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LIST OF TERMS

Aroclor	Any of several commercial polychlorinated biphenyl mixtures
DOE	U.S. Department of Energy
DOE-RL	U.S. Department of Energy, Richland Operations Office
DQO	data quality objective
DST	double-shell tank
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
g	gram
mL	milliliters
mR	millirem
mR/hr	millirem per hour
ORP	U.S. Department of Energy, Office of River Protection
PCB	polychlorinated biphenyl
ppb	parts per billion
ppm	parts per million
RPD	relative percent difference
SST	single-shell tank
TSCA	*Toxic Substance Control Act*
UCL	upper confidence limit
WTP	waste treatment plant
%	percent

INERIM BASIS FOR PCB SAMPLING AND ANALYSES

1.0 INTRODUCTION

This document was developed as an interim basis for sampling and analysis of polychlorinated biphenyls (PCBs) and will be used until a formal data quality objective (DQO) document is prepared and approved.

On August 31, 2000, the *Framework Agreement for Management of Polychlorinated Biphenyls (PCBs) in Hanford Tank Waste* was signed by the U.S. Department of Energy (DOE), the Environmental Protection Agency (EPA), and the Washington State Department of Ecology (Ecology) (Ecology et al. 2000). This agreement outlines the management of double shell tank (DST) waste as *Toxic Substance Control Act* (TSCA) PCB remediation waste based on a risk-based disposal approval option per Title 40 of the Code of Federal Regulations 761.61 (c). The agreement calls for "Quantification of PCBs in DSTs, single shell tanks (SSTs), and incoming waste to ensure that the vitrification plant and other ancillary facilities PCB waste acceptance limits and the requirements of the anticipated risk-based disposal approval are met." Waste samples will be analyzed for PCBs to satisfy this requirement.

This document describes the DQO process undertaken to assure appropriate data will be collected to support management of PCBs and is presented in a DQO format. The DQO process was implemented in accordance with the U.S. Environmental Protection Agency EPA QA/G4, *Guidance for the Data Quality Objectives Process* (EPA 1994) and the *Data Quality Objectives for Sampling and Analyses*, HNF-IP-0842, Rev. 1A, Vol. IV, Section 4.16 (Banning 1999).

2.0 PROBLEM STATEMENT

The primary reason for managing the PCB concentrations in the existing DST system waste is to maintain the PCB concentration levels within the waste acceptance criteria for the waste treatment plant (WTP). In addition, the PCB concentration levels for waste coming into the DST system must be managed within the WTP waste acceptance criteria levels and in accordance with TSCA PCB regulations. The problem statement for managing the DST system waste for PCB concentrations can be stated as follows:

> Determine PCB concentrations in the DST and incoming waste (including SST waste) to (1) manage PCB concentrations in the DST system in accordance with DST waste acceptance criteria and (2) support WTP design and risk assessment requirements.

3.0 DECISION STATEMENTS

Two decision statements were developed to manage the PCB concentration in DST system waste. The first decision statement addresses PCB concentrations in waste that is currently in the DST system while the second decision statement addresses waste entering the DST system. Waste entering the DST system includes waste transfers from the SST system, as well as other onsite facilities (e.g., Plutonium Finishing Plant and T Plant). The third decision statement addresses the need to manage the DST system waste so the WTP's waste acceptance criteria can be met.

The first two decision statements address the first part of the problem statement while the third decision statement addresses the second part of the problem statement.

The decision statements are:

1. Determine whether or not existing DST system waste and waste being transferred within the DST system contain PCB concentrations above the action levels and require additional transfer controls or require no action.

2. Determine whether or not waste entering the DST system contains PCB concentrations above levels that requires transfer controls, the U.S. Department of Energy, Office of River Protection (ORP) approval for acceptance, or requires no action.

3. Determine whether or not PCB concentrations exceed the waste acceptance criteria for the WTP prior to pretreatment (based on risk assessment, initial design criteria, and environmental regulations) and may require revision of the design criteria, revision of the risk assessment, or require no action.

4.0 DATA INPUTS

At this time, the only data needed for the above decisions is total PCB concentrations. This information will be required for both waste currently in the DST system and waste entering the DST system.

