Appendix F

Barr Data Validation Standard Operating Procedures

- For Routine Level Volatile Organic Compounds (VOC), Gasoline Range Organics (GRO) and Total Petroleum Hydrocarbons (TPH) Data Validation (pg.1)
- For Routine Level Semivolatile Organic Compounds (SVOC) and Polycyclic Aromatic Hydrocarbons (PAH) Data Validation (pg. 22)
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STANDARD OPERATING PROCEDURE

for Routine Level Volatile Organic Compounds (VOC), Gasoline Range Organics (GRO) and Total Petroleum Hydrocarbons (TPH) Data Validation

PCDOCS No.: 248819

Revision 3.1

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Annual Review of the SOP has been performed and the SOP still reflects current practice.

Initials:	_____	Date:	_____
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Initials:	_____	Date:	_____

Standard Operating Procedures for Routine Level Volatile Organic Compounds (VOC) Gasoline Range Organics (GRO) and Total Petroleum Hydrocarbons (TPH) Data Validation

Purpose

This SOP is intended as a guidance SOP for the routine level validation of volatile organic compounds (VOC) data provided by laboratories to be used in Barr Engineering Company (Barr) projects or by Barr clients.

Applicability

This SOP applies to routine VOC (including BTEX and TPH) and gasoline range organics (GRO) data validation by the analytical methods including, but not limited to:

- GC/MS and GC/MS SIM (EPA Method 8260B)
- GC/PID or GC/ECD (EPA Method 8021B)
- Wisconsin (WI) GRO (EPA Method 8015C)
- TCLP VOCs (EPA Methods 1311/8260B)

Validation of Contract Laboratory Program (CLP) data should be performed in accordance with to the *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (June 2008)*.

Definitions

Blank. An analytical sample designed to assess specific sources of contamination. See individual definitions for types of blanks.

BTEX. An acronym that stands for Benzene, Toluene, Ethylbenzene, and Xylenes.

Contamination. A component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

Deuterated Monitoring Compounds (DMCs). Compounds added to every volatile calibration standard, blank, and sample used to evaluate the efficiency of the extraction/purge and trap procedures, and the performance of the Gas Chromatograph/Mass Spectrometer (GC/MS) systems. DMCs are isotopically labeled (deuterated) analogs of native target compounds. DMCs are not expected to be naturally detected in the environmental media.

Field Blank. A blank used to provide information about contaminants that may be introduced during sample collection.

GC/ECD. Gas Chromatography/Electron Capture Detector. Measures electron capturing compounds (usually halogenated) by creating an electrical field in which molecules exiting a GC column can be detected by the drop in current in the field. Identifies potential compounds based on retention time in a GC column, but the identification of the compound is not selective with one

detector. Additional conformational analyses must be performed (either GC/MS or a separate GC/ECD with a different stationary phase on the column).

GC/FID. Gas Chromatography/Flame Ionization Detector. As components elute from the GC's column they pass through the flame and are burned, producing ions. The ions propagate an electric current, which is the signal output of the detector. The greater the concentration of the component, the more ions are produced, and the greater the current.

GC/MS. Gas Chromatography/Mass Spectrometry (sometimes Mass Selective Detector (MSD)). An analytical technique used to measure the mass-to-charge ratio of ions. A MS detector can selectively identify a compound based on the compound's mass-to-charge ratio and generally does not require secondary confirmation.

GC/PID. Gas Chromatography/Photoionization Detector. Uses ultraviolet light to ionize analyte exiting from a GC column. The resultant electrical charge produces a measurable current on a detector.

GRO. Gasoline Range Organics. Light-range petroleum products, including gasoline, with petroleum hydrocarbon compounds corresponding to an alkane range from the beginning of n-hexane (C_6) to beginning of n-decane (C_{10}) and with a boiling point range between approximately 60 - 170 degrees Centigrade.

HCl. Hydrochloric acid.

Initial Calibration. Analysis of analytical standards at different concentrations to define the linear range of an analytical instrument.

Internal Standards. Compounds added to every volatile calibration standard, blank, sample, or sample extract, including the Laboratory Control Sample (LCS), at a known concentration, prior to analysis. Internal standards are used to monitor instrument performance and quantitation of target compounds.

Instrument Blank. A blank designed to determine the level of contamination either associated with the analytical instruments, or resulting from carryover.

Laboratory Control Sample (LCS). The LCS is an internal laboratory Quality Control (QC) sample designed to assess the capability of the laboratory to perform the analytical method.

Matrix. The predominant material of which the sample to be analyzed is composed.

Matrix Effect. In general, the effect of a particular matrix on the constituents with which it contacts. Matrix effects may prevent efficient purging/extraction of target analytes, and may affect DMC and surrogate recoveries. In addition, non-target analytes may be extracted from the matrix causing interferences.

Matrix Spike (MS). Aliquot of the sample fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

Matrix Spike Duplicate (MSD). A second aliquot of the same as the MS sample that is fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to determine precision of the method.

MeOH. Methanol.

Method Blank. A reagent aqueous sample spiked with internal standards, and surrogate standards (or DMCs), that is carried throughout the entire analytical procedure. The method blank

is used to define the level of contamination associated with the processing and analysis of samples.

MTBE. Methyl-Tertiary-Butyl-Ether. A gasoline additive, intended to reduce air pollution, that has sometimes contaminated groundwater through releases from leaking underground fuel storage tanks.

Narrative. The portion of the data package which includes laboratory, contact person, sample number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution.

NELAP. National Environmental Laboratory Accreditation Program. NELAP adopts standards (e.g. rules) that are based on the International Organization for Standardization (ISO) and are developed through a consensus process. Oversight is provided by the NELAP Board which consists of one representative and one alternate from each of the recognized accreditation bodies.

$Na_2S_2O_4$. Sodium Hydrosulfite. A chemical used to preserve aqueous VOC samples if residual chlorine is present.

PE Sample. Performance Evaluation Sample. A reference sample provided to a laboratory for the purpose of demonstrating that the laboratory can successfully analyze the sample within limits of performance specified.

PT Sample. Proficiency Testing Sample. A sample, the composition of which is unknown to the laboratory and is provided to test whether a laboratory can produce analytical results within the specified acceptance criteria. Required for accreditation by MN Rules and NELAP.

QAPP. Quality Assurance Project Plan. A formal document describing in comprehensive detail the necessary quality assurance (QA), quality control (QC), and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria.

QA/QC. Quality Assurance/Quality Control.

Retention Time (RT). The time a target analyte is retained on a Gas Chromatograph (GC) column before elution. The identification of a target analyte is dependent on a target compound's RT falling within the specified RT Window established for that compound. The RT is dependent on the nature of the column's stationary phase, column diameter, temperature, flow rate, and other parameters.

SAP. Sampling and Analysis Plan. The purpose of the SAP is to ensure that sampling data collection activities are comparable to and compatible with previous data collection activities performed at the site and to document the details of all field activities and laboratory analyses prior to the work being conducted.

Sample Delivery Group (SDG). Identifies a group of samples for delivery, A sample delivery group is defined by the following, whichever is most frequent:

- Each set of field samples received; or
- Each 20 field samples within a sampling event; or
- Each 7 calendar day period (3 calendar day period for 7-day turnaround) during which field samples are received.

SIM. Selected Ion Monitoring. Method of GC/MS scanning that focuses on only a few ions for detection. Using this technique increases the sensitivity of a mass spectrometry detector as much as 500-fold.

Surrogates (Surrogate Standard). Compounds added to every blank, sample, including Laboratory Control Sample (LCS/LCSD), Matrix Spike/Matrix Spike Duplicate (MS/MSD), and standards; used to evaluate analytical efficiency by measuring recovery. Surrogates are not expected to be detected in environmental media.

