for Each Waste Code

The validated data are plotted on log-normal probability coordinates on the subsequent plots. The benzene TCLP concentration is plotted along the horizontal axis while probability of a concentration equal to or less than that concentration is plotted along the vertical axis. A log-normal probability distribution of concentrations should appear as a straight line on such plots.

The following data is plotted on each figure.

- C Data points represent validated benzene concentration measurements and the raw probability of their occurrence. Only measured concentrations are shown on the figures. Valid samples in which benzene was not detected are included only in that they decrease the probability of observing any particular measured concentration. For example, for waste code 01, approximately 1/3 of the validated samples did not detect benzene. These are indicated on the figure by the fact that the first data point represents approximately a 1/3 probability of observing a concentration equal to or less than the value obtained in that batch.
- C The solid line through the data represents the fitted log-normal probability distribution for the benzene TCLP concentration. The equation for this curve is given in Table 11.
- C The broken lines on each side of the solid lines represent the 95% confidence limits of the predictions of the fitted log-normal probability distribution. That is, it can be stated with 95% confidence that, based on the collected and validated data, that the probability of observing a concentration equal to or below a given concentration is between these two lines. For waste code 01, this suggests that it can be stated with 95% confidence that the benzene TCLP concentration is less than the reference level in 55 to 85% of the samples. It is thus very unlikely that more than 45% of any collection of waste code 01 samples would exceed the TCLP reference for benzene. It is also very unlikely that only 15% or less of the samples would exceed the TCLP reference for benzene.
- C The fine vertical solid line on the plots represents the TCLP reference concentration (0.5 mg/L).