4.1 TOTAL PCB CONCENTRATIONS

Total PCB concentrations will be determined by using SW-846 method 8082 (EPA 1996). Total PCB concentrations will be calculated by summing the concentrations of seven Aroclors (1016, 1221, 1232, 1242, 1248, 1254, and 1260) found in a sample. The total PCBs in a sample will be calculated by summing only the detected Aroclors. If no Aroclors are detected, the total PCB concentration is considered to be the detection limit for the single most common Aroclor expected in the sample. This follows EPA's

present procedures for determining the total PCBs in a sample and was specified by agreement in a meeting with representatives from EPA Region 10, EPA Manchester Laboratory, Ecology, and DOE.

During the technical meetings, analyses of coplanar PCBs was considered. However, after discussions concerning the need for coplanar PCBs, concurrence was reached that analyses of coplanar PCBs would not be required because there are no current regulations requiring these analyses. According to guidance from EPA, the fate analysis model default fraction for coplanar PCBs (i.e., 1% of the total PCB is coplanar) will be used in risk assessment calculations. If the present situation changes or additional requirements for coplanar PCBs are found, this decision will be revisited.

Separate analyses will be conducted on liquids and solids. If a liquid sample contains > 0.5% solids by weight, liquids with greater than 0.5% solids must be filtered before analysis of the liquids.

4.2 QUALITY ASSURANCE/QUALITY CONTROL REQUIREMENTS

The 222-S Laboratory will perform the analyses required by this document. The *222-S Laboratory Quality Assurance Plan* (Markel 2000) specifies the requirements to assure the quality of the analyses conducted at the laboratory. The requirements shall meet the *Hanford Analytical Services Quality Assurance Requirements Document* (DOE-RL 1998) baseline requirements for laboratory quality systems. All of the analyses conducted to support this document shall be performed in accordance with these requirements.

All sampling events will be conducted using established quality assurance and quality control procedures. At a minimum, trip blanks and field blanks will be utilized. The requirements for tank sampling will be detailed in the sampling and analysis plan prepared for a particular sampling event.

Laboratory quality control will be conducted according to the following criteria:

> Surrogate Standards must fall within the established laboratory control limits. Interim limits until in-house limits are established are to be set at 50 to 150% recovery.
>
> Spike recovery will be within 50 to 150% and the spikes must be done in a valid concentration range.
>
> One laboratory control sample is required for each 20 samples or each batch of samples; whichever is more frequent. Interim limits until in-house limits are established are to be set at 70 to 130% recovery.

Continuing Calibration checks must be made at the beginning of each shift (not to exceed 12 hours) and once every 20 samples or less. If response is not within 15% of the predicted response for all analytes, recalibration is required. Retention times must also fall within the determined retention time window for each analyte. Samples exceeding these criteria must be reanalyzed.

Sample duplicate analyses must be performed at least once for each 20 samples or each batch of samples whichever is more frequent. The relative percent difference (RPD) for the duplicate analyses will be < 30%.

One method blank must be analyzed for each extraction batch or at least once, for each 20 samples or each batch of samples, whichever is more frequent. Additional extraction blanks are required if there is a change in the source or batch of reagents being used.

If the analytical results fall outside of the specified QC ranges, the laboratory personnel will investigate and correct the condition. If the condition cannot be corrected, the data will be flagged in the Tank Characterization Database.

Detection limits for PCB concentrations required by this document are one order of magnitude below the action levels (see Section 6.0). The detection limit for liquid analyses is 0.29 ppm and the detection limit for solid analyses is 5 ppm.

The 222-S Laboratory can achieve the detection limits shown above with the specified 8082 methodology. However, detection limits are largely dependent on the sample size, with the larger sample sizes producing lower detection limits. The sample size the laboratory can use depends on the radioactivity of the sample. Under a best case scenario for liquids, the laboratory can reach a detection limit of 0.54 ppb per Aroclor with a 100-mL sample that has a dose rate of <100 mR/hr. Under a best case scenario for solids, the laboratory can reach detection limits of 57 ppb per Aroclor with a 10-g sample that has a dose rate of <10 mR. Smaller samples would increase the detection limits.

Sample size requirements will be specified in the sampling and analysis plan.

5.0 STUDY BOUNDARIES

This step in the DQO process defines the spatial and temporal boundaries for the required sampling and analyses needed for the decisions to be made. The spatial boundaries define the physical area to which the decisions will apply and where the samples should be taken. The temporal boundaries describe the timeframe that the data will represent and when the samples should be taken.