TCLP. Toxicity Characteristic Leaching Procedure. A test designed to determine whether a waste is hazardous or requires treatment to become less hazardous; also can be used to monitor treatment techniques for effectiveness.

TPH. Total Petroleum Hydrocarbons. A measure of the concentration or mass of petroleum hydrocarbon constituents present in a given amount of soil or water. The term "total" is a misnomer--few, if any, of the procedures for quantifying hydrocarbons are capable of measuring all fractions of petroleum hydrocarbons present in the sample. Volatile hydrocarbons are usually lost in the process and not quantified, and some non-petroleum hydrocarbons are sometimes included in the analysis.

Trip Blank. A blank used to provide information about contaminants that may be introduced during sample transport.

Volatile Organic Compounds (VOC). Organic chemical compounds that have high enough vapor pressures under normal conditions to significantly vaporize and enter the atmosphere.

Equations

For % Recovery (%R or %Rec):

$$\%R = \frac{SSR - SR}{SA} \times 100$$

Where,

%R = % recovery
SSR = spiked sample result
SR = sample result
SA = spike added to native sample
In the case of LCS and other laboratory-prepared samples, the sample result (SR) is zero.

For RPD:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where,

RPD = relative percent difference
S = original sample result
D = duplicate sample result

References

This SOP is based on the recommendations of *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (January 2005),* and quality control recommendations outlined in:

- **Minnesota Rules 4740.2020 – 4740.2120** – *State of Minnesota Rules,* October 2006,
- **SW-140 –** *Wisconsin GRO (WI GRO),* September 1995,
- **EPA Method 8260B** – *"Volatile Organic Compounds by GC/MS"*, December 1996,
- **EPA Method 8015C** – *"Nonhalogenated Organics Using GC/FID"*, February 2007,
- **EPA Method 8021B** – *"Aromatic and Halogenated Volatiles by GC using PID and/or ECD"*, December 1996, and
- **EPA Method 1311** – *"Toxicity Characteristic Leaching Procedure"* July 1992.

Responsibilities

The laboratory is responsible for generating data from the samples submitted for analysis. In instances where QC criteria are not met for the analysis of samples, the laboratory is responsible for reanalysis of the samples, provided reanalysis is possible (considering matrix interference, holding times and sample volume, etc.).

The QA/QC officer is responsible for validating the data in accordance with this SOP, in addition to using professional judgment where necessary or appropriate.

Procedure

I. Hold Time and Preservation Evaluation

The purpose of hold time evaluation is to ascertain the validity of the analytical results based on the sample condition, proper preservation and the time elapsed between the date of sample collection and date of analysis.

The recommended hold time and preservation acceptance criteria are in *Table 1*.

Table 1 – Recommended Hold Times and Preservation

Compound	Matrix	Temperature	Preservative	Maximum Hold Time
VOC (including BTEX and MTBE)	aqueous	< 6° C	HCl <2 pH	14 days
	aqueous	< 6° C	unpreserved	7 days
	sediment/soil	< 6° C	25 mL MeOH in jar pre-weighed by laboratory	14 days
WI GRO	aqueous	< 6° C	HCl <2 pH	14 days
	sediment/soil	< 6° C	25 mL MeOH in jar pre-weighed by laboratory	14 days
TPH	aqueous	< 6° C	HCl or H_2SO_4 <2 pH	7 day extraction/ addl. 40 days analysis
	sediment/soil	< 6° C	not required	14 days extraction/ addl.40 days analysis
TCLP	all matrices	< 6° C	no preservative	14 days extraction/ addl. 14 days analysis

If samples do not meet hold time, preservation and extraction/analysis recommendations in *Table 1*, consider qualification with an "**h**". Other matrices, such as product samples (e.g. oil,) may not be necessarily be subjected to the same hold time recommendations.

It is noted that the temperature of sample upon laboratory receipt may exceed the recommended temperature if the sample was collected the same day or shortly before receipt by the laboratory. While Minnesota requires that samples are stored and received on ice this may have little impact on the temperature of samples collected within five (5) hours before submission to the laboratory. Other states may have additional or different requirements. Use professional judgment when evaluating the application of qualifiers in these cases.

Professional judgment should be applied (considering matrix and magnitude of exceedence, etc.) when evaluating the application of qualifiers when criteria are not met.

Special considerations for Holding Times of VOC samples

Aqueous samples should be received without headspace and soil samples typically require 25 grams of soil to 25 mL methanol (other volumes may be used, but the ratio of grams of soil to mL of methanol should be 1:1). Some headspace may be self-evolving in aqueous samples at sites with characteristically high pH levels and this should be considered before qualification of the results.

Aqueous samples with residual chlorine present should additionally have a 10% $Na_2S_2O_4$ solution added in addition to the HCl preservative to dechlorinate the sample. Samples with residual chlorine might warrant qualification with an "**h**" if not preserved correctly.

A separate sample (without preservative) should be collected for each soil sample to be analyzed for VOC, BTEX or WI GRO for the determination of moisture content. Samples without moisture content determination should be reported as wet weight.

II. Blanks

Blank evaluation is conducted to determine the existence and magnitude of target analyte contamination as a result of activities in the field during collection and transport or from inter-laboratory sources.

- For each matrix, at least one method blank should be prepared and analyzed with each sample delivery group, or each batch digested (whichever is more frequent). The laboratory should analyze a method blanks at least once every 12 hours.

- Field blank collection and analysis frequency is project-specific.

- Trip blanks should be placed in each transport cooler containing VOC sample containers prior to shipment into the field and remain with the associated VOC samples submitted to the laboratory for VOC analysis; including sample storage through analysis.

Table 2 – Guidance for the Evaluation of Blank Contamination		
Positive Detection in Blank	**Sample Result**	**Recommended Action**
Common laboratory contaminants (e.g. methylene chloride, acetone, toluene, 2-butanone (MEK), carbon disulfide, and cyclohexane)	Non-detect	No action required
	<10x blank concentration	Qualify with "**b**"
	>10x blank concentration	Use professional judgment
All other target parameters	Non-detect	No action required
	<5x blank concentration	Qualify with "**b**"
	>5x blank concentration	Use professional judgment
Gross contamination (e.g. saturated peaks of target analytes in blanks)	All detections	Qualify with "******"

Note: "*****"indicates that the reported value is estimated and QA/QA criteria were not met;
"******" indicates that the reported value is unusable and QA/QC criteria were not met;
"b" indicates the reported value may be a potential false positive based on blank data validation procedures.

III. Deuterated Monitoring Compounds (DMC aka Surrogates)

Deuterated Monitoring Compounds (DMC) are also frequently known as System Monitoring Compounds (SMC) or Surrogates. Keep in mind that the laboratory may have different limits and compounds than those recommended. *Table 6* in **Section IX** presents the *recommended* compounds and recovery limits (per Guidelines) for DMCs used by laboratories (VOCs only). Laboratory-assigned limits should be used where provided.

All samples (blanks, spiked samples, project samples, QC samples) should contain DMCs or surrogates. If a sample does not contain DMCs or surrogates, professional judgment should be used to determine if the reported results are useable or not. Acceptable evaluation of DMCs or surrogates may not be applicable if dilution of the sample was required.

Table 3 – Guidance for the Recovery of Deuterated Monitoring Compounds		
Sample Concentration	**DMC or surrogate recovery**	**Recommended Action**
Sample is non-detect or has concentrations of associated target compounds less than reporting limit (RL)	< 10% recovery	Qualify associated target compounds with "******"
	< lower recovery limit	Qualify with associated target compounds with "*****"
	within acceptance limits	No action
	> upper recovery limits	No action
Sample has detectable concentrations of associated target compounds above reporting limit (RL)	< 10% recovery	Qualify with associated target compounds with "*****"
	< lower recovery limit	Qualify with associated target compounds with "*****"
	within acceptance limits	No action
	> upper recovery limits	Qualify with associated target compounds with "*****"

Note: "*****"indicates that the reported value is estimated and QA/QA criteria were not met;
"******" indicates that the reported value is unusable and QA/QC criteria were not met;

In instances where the DMC or surrogate recoveries are marginally outside acceptance criteria (within 10% of recovery limits), additional consideration should be given to historical results (where available) and general recovery trends in related samples of the same report before qualifying the sample.