5.1 SPATIAL BOUNDARIES

The spatial boundaries for the PCB sampling and analyses cover waste currently in the DST system and waste entering the DST system, including SST system waste. Approximately ninety percent of the waste entering the DST system will be SST waste (Strode and Boyles 1999). Therefore, samples from SST tanks will be used to help establish a PCB concentration baseline for the DST system and allow management of the majority of the waste expected to enter the DST system.

Archive samples, as well as samples from future sampling events, will be used to establish a PCB concentration baseline for each DST. PCB analyses on new samples will be performed on an "opportunistic" basis. That is, PCB analyses will be performed on samples obtained for other purposes, providing sufficient sample quantity exists. Archive samples are acceptable because PCBs are persistent and considered to have very low volatility. Archive samples will allow a PCB concentration baseline to be established in a more cost effective and timely manner than obtaining new tank waste samples. The determination and selection of the tank sampling order is described in *Characterization Plan for Establishing a PCB Baseline Inventory in Hanford Waste Tanks* (Nguyen 2000).

The tank sampling order is determined by a prioritization method described in Nguyen (2000). The prioritization is based on giving a number to each tank based on the criteria listed below. See Nguyen (2000) for details on the prioritization.

The prioritization criteria are:

1. Tanks that have received waste from facilities that may have used PCBs,
2. Tanks that receive waste from outside of the DST system,
3. Phase I tank treatment schedule,
4. SST saltwell pumping schedule,
5. Remaining DSTs,
6. Phase II SSTs, and
7. SSTs where PCBs were tentatively identified in vapor samples.

5.2 TEMPORAL BOUNDARIES

Analyses to be performed in fiscal year 2001, for the highest priority tanks, are identified in Nguyen (2000). The waste from 24 tanks will be sampled each year (Nguyen 2000) until sufficient data are available to satisfy the establishment of a PCB baseline in the DST system and make the decisions stated above.

In order to manage PCB concentrations in the DST system, sampling of waste entering the DST system will be required as long as waste is accepted for storage and the waste is processed by the WTP.

5.3 SAMPLING CONSTRAINTS

As stated above, PCB concentrations in the tank waste will be obtained from archived samples. Along with the usual sampling constraints encountered in sampling tank waste (e. g., potential waste stratification, limitations on the number of samples, sample location restrictions, etc.), archive samples from any particular tank will depend on the material that was archived from previous sampling events. The sampling plan is discussed in Section 8.0.

6.0 DECISION RULES

Decision rules are developed based on the first four steps of the DQO process. The decision rules contain the parameters of interest, the boundary of the decisions, the action levels, and the alternative actions. The decision rules define how to evaluate the actions to be taken determined by the analytical results.

The agreement (Ecology et al. 2000) states that "the initial engineering design basis for the vitrification plant will assume up to 50 parts per million of PCBs in the waste feed to the vitrification plant." In addition, the request for proposal for the WTP contract indicates the WTP would be designed to accept a PCB concentration up to 50 ppm. Therefore, action levels for the solids in the first and third decision statements are based on the present requirements for the WTP waste acceptance criteria. However, for the PCBs in liquids, an action level of 2.9 ppm has been selected based on a risk assessment for the WTP. The risk assessment, documented in the *Integrated Emissions Baseline Report*, is scheduled for release January 31, 2001. If the action levels change, this document will be revised accordingly.

The action level for solids in the second decision rule is based on the TSCA regulations (40 CFR 761) that mandate additional disposal requirements (i.e., incineration) for PCB concentrations above a certain level. The action level for liquids (2.9 ppm) is the same in the second decision rule as the first and third decision rules (see above).

If the PCB concentrations discussed above change (e.g., WTP or DST waste acceptance criteria), the action levels will be revised accordingly.

The decision rules developed for this document are listed below. Each decision rule number corresponds to the appropriate decision statement (same number) listed in Section 3.0.

1. If the 95 % upper confidence limit (UCL) for PCB concentrations in the DST system waste or waste planned for transfer within the DST system is >50 ppm for solids or 2.9 ppm for liquids, then PCB transfer controls will be required; otherwise PCB transfer controls will not be required.

2. If the 95 % UCL for PCB concentrations in the waste entering the DST is >450 ppm for solids or >2.9 ppm for liquids, then the waste will be rejected or accepted with DOE approval; otherwise the waste can be accepted.

3. If the 95 % UCL for PCB concentrations in the DST waste feed is >50 ppm for solids or 2.9 ppm for liquids, then the WTP risk assessment may require revision, the WTP design may require changes, or both; otherwise no action is required.