In all cases, only the target compound(s) associated with the DMC that fails to meet acceptance criteria may require qualification.

Table 7 in **Section IX** presents the recommended DMCs with their associated target compounds. Bear in mind that laboratory methods may deviate from the recommended guidance and surrogate failures should be evaluated based on laboratory SOPs, especially in regard to which DMCs (surrogates) are associated with which target compounds.

For WI GRO analysis, surrogates are not required by the method. If used, the method requires that the surrogates must not elute within the gasoline range organics (GRO) window. Surrogates recommended by the method are nonane (C_9) and nonacosane (C_{29}). Use professional judgment and the above table as guidance for evaluating surrogates in WI GRO samples.

IV. Laboratory Control Samples (LCS) and Laboratory Control Sample Duplicates (LCSD)

The laboratory control sample is used to monitor the overall performance of each step during analysis, including sample preparation. Per method (laboratories may have developed other acceptable QC measures), LCSs should be analyzed:

- Once every preparation batch
- Once for each matrix
- One LCS/LCSD pair every 20 samples of the same matrix for WI GRO analysis

Laboratory control samples contain a known amount of a prescribed number of target compounds (per MN Rules and NELAP; see Table 9) and the percent recoveries are evaluated based either on the laboratory's internally generated acceptance windows or default method criteria (as given below).

Table 4 – Guidelines for Evaluating Laboratory Control Sample Recoveries

Analysis	Matrix	Acceptance Criteria	Recommended Action
VOC and associated analyses	aqueous/ sediment/ soil	no guidance from EPA, use laboratory acceptance criteria or professional judgment (generally, 75-125% recovery is acceptable)	if LCS > upper limit & samples are non-detect, no action; if detections, qualify with "*"
			if LCS < lower limit, qualify samples with "*****"
			if LCS << lower limit, qualify detects with "*****" qualify non-detects with "******"
GRO	aqueous	75-115% recovery <20% RPD	if LCS > 115% & samples are non-detect, no action; if detections, qualify with "*"
			if LCS < 75%, qualify samples with "*****"
	soil/sediment	70-120% recovery <20%RPD	if LCS > 120% & samples are non-detect, no action; if detections, qualify with "*****"
			if LCS < 70%, qualify samples with "*****"

Note: "*****"indicates that the reported value is estimated and QA/QA criteria were not met;
"******" indicates that the reported value is unusable and QA/QC criteria were not met.

RPDs are calculated for LCS/LCSD pairs using the equation as provided in the *Equations* section found in the beginning of this SOP, and are not calculated where data is already qualified with b, U, < or **.

V. Field Duplicates

Field duplicates (also known as "masked or "blind" duplicates) are also used to demonstrate acceptable precision and reproducibility of results by the laboratory. Frequency of collection is project-specific. RPDs are calculated using the equation as provided in the *Equations* section found in the beginning of this SOP, and are not calculated where data is already qualified with b, U, < or **.

Acceptance criteria for field duplicates is subject to the professional judgment of the QC officer, but typically RPDs between 20-30% for aqueous samples and 30-40% for soil and sediment samples are considered acceptable. In cases where the either of samples (native or field duplicate) is non-detect for a parameter and the other corresponding sample is detected and greater than two times (>>2x) the RL, professional judgment should be used to determine if qualification is appropriate.

It is noted that RPD results will be dependent on the heterogeneity of the samples. Higher RPDs are expected when results are at or near the reporting limits and are not always indicative of poor precision. Use professional judgment when considering qualification of associated results based upon field duplicate RPDs.

VI. Matrix Spikes (MS) and Matrix Spike Duplicates (MSD)

Matrix spikes provide information about the effect of each samples' matrix on the sample preparation procedures and analytical results. Matrix spike and matrix spike duplicate samples contain a known amount of a prescribed number of target compounds (per MN Rules and NELAP; see Table 9).

Matrix spikes are typically analyzed at the following frequencies:

- 1 (MS/MSD pair) in every 20 samples
- 1 per preparation batch per matrix, or
- 1 per sample delivery group

However, the frequency may be project-specific and the QC officer should review the documents outlining the needs of the project (SAP, QAPP, etc.). In some cases, MS/MSD analysis is not required.

If a matrix spike does not meet acceptance criteria and is not associated with a project sample, no further action is required unless other systematic evidence warrants qualification.

If the native concentration of a spiked sample is significantly greater than the spike added (greater than four times (>4x)), spike recovery cannot be accurately evaluated, therefore the criteria do not apply. Professional judgment should be used for percent recoveries nominally outside laboratory acceptance criteria prior to qualifying data.

Percent recoveries of matrix spikes (and matrix spike duplicates) should be calculated using the appropriate equation for percent recovery provided in the *Equations* section in the beginning of this SOP.

If laboratory acceptance criteria are provided for the percent recoveries of matrix spikes, those criteria should be used for the evaluation of the data. If acceptance criteria are not provided by the laboratory, the percent recoveries recommended by the Guidelines are presented in *Table 8* in **Section IX** may be used for guidance.

Solid samples may have highly variable concentrations of target analytes and percent recoveries (%R) may be influenced by the sampling precision and inherent sample homogeneity.

In general, matrix spikes and matrix spike duplicates may be evaluated as follows:

Table 5 – Guidance for Matrix Spike Evaluation

Spike Result	Recommended Action
% recovery > upper acceptance limit	Non-detects, no qualification
	Detects, qualify with "*****"
% recovery meets acceptance limits	No qualification
% recovery is between 20% and lower acceptance limit	Non-detects, qualify with "*****"
	Detects, qualify with "*****"
% recovery is below 20%	Non-detects, use professional judgment; consider qualifying with "******"
	Detects, qualify with "*****"

While matrix spike duplicates are not required by all methods, if results for MSD analyses are reported, evaluate the RPD for MS and MSD pairs using the equation for RPD evaluation provided in the *Equations* section in the beginning of this SOP. Generally, acceptance criteria for MS/MSD is <20-30% RPD for aqueous samples and <30-40% for soils/sediments, but professional judgment should be used for difficult matrices and the acceptance criteria should be adjusted accordingly.

VII. Overall Assessment

The chain-of-custody should be reviewed to determine if the laboratory report matches the requested analyses and that project-specific parameters were analyzed as requested. The narrative and other supporting documentation should be evaluated to ensure that sample condition was appropriately documented by the laboratory upon receipt. If available, historical data should be used to assist with data evaluation. Any additional anomalies should be documented and evaluated, if necessary.

VIII. Documentation

The QC officer performing the validation should complete a Routine Level Quality Control Report as part of the validation process, making sure that all exceedances of acceptance criteria are documented in the appropriate sections. If revised reports are required, copies should be given to the appropriate data management personnel for record maintenance.

All qualifiers, added, removed or retained, should be documented on the Control Report.

IX. Additional Tables

The following tables should be used for guidance purposes *only*. Priority should be given to laboratory limits and associated target compounds when provided by the laboratory. Use professional judgment before applying any of the data in the following tables to the validation process.

Table 6 – Recommended Guidance for DMC/Surrogate Recovery (alphabetical)

DMC	Recovery limits (%) for aqueous samples	Recovery limits (%) for soil samples
1,1,2,2-Tetrachloroethane-d_2	73-125	56-161
1,1-Dichloroethane-d_2	55-104	45-132
1,2-Dichlorobenzene-d_4	80-131	70-131
1,2-Dichloroethane-d_4	78-129	79-122
1,2-Dicloropropane-d_6	79-124	74-124
1,4-Dioxane-d_8	50-150	50-150
2-Butanone-d_5	49-155	20-182
2-Hexanon-d_5	28-135	17-184
Benzene-d_6	77-124	80-121
Chloroethane-d_5	71-131	61-130
Chloroform-d	78-121	72-123
Toluene-d_8	77-121	78-121
trans-1,3-Dichloropropene-d_4	73-121	72-130
Vinyl Chloride-d_3	65-131	68-122

Table 7 – Target Compounds Associated with DMCs (alphabetical)		
DMC	**Associated Target Compounds**	
1,1,2,2-Tetrachloroethane-d_2	1,1,2,2-Tetrachloroethane	1,2-Dibromo-3-chloropropane
1,1-Dichloroethane-d_2	trans-1,2-Dichloroethene 1,1-Dichloroethene	cis-1,2-Dichloroethene
1,2-Dichlorobenzene-d_4	Chlorobenzene 1,3-Dichlorobenzene 1,4-Dichlorobenzene	1,2-Dichlorobenzene 1,2,4-Trichlorobenzene 1,2,3-Trichlorobenzene
1,2-Dichloroethane-d_4	Trichlorofluoromethane 1,1,2-Trichloro-1,2,2-trifluoroethane Methyl acetate Methylene chloride	Methyl-tert-butyl ether 1,1,1-Trichloroethane Carbon tetrachloride 1,2-Dibromoethane 1,2-Dichloroethane
1,2-Dicloropropane-d_6	Cyclohexane Methylcyclohexane	1,2-Dichloropropane Bromodichloromethane
1,4-Dioxane-d_8	1,4-Dioxane	
2-Butanone-d_5	Acetone	2-Butanone
2-Hexanon-d_5	4-Methyl-2-pentanone	2-Hexanone
Benzene-d_6	Benzene	
Chloroethane-d_5	Dichlorodifluoromethane Chloromethane Bromomethane	Chloroethane Carbon disulfide
Chloroform-d	1,1-Dichloroethane Bromochloromethane Chloroform	Dibromochloromethane Bromoform
Toluene-d_8	Trichloroethene Toluene Tetrachloroethene Ethylbenzene	o-Xylene m,p-Xylene Styrene Isopropylbenzene
trans-1,3-Dichloropropene-d_4	cis-1,3-Dichloropropene trans-1,3-Dichloropropene	1,1,2-Trichloroethane
Vinyl Chloride-d_3	Vinyl chloride	

Table 8 – EPA-recommended MS/MSD limits for VOCs				
Compound	**% Rec., Aqueous**	**% RPD, Aqueous**	**% Rec., Soil/Sediment**	**% RPD, Soil/Sediment**
1,1-Dichloroethane	61-145	< 14	59-172	< 22
Trichloroethene	71-120	< 14	62-137	< 24
Benzene	76-127	< 11	66-142	< 21
Toluene	76-125	< 13	59-139	< 21
Chlorobenzene	75-130	< 13	60-133	< 21

Table 9 – Number of Target Compounds Required by NELAP and MN Rules for LCS/LCSD and MS/MSD samples	
Number of Target Parameters	**Required Number of Spiked Compounds**
1-10 analytes	Spike *all* compounds
11-20 analytes	*At least* 10 compounds or 80% of all analytes, whichever is greater
More than 20 analytes	Spike *at least* 16 compounds

X. Attachments

Attachment 1: Routine Level Quality Control Report
Attachment 2: Barr Qualifiers/Footnotes
Attachment 3: Revisions to SOP

Attachment 1
Routine Level Quality Control Report

Barr Project # _____	***Project Name:*** _____		
Laboratory: _____	***Sample ID Event or COC#*** _____		
Lab Report # _____	***Matrix:*** ***Soil*** _____	***Required Analysis:***	***VOC*** _____
Report Date: _____	***Water*** _____		***SVOC*** _____
Review By: _____ ***Date:*** _____	***Air*** _____		***Metal*** _____
	Other _____		***GenChem*** _____
	Holding Times Met: ☐ ***Yes*** ☐ ***No***		
	Comments:		

Accuracy Data:	MS/MSD % Recovery Yes / No Sample ID_____	LCS/LCSD % Recovery
VOC		
SVOC		
Metals		
Other		

Precision Data:	MS/MSD RPDs, % Yes / No Sample ID_____	LCS/LCSD RPDs, %
VOC		
SVOC		
Metals		
Other		

Surrogate Standards Data		
Organics:		Inorganic Sample Dups:
VOC		Frequency: ____
SVOC		Results:

Blank Data:	Field Blank	Trip Blank (VOC Only)	Laboratory/Method Blank
VOC			
SVOC			
Metals			
Other			

Attachment 1 (continued)
Routine Level Quality Control Report

Completeness Check: 100% Yes / No Comments:	**Historical Comparison:** N/A ____ Comments:

Masked/Blind Duplicate Results: **N/A**____ **Sample**_____

	Native Result	Duplicate Result	Native Result	Duplicate Result
VOC				
SVOC				
Metals				
Other				

Qualifiers/Qualifier Summary: **Yes / No** **(Note any TB, FB and MB affected)**

Sample Parameter	Add Qualifier	Remove Qualifier	Retain Qualifier

Other Actions Taken: Revised Report Requested _____	Lab Exception Report Completed: _____

Summary:

Attachment 2
Barr Qualifiers/Footnotes

Data Qualifiers/Footnotes

--	Not analyzed/not available.
DLND	Not detected, detection limit not determined.
ND	Not detected.
AT	Sample chromatogram is noted to be atypical of a petroleum product.
a	Estimated value, calculated using some or all values that are estimates.
B	The reported value is less that the Contract Required Detection Limit (CRDL) but greater than or equal to the Instrument Detection Limit (IDL).
b	Potential false positive value based on blank data validation procedures.
c	Coeluting compound.
e	Estimated value, exceeded the instrument calibration range.
h	EPA recommended sample preservation, extraction or analysis holding time was exceeded.
I	Indeterminate value based on failure of blind duplicate data to meet quality assurance criteria.
J	Associated value is an estimate.
j	Reported value is less than the stated laboratory quantitation limit and is considered an estimated value.
p	Small peak in chromatogram below method detection limit.
r	The presence of the compound is suspect based on the ID criteria of the retention time and relative retention time obtained from the examination of the chromatograms.
s	Potential false positive value based on statistical analysis of blank sample data.
U	Not detected.
*	Estimated value, QA/QC criteria not met.
**	Unusable value, QA/QC criteria not met.

Attachment 3:
Revisions to PCDOCS No.: 248819

Revision Number	Date of Revision	Section	Revision Made
3.1	02/2009	Document Wide	Edits to references, formatting; minor language additions and corrections;
		IX	Added Table 9
		Attachments	Added Attachment 3

STANDARD OPERATING PROCEDURE

for Routine Level Semivolatile Organic Compounds (SVOC) and Polycyclic Aromatic Hydrocarbons (PAH) Data Validation

PCDOCS No.: 248818

Revision 3.1

March 16, 2009

Approved By:	Michael Dupay		03-16-09
	Print QA Manager(s)	Signature	Date

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Annual Review of the SOP has been performed and the SOP still reflects current practice.

Initials:		Date:	
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Standard Operating Procedures for Routine Level Semivolatile Organic Compounds (SVOC) and Polycyclic Aromatic Hydrocarbons (PAH) Data Validation

Purpose

This SOP is intended as a guidance document for the routine level validation of semivolatile organic compounds (SVOC) and Polycyclic Aromatic Hydrocarbons (PAH) data provided by laboratories to be used in Barr Engineering Company (Barr) projects or by Barr clients.

Applicability

This SOP applies to routine SVOC (including PAHs, PCPs) and diesel range organics (DRO) data validation by the analytical methods including, but not limited to:

- GC/MS for SVOCs (EPA Method 8270D and 8270D SIM)
- GC/FID for PAHs (EPA Method 8100)
- HPLC for PAHs (EPA Method 8310)
- Wisconsin (WI) DRO (SW-141)
- GC/FID for DRO (EPA Method 8015C)
- TCLP/SVOC (EPA Methods 1311/8270D)

Validation of Contract Laboratory Program (CLP) data should be performed in accordance with to the *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (June 2008)*.

Definitions

Blank. An analytical sample designed to assess specific sources of contamination. See individual definitions for types of blanks.

Contamination. A component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

DRO. Diesel Range Organics. Organic range corresponding to a hydrocarbon range of C_{10} - C_{28} and a boiling point range between approximately 170°C and 430°C. Other organic compounds, including chlorinated hydrocarbons, phenols, phthalate esters, polynuclear aromatic hydrocarbons, kerosene, fuel oils and heavier oils, are measurable.

Deuterated Monitoring Compounds (DMCs). Compounds added to every semivolatile calibration standard, blank, and sample used to evaluate the efficiency of the extraction/purge and trap procedures, and the performance of the Gas Chromatograph/Mass Spectrometer (GC/MS) systems. DMCs are isotopically labeled (deuterated) analogs of native target compounds. DMCs are not expected to be naturally detected in the environmental media.

Field Blank. A blank used to provide information about contaminants that may be introduced during sample collection.

GC/FID. Gas Chromatography/Flame Ionization Detector. As components elute from the GC's column they pass through the flame and are burned, producing ions. The ions propagate an electric current, which is the signal output of the detector. The greater the concentration of the component, the more ions are produced, and the greater the current.

GC/MS. Gas Chromatography/Mass Spectrometry (sometimes Mass Selective Detector (MSD)). An analytical technique used to measure the mass-to-charge ratio of ions. A MS detector can selectively identify a compound based on the compound's mass-to-charge ratio and generally does not require secondary confirmation.

HCl. Hydrochloric acid.

HPLC. High Performance Liquid Chromatography. A chromatographic technique for separating and analyzing mixtures of substances, using a packed column with small particles coated with the stationary phase and where the mobile phase is pumped through the column with a high pressure pump. For the purposes of these analyses, a fluorescence or UV (ultraviolet) detector is used to identify the chromatographic separations.

Initial Calibration. Analysis of analytical standards at different concentrations to define the linear range of an analytical instrument.

Internal Standards. Compounds added to every volatile calibration standard, blank, sample, or sample extract, including the Laboratory Control Sample (LCS), at a known concentration, prior to analysis. Internal standards are used to monitor instrument performance and quantitation of target compounds.

Instrument Blank. A blank designed to determine the level of contamination either associated with the analytical instruments, or resulting from carryover.

Laboratory Control Sample (LCS). The LCS is an internal laboratory Quality Control (QC) sample designed to assess the capability of the laboratory to perform the analytical method.

Matrix. The predominant material of which the sample to be analyzed is composed.

Matrix Effect. In general, the effect of a particular matrix on the constituents with which it contacts. Matrix effects may prevent efficient purging/extraction of target analytes, and may affect DMC and surrogate recoveries. In addition, non-target analytes may be extracted from the matrix causing interferences.

Matrix Spike (MS). Aliquot of the sample fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

MeOH. Methanol.

Method Blank. A reagent aqueous sample spiked with internal standards, and surrogate standards (or DMCs), that is carried throughout the entire analytical procedure. The method blank is used to define the level of contamination associated with the processing and analysis of samples.

Narrative. Portion of the data package which includes laboratory, contact, sample number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution.

NELAP. National Environmental Laboratory Accreditation Program. NELAP adopts standards (e.g. rules) that are based on the International Organization for Standardization (ISO) and are developed through a consensus process. Oversight is provided by the NELAP Board which consists of one representative and one alternate from each of the recognized accreditation bodies.

PE Sample. Performance Evaluation Sample. A reference sample provided to a laboratory for the purpose of demonstrating that the laboratory can successfully analyze the sample within limits of performance specified.

PT Sample. Proficiency Testing Sample. A sample, the composition of which is unknown to the laboratory and is provided to test whether a laboratory can produce analytical results within the specified acceptance criteria. Required for accreditation by MN Rules and NELAP.

QAPP. Quality Assurance Project Plan. A formal document describing in comprehensive detail the necessary quality assurance (QA), quality control (QC), and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria.

QA/QC. Quality Assurance/Quality Control.

Retention Time (RT). The time a target analyte is retained on a Gas Chromatograph (GC) column before elution. The identification of a target analyte is dependent on a target compound's RT falling within the specified RT Window established for that compound. The RT is dependent on the nature of the column's stationary phase, column diameter, temperature, flow rate, and other parameters.

SAP. Sampling and Analysis Plan. The purpose of the SAP is to ensure that sampling data collection activities are comparable to and compatible with previous data collection activities performed at the site and to document the details of all field activities and laboratory analyses prior to the work being conducted.

Sample Delivery Group (SDG). Identifies a group of samples for delivery, A sample delivery group is defined by the following, whichever is most frequent:

- Each set of field samples received; or
- Each 20 field samples within a sampling event; or
- Each 7 calendar day period (3 calendar day period for 7-day turnaround) during which field samples are received.

SIM. Selected Ion Monitoring. Method of GC/MS scanning that focuses on only a few ions for detection. Using this technique increases the sensitivity of a mass spectrometry detector as much as 500-fold.

Semivolatile Organic Compounds (SVOC). An organic compound which has a boiling point higher than water and which may vaporize when exposed to temperatures above room temperature. Semivolatile organic compounds include phenols and polynuclear aromatic hydrocarbons (PAH)

Surrogates (Surrogate Standard). Compounds added to every blank, sample, including Laboratory Control Sample (LCS/LCSD), Matrix Spike/Matrix Spike Duplicate (MS/MSD), and standards; used to evaluate analytical efficiency by measuring recovery. Surrogates are not expected to be detected in environmental media.

TCLP. Toxicity Characteristic Leaching Procedure. A test designed to determine whether a waste is hazardous or requires treatment to become less hazardous; also can be used to monitor treatment techniques for effectiveness.

Equations

For % Recovery (%R or %Rec):

$$\%R = \frac{SSR - SR}{SA} \times 100$$

Where,

%R = % recovery
SSR = spiked sample result
SR = sample result
SA = spike added to native sample
In the case of LCS and other laboratory-prepared samples, the sample result (SR) is zero.

For RPD:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where,

RPD = relative percent difference
S = original sample result
D = duplicate sample result

References

This SOP is based on the recommendations of *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (January 2005)*, and quality control recommendations outlined in:

- **SW-141** – *"Wisconsin DRO"*, September 1995;
- **EPA Method 1311** – *"Toxicity Characteristic Leaching Procedure"*, July 1992;
- **EPA Method 8015B** – *"Nonhalongenated Organics Using GC/FID"*, February 2007;
- **EPA Method 8100** – *"Polynuclear Aromatic Hydrocarbons"*, September 1986;
- **EPA Method 8270** – *"Semivolatile Organic Compounds by GC/MS"*, February 2007; and
- **EPA Method 8310** – *"Polynuclear Aromatic Hydrocarbons*, September 1986.

Responsibilities

The laboratory is responsible for generating data from the samples submitted for analysis. In instances where QC criteria are not met for the analysis of samples, the laboratory is responsible for reanalysis of the samples, provided reanalysis is possible (considering matrix interference, holding times and sample volume, etc.).

The QA/QC officer is responsible for validating the data in accordance with this SOP, in addition to using professional judgment where necessary or appropriate.

Procedure

I. Hold Time and Preservation Evaluation

The purpose of hold time evaluation is to ascertain the validity of the analytical results based on the sample condition, proper preservation and the time elapsed between the date of sample collection and date of analysis.

The recommended hold time and preservation acceptance criteria are in *Table 1*.

Table 1 – Recommended Hold Times and Preservation

Compound	Matrix	Temperature	Preservative	Maximum Hold Time
SVOCs /PAHs	aqueous	< 6° C	ice	7 days extraction/ addl. 40 days analysis
	sediment/soil	< 6° C	ice	14 days extraction/ addl. 40 days analysis
WI DRO	aqueous	< 6° C	HCl <2 pH	7 days extraction/ addl. 40 days analysis
	sediment/soil	< 6° C	ice	14 days extraction/ addl. 40 days analysis
TCLP	all matrices	< 6° C	ice	14 days TCLP extraction / 7 days prep. extraction / addl. 40 days analysis

If samples do not meet hold time, preservation and extraction/analysis recommendations in *Table 1*, consider qualification with an "**h**". Other matrices, such as product samples (e.g. oil) may not be necessarily be subjected to the same hold time recommendations.

It is noted that the temperature of sample upon laboratory receipt may exceed the recommended temperature if the sample was collected the same day or shortly before receipt by the laboratory. While Minnesota requires that samples are stored and received on ice this may have little impact on the temperature of samples collected within five (5) hours before submission to the laboratory. Other states may have additional or different requirements. Use professional judgment when evaluating the application of qualifiers in these cases.

Professional judgment should be applied (considering matrix and magnitude of exceedence, etc.) when evaluating the application of qualifiers when criteria are not met.

A separate sample (without preservative) should be collected for each soil/sediment sample to be analyzed for DRO for the determination of moisture content. Samples without moisture content determination should be reported as wet weight.

II. Blanks

Blank evaluation is conducted to determine the existence and magnitude of target analyte contamination as a result of activities in the field during collection and transport or from inter-laboratory sources.

- For each matrix, at least one method blank should be prepared and analyzed with each sample delivery group, or each batch digested (whichever is more frequent).
- The laboratory should analyze a method blanks at least once every 20 samples.
- At least one method blank should be analyzed with each concentration level (e.g. low or medium).
- Field blank collection and analysis frequency is project-specific.

Table 2 – Guidance for the Evaluation of Blank Contamination

Analyses	Positive Detection in Blank	Sample Result	Recommended Action
SVOCs/ DRO/ PAHs	Common laboratory contaminants (e.g. common phthalate esters)	Non-detect	No action required
		<10x blank concentration	Qualify with "**b**"
		>10x blank concentration	Use professional judgment
	All other target parameters	Non-detect	No action required
		<5x blank concentration	Qualify with "**b**"
		>5x blank concentration	Use professional judgment
Any analysis	Gross contamination (e.g. saturated peaks of target analytes in blanks)	All detections	Qualify with "******"
SVOC 8270 SIM	All target parameters	Non-detect	No action required
		< 20x blank concentration	Qualify with "**b**"
		> 20x blank concentration	Use professional judgment

Note: "******" indicates that the reported value is unusable and QA/QC criteria were not met;
"b" indicates the reported value may be a potential false positive based on blank data validation procedures.

III. Deuterated Monitoring Compounds (DMC), (Surrogates)

Deuterated Monitoring Compounds (DMC) are also frequently known as System Monitoring Compounds (SMC) or Surrogates. Keep in mind that the laboratory may have different limits and compounds than those recommended. *Table 7* in **Section IX** presents the *recommended* compounds and recovery limits (per Guidelines) for DMCs used by laboratories (SVOCs only). Associated methods may provide additional guidance. Laboratory or QAPP assigned limits should be used where provided.

All samples (blanks, spiked samples, project samples, QC samples) should contain DMCs or surrogates. If a sample does not contain DMCs or surrogates, professional judgment should be used to determine if the reported results are useable or not. Acceptable evaluation of DMCs or surrogates may not be applicable if dilution of the sample was required.

Table 3 – Guidance for the Recovery of Deuterated Monitoring Compounds

Analysis	Sample Concentration	DMC/surrogate recovery	Recommended Action
SVOC/ SVOC SIM	Sample is non-detect or has concentrations of associated target compounds less than reporting limit (RL)	< 10% recovery	Qualify associated target compounds with "**"
		< lower recovery limit	Qualify with associated target compounds with "*"
		within or > acceptance limits	No action
	Sample has detectable concentrations of associated target compounds above reporting limit (RL)	< lower recovery limit	Qualify with associated target compounds with "*"
		within acceptance limits	No action
		> upper recovery limits	Qualify with associated target compounds with "*"

Note: "*"indicates that the reported value is estimated and QA/QA criteria were not met;
"**" indicates that the reported value is unusable and QA/QC criteria were not met.

In instances where the DMC or surrogate recoveries are marginally outside acceptance criteria (within 10% of recovery limits), additional consideration should be given to historical results (where available) and general recovery trends in related samples of the same report before qualifying the sample.

In all cases, only the target compound(s) associated with the DMC that fails to meet acceptance criteria may require qualification.

Table 8 in **Section IX** presents the recommended DMCs with their associated target compounds for SVOCs *only*. Bear in mind that laboratory methods may deviate from the recommended guidance and surrogate failures should be evaluated based on laboratory SOPs, especially in regard to which DMCs (surrogates) are associated with which target compounds.

Not all DMC/surrogates are utilized in all SVOC analyses. If alternate or fewer surrogates are used, the following guidelines are recommended:

Table 4 – Guidance for the Recovery of Deuterated Monitoring Compounds (If Fewer DMCs than National Function Guidelines Recommend Are Used)

DMC/Surrogate recoveries	Recommended Action
One DMC < 10% recovery	All detects of same fraction (Acid or Base/Neutral), qualify with "*"
	All non-detects, qualify with "**"
One DMC (or two DMC of different fractions), between 10% recovery and lower recovery limit	No action required
Two or more DMC of the same acid or base/neutral fraction between 10% recovery and lower recovery limit	All detects of same fraction (Acid or Base/Neutral), qualify with "*"
	All non-detects, qualify with "**"
Two or more DMC of the same acid or base/neutral fraction above the upper recovery limit	All detects of same fraction (Acid or Base/Neutral), qualify with "*"
	All non-detects, qualify with "**"
One DMC above the upper recovery limit	No action

Note: "*"indicates that the reported value is estimated and QA/QA criteria were not met;
"**" indicates that the reported value is unusable and QA/QC criteria were not met.

PAH analysis by Method 8100 (GC/FID) requires only that one surrogate be used and does not specify which surrogate is to be used. 2-fluorobiphenyl and 1-fluoronaphthalene are the recommended surrogate compounds, but the choice is open to the laboratory performing the analysis, provided adequate chromatographic separations can be demonstrated. PAH analysis by Method 8310 (HPLC) has similar recommendations and requirements. The recommended (but not required) surrogate is decafluorobiphenyl for this method.

For DRO analysis, surrogates are not required by the method. If used, the method requires that the surrogates must not elute within the diesel range organics (DRO) window. Surrogates recommended by the method are nonane (C_9) and nonacosane (C_{29}). Use professional judgment and the above table as guidance for evaluating surrogates in DRO samples.

IV. Laboratory Control Samples (LCS) and Laboratory Control Sample Duplicates (LCSD)

The laboratory control sample is used to monitor the overall performance of each step during analysis, including sample preparation. Per method (laboratories may have developed other acceptable QC measures), LCSs should be analyzed:

- Once every preparation batch
- Once for each matrix
- One LCS every 20 samples of the same matrix (WI DRO methods require an additional LCSD analysis every 20 samples)

Laboratory control samples contain a known amount of a prescribed number of target compounds (per MN Rules and NELAP; see Table 10) and the percent recoveries are evaluated based either on the laboratory's internally generated acceptance windows or default method criteria (as presented in the following table).

Table 5 – Guidelines for Evaluating Laboratory Control Sample Recoveries

Analysis	Matrix	Acceptance Criteria	Recommended Action
SVOC and associated analyses	aqueous/ sediment/ soil	no guidance from EPA, use laboratory acceptance criteria or professional judgment (generally, 75-125% recovery is acceptable)	if LCS > upper limit & samples are non-detect, no action; if detections, qualify with "*"
			if LCS < lower limit, qualify samples with "**"
			if LCS << lower limit, qualify detects with "**" qualify non-detects with "**"
DRO	aqueous	75-115% recovery <20% RPD	if LCS > 115% & samples are non-detect, no action; if detections, qualify with "*"
			if LCS < 75%, qualify samples with "**"
	soil/sediment	70-120% recovery <20%RPD	if LCS > 120% & samples are non-detect, no action; if detections, qualify with "**"
			if LCS < 70%, qualify samples with "**"

Note: "**"indicates that the reported value is estimated and QA/QA criteria were not met;
"**" indicates that the reported value is unusable and QA/QC criteria were not met.

RPDs are calculated for LCS/LCSD pairs using the equation as provided in the *Equations* section found in the beginning of this SOP, and are not calculated where data is already qualified with b, U, < or **.

V. Field Duplicates

Field duplicates (also known as "masked or "blind" duplicates) are also used to demonstrate acceptable precision and reproducibility of results by the laboratory. Frequency of collection is project-specific. RPDs are calculated using the equation as provided in the *Equations* section found in the beginning of this SOP, and are not calculated where data is already qualified with b, U, < or **.

Acceptance criteria for field duplicates is subject to the professional judgment of the QC officer, but typically RPDs <20-30% for aqueous samples and <30-40% for soil and sediment samples are considered acceptable. In cases where the either of samples (native or field duplicate) is non-detect for a parameter and the other corresponding sample is detected and much greater than two times (>>2x) the RL, professional judgment should be used to determine if qualification is appropriate.

It is noted that RPD results will be dependent on the heterogeneity of the samples. Higher RPDs are expected when results are at or near the reporting limits and are not always indicative of poor precision. Use professional judgment when considering qualification of associated results based upon field duplicate RPDs.

VI. Matrix Spikes (MS) and Matrix Spike Duplicates (MSD)

Matrix spikes provide information about the effect of each samples' matrix may have on the sample preparation procedures and analytical results. Matrix spike and matrix spike duplicate samples contain a known amount of a prescribed number of target compounds (per MN Rules and NELAP; see Table 10).

Matrix spikes are typically analyzed at the following frequencies:

- 1 (MS/MSD pair) in every 20 samples (does not apply to WI DRO)
- 1 per preparation batch per matrix, or
- 1 per sample delivery group

However, the frequency may be project-specific and the QC officer should review the documents outlining the needs of the project (SAP, QAPP, etc.). In some cases, MS/MSD analysis is not required.

If a matrix spike does not meet acceptance criteria and is not associated with a project sample, no further action is required unless other systematic evidence warrants qualification.

If the native concentration of a spiked sample is significantly greater than the spike added (greater than four times (>4x)), spike recovery cannot be accurately evaluated, therefore the criteria do not apply. Professional judgment should be used for percent recoveries nominally outside laboratory acceptance criteria prior to qualifying data.

Percent recoveries of matrix spikes (and matrix spike duplicates) should be calculated using the appropriate equation for percent recovery provided in the *Equations* section in the beginning of this SOP.

If laboratory acceptance criteria are provided for the percent recoveries of matrix spikes, those criteria should be used for the evaluation of the data. If acceptance criteria are not provided by the laboratory, the percent recoveries recommended by the Guidelines are presented in *Table 9* in **Section IX** can be used for guidance.

Solid samples may have highly variable concentrations of target analytes and percent recoveries (%R) may be limited by the sampling precision and inherent sample homogeneity.

In general, matrix spikes and matrix spike duplicates may be evaluated as follows:

Table 6 – Guidance for Matrix Spike Evaluation

Spike Result	Recommended Action
% recovery > upper acceptance limit	Non-detects, no qualification
	Detects, qualify with "*****"
% recovery meets acceptance limits	No qualification
% recovery is between 20% and lower acceptance limit	Non-detects, qualify with "*****"
	Detects, qualify with "*****"
% recovery is below 20%	Non-detects, use professional judgment; consider qualifying with "******"
	Detects, qualify with "*****"

While matrix spike duplicates are not required by all methods, if results for MSD analyses are reported, evaluate the RPD for MS/MSD pairs using the equation for RPD evaluation provided in the *Equations* section in the beginning of this SOP. Generally, acceptance criteria for MS/MSD is <20-30% RPD for aqueous samples and <30-40% for soils/sediments, but professional judgment should be used for difficult matrices and the acceptance criteria adjusted accordingly.

VII. Overall Assessment

The chain-of-custody should be reviewed to determine if the laboratory report matches the requested analyses and that project-specific parameters were analyzed as requested. The narrative and other supporting documentation should be evaluated to ensure that sample condition was appropriately documented by the laboratory upon receipt. If available, historical data should be used to assist with data evaluation. Any additional anomalies should be documented and evaluated, if necessary.

VIII. Documentation

The QC officer performing the validation should complete a Routine Level Quality Control Report as part of the validation process, making sure that all exceedances of acceptance criteria are documented in the appropriate sections. If revised reports are required, copies should be given to the appropriate data management personnel for record maintenance.

All qualifiers, added, removed or retained, should be documented on the Control Report.

IX. Additional Tables

The following tables should be used for guidance purposes *only* for samples being analyzed for SVOCs. Priority should be given to laboratory limits and associated target compounds when provided by the laboratory. Use professional judgment before applying any of the data in the following tables to the validation process.

Table 7 – Recommended Guidance for DMC/Surrogate Recovery		
DMC	**Recovery limits (%) for aqueous samples**	**Recovery limits (%) for soil/sediment samples**
2,4-Dichlorophenol-d_3	37-105	23-104
2-Chlorophenol-d_4	41-106	13-101
2-Nitrophenol-d_4	40-108	16-104
4-6-Dinitro-2-methylphenol-d_2	22-104	1-121
4-Chloroaniline-d_4	1-145	1-145
4-Methylphenol-d_8	25-111	8-100
4-Nitrophenol-d_4	33-116	16-166
Acenaphthylene-d_8	41-107	20-97
Anthracene-d_{10}	44-110	22-98
Benzo(a)pyrene-d_{12}	32-121	43-111
Bis-(2-chloroethyl) ether-d_8	40-105	12-98
Dimethylphthalate-d_6	47-114	43-111
Fluorene-d_{10}	42-111	40-108
Nitrobenzene-d_5	43-108	16-103
Phenol-d_5	39-106	17-103
Pyrene-d_{10}	52-119	51-120
Fluoranthene-d_{10} **(SIM)**	50-150	50-150
2-Methylnaphthalene-d_{10} **(SIM)**	50-150	50-150

Table 8 – DMC and Associated Target Compounds		
DMC (alphabetical)	**Associated Target Compounds**	
2,4-Dichlorophenol-d_3	2,3-Dichlorophenol Hexachlorobutadiene 4-Chloro-3-methylphenol 2,4,6-Trichlorophenol	2,3,5-Trichlorophenol 1,2,4,5-Tetrachlorobenzene Pentachlorophenol 2,3,4,6-Tetrachlorophenol
2-Chlorophenol-d_4	2-Chlorophenol	
2-Nitrophenol-d_4	Isophorone	2-Nitrophenol
4-6-Dinitro-2-methylphenol-d_2	4,6-Ditritro-2-methylphenol	
4-Chloroaniline-d_4	4-Chloroaniline Hexachlorocyclopentadiene	3,3'-Dichlorobenzidine
4-Methylphenol-d_8	2-Methylphenol 4-Methylphenol	2,4-Dimethylphenol
4-Nitrophenol-d_4	2-Nitroaniline 3-Nitroaniline 2,4-Dinitrophenol	4-Nitrophenol 4-Nitroaniline
Acenaphthylene-d_8	Naphthalene 2-Methylnaphthalene 2-Chloronapthalene	Acenaphthylene Acenaphthene
Anthracene-d_{10}	Hexachlorobenzene Atrazine	Phenanthrene Anthracene
Benzo(a)pyrene-d_{12}	Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene Dibenzo(a,h)anthracene Benzo(g,h,i)perylene
Bis-(2-chloroethyl) ether-d_8	Bis-(2-chloroethyl) ether 2,2'-oxybis(1-chloropropane)	bis(2-Choloethoxy) methane
Dimethylphthalate-d_6	Caprolactum 1,1'-Biphenyl Dimethylphthalate Diethylphthalate	Di-n-butylphthalate Butylbenzylphthalate bis(2-ethylhexyl)phthalate Di-n-octylphthalate
Fluorene-d_{10}	Dibenzofuran Fluorene 4-Chlorophenyl-phenylether	4-Bromophenyl-phenylether Carbazole

Table 8 – DMC and Associated Target Compounds (Continued)		
DMC	**Associated Target Compounds**	
Nitrobenzene-d_5	Acetophenone N-Nitroso-di-n-propylamine Hexachloroethane Nitrobenzene	2,6-Dinitrotoluene 2,4-Dinitrotoluene N-Nitrosdiphenylamine
Phenol-d_5	Benzaldehyde	Phenol
Pyrene-d_{10}	Fluoranthrene Pyrene	Benzo(a)anthracene Chrysene
SIM DMC and Associated Target Compounds		
Fluoranthene-d_{10}	Fluoranthene Pyrene Benzo(a)antheacene Chrysene Benzo(b)fluoranthene	Benzo(k)fluoranthene Benzo(a)pyrene Indeno(1,2,3-cd)pyrene Dibenzo(a,h)anthracene Benzo(g,h,i)perylene
2-Methylnaphthalene-d_{10}	Naphthalene 2-Methylnaphthalene Ancenaphthylene Acenaphthene	Fluorene Pentachlorophenol Phenanthrene Anthracene

Table 9 – Recommended MS/MSD Recoveries and RPD				
Compound	**%Recovery for Water Samples**	**RPD for Water Samples**	**%Recovery for Soil/Sediment Samples**	**RPD for Soil/Sediment Samples**
2,4-Dinitrotoluene	24 – 96	0 – 38	28 – 89	0 – 47
2-Cholorphenol	27 – 123	0 – 40	25 – 102	0 - 50
4-Chloro-3-methylphenol	23 - 97	0 – 42	26 – 103	0 – 33
4-Nitrophenol	10 – 80	0 – 50	11 – 114	0 – 50
Acenaphthene	46 – 118	0 – 31	31 – 137	0 – 19
N-Nitroso-di-n-propylamine	41 – 116	0 – 38	41 – 126	0 – 38
Pentachlorophenol	9 – 103	0 – 50	17 – 109	0 – 47
Phenol	12 - 110	0 - 42	26 - 90	0 - 35
Pyrene	26 – 127	0 - 31	35 – 142	0 – 36

Table 10 – Number of Target Compounds Required by NELAP and MN Rules for LCS/LCSD and MS/MSD samples	
Number of Target Parameters	**Required Number of Spiked Compounds**
1-10 analytes	Spike *all* compounds
11-20 analytes	*At least* 10 compounds or 80% of all analytes, whichever is greater
More than 20 analytes	Spike *at least* 16 compounds

X. Attachments

Attachment 1: Routine Level Quality Control Report
Attachment 2: Barr Qualifiers/Footnotes
Attachment 3: Revisions to SOP

Attachment 1
Routine Level Quality Control Report

Barr Project # _____	***Project Name:*** _____		
Laboratory: _____	***Sample ID Event or COC#*** _____		
Lab Report # _____	***Matrix:*** ***Soil*** _____	***Required Analysis:*** ***VOC***	_____
Report Date: _____	***Water*** _____	***SVOC***	_____
Review By: _____ ***Date:*** _____	***Air*** _____	***Metal***	_____
	Other _____	***GenChem***	_____
	Holding Times Met: ☐ ***Yes*** ☐ ***No***		
	Comments:		

Accuracy Data:	MS/MSD % Recovery Yes / No Sample ID_____	LCS/LCSD % Recovery
VOC		
SVOC		
Metals		
Other		

Precision Data:	MS/MSD RPDs, % Yes / No Sample ID_____	LCS/LCSD RPDs, %
VOC		
SVOC		
Metals		
Other		

Surrogate Standards Data		
Organics:		Inorganic Sample Dups:
VOC		Frequency: ____
SVOC		Results:

Attachment 1
Routine Level Quality Control Report

Blank Data:	Field Blank	Trip Blank (VOC Only)	Laboratory/Method Blank
VOC			
SVOC			
Metals			
Other			

Completeness Check: 100% Yes / No Comments:	**Historical Comparison:** N/A ____ Comments:

Masked/Blind Duplicate Results: **N/A**____ **Sample**_____

	Native Result	Duplicate Result	Native Result	Duplicate Result
VOC				
SVOC				
Metals				
Other				

Qualifiers/Qualifier Summary: **Yes / No** **(Note any TB, FB and MB affected)**

Sample Parameter	Add Qualifier	Remove Qualifier	Retain Qualifier

Attachment 1
Routine Level Quality Control Report

Other Actions Taken: Revised Report Requested _____	Lab Exception Report Completed: _____
Summary:	

Attachment 2
Barr Qualifiers/Footnotes

Data Qualifiers/Footnotes

--	Not analyzed/not available.
DLND	Not detected, detection limit not determined.
ND	Not detected.
AT	Sample chromatogram is noted to be atypical of a petroleum product.
a	Estimated value, calculated using some or all values that are estimates.
B	The reported value is less that the Contract Required Detection Limit (CRDL) but greater than or equal to the Instrument Detection Limit (IDL).
b	Potential false positive value based on blank data validation procedures.
c	Coeluting compound.
e	Estimated value, exceeded the instrument calibration range.
h	EPA recommended sample preservation, extraction or analysis holding time was exceeded.
I	Indeterminate value based on failure of blind duplicate data to meet quality assurance criteria.
J	Associated value is an estimate.
j	Reported value is less than the stated laboratory quantitation limit and is considered an estimated value.
p	Small peak in chromatogram below method detection limit.
r	The presence of the compound is suspect based on the ID criteria of the retention time and relative retention time obtained from the examination of the chromatograms.
s	Potential false positive value based on statistical analysis of blank sample data.
U	Not detected.
*	Estimated value, QA/QC criteria not met.
**	Unusable value, QA/QC criteria not met.

Attachment 3
Revisions to PCDOCS No.: 248818

Revision Number	Date of Revision	Section	Revision Made
3.1	02/2009	Document Wide	Edits to references, formatting; minor language additions and corrections
		IX	Added Table 10
		Attachments	Added Attachment 3

STANDARD OPERATING PROCEDURE

for Routine Level Metals Data Validation

PCDOCS No.: 248176

Revision 2.1

March 16, 2009

Approved By:	Michael Dupay		03-16-09
	Print QA Manager(s)	Signature	Date

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Annual Review of the SOP has been performed
and the SOP still reflects current practice.

Initials:	_____	Date:	_____
Initials:	_____	Date:	_____
Initials:	_____	Date:	_____
Initials:	_____	Date:	_____
Initials:	_____	Date:	_____

Standard Operating Procedures for Routine Level Metals Data Validation

Purpose

This SOP is intended as a guidance document for the routine level validation of metals data provided by laboratories to be used in Barr Engineering Company (Barr) projects