The transfer controls in decision rule 1 will be used to manage the PCB concentration in the tanks so PCB concentrations will not exceed the present WTP waste acceptance for PCBs.

The actions or alternative actions will be taken as a result of the analytical results for PCB concentrations in a tank. The statistical method used to estimate the 95 % UCL for the PCB concentrations in liquid and solid samples is described in Section 7.0.

7.0 ERROR TOLERANCE

The statistical method for estimating the 95 % UCL for the PCB concentrations in liquid and solid samples to support this document is discussed below.

For liquid samples: Let $\overline{X}_1$, S_1^2, n_1, and df_1 be the sample mean, sample variance, number of observations, and degrees of freedom from the observations from the liquid samples. The upper limit to a one-sided 95% confidence interval on the mean is used to compare the sample results with the action level. Based on the data from the liquid samples, the upper limit is:

$$UL(95\%, \text{Liquid}) = \overline{X}_1 + t_{(0.05,\, df_1)} \times \sqrt{S_1^2/n_1}$$

where: $t_{(0.05,\, df_1)}$ is the appropriate quantile from the Student's t distribution with df_1 degrees of freedom.

If UL(95%, Liquid) is less than the action level, then the hypothesis that the concentration in liquid waste is greater than the action level is rejected.

For solid samples: Let $\overline{X}_2$, S_2^2, n_2, and df_2 be the corresponding sample mean, sample variance, number of observations, and degrees of freedom from the observations from the solid samples. The upper limit to a one-sided 95% confidence interval on the mean is

used to compare the sample results with the action levels. Based on the data from the solid samples, the upper limit is:

$$UL(95\%, Solid) = \overline{X}_2 + t_{(0.05, df_2)} \times \sqrt{S_2^2/n_2}$$

where: $t_{(0.05, df_2)}$ is the appropriate quantile from Student's t distribution with df_1 degrees of freedom.

If UL(95%, Solid) is less than the regulatory limit, then the hypothesis that the concentration in solid waste is greater than the action level is rejected.

If the results of the analyses do not meet the action levels, additional analyses may be performed to reduce the PCB concentration at the 95 % UCL.

8.0 SAMPLE DESIGN

As mentioned in Section 5.3, the data collection design is constrained by the available archive material, the opportunistic nature of obtaining future PCB samples, and the normal operational restrictions (e.g., available risers, etc.) of tank sampling activities. In addition, the results of current PCB analyses for tank waste are all non-detect. Non-detect analytical results do not allow statistical evaluations such as variances calculations. Therefore, a probabilistic sampling design cannot be conducted. However, statistical calculations (see Section 7.0) will be performed on the analytical results.

Present data indicate PCB concentrations in the tank waste are well below action levels. Therefore, the sampling scheme discussed below (two samples for solids and two for liquids from two separate risers) should be adequate to satisfy action level requirements.

Available archive samples are selected to optimize the representativeness of the final data. Analyses of four samples (if available) will be conducted on the archived material from the selected tanks. The four samples will consist of two samples from each phase (liquids and solids) from separate risers. However, when there is only one archive sample for a phase in a high priority tank, a PCB analysis will be performed on that sample. The available archive samples are selected according to the following order of preference (Nguyen 2000).

1. Core composite samples from different risers,
2. Core composite samples from the same riser,
3. Segment samples from cores taken from different risers,
4. Segment samples from the same core or riser,

5. Grab samples taken from different risers, and

6. Grab samples taken from the same riser.

In addition, most recent samples are used if everything else is equal. Archive samples are not used if the sample size is insufficient for analysis (i.e., less than approximately 2 g for solids or 100 mL for liquids). Archive samples may not be used if characteristics of the waste in the tank have been altered due to addition of other waste since the samples were taken. Analyses planned for fiscal year 2001 are listed in Nguyen (2000).

Selection of the tanks for sampling is based on a prioritization system (Nguyen 2000) briefly described in Section 5.1. Twenty-four of the top 25 tanks are scheduled for sampling in fiscal year 2001. While five of these tanks are from current sampling events and nineteen from archive samples, there exists flexibility in the actual split between archive and opportunistic samples. See Nguyen (2000) for a list of tanks.

The characterization plan will be updated annually to provide a sampling update (tanks to be sampled) for the following year.

9.0 REFERENCES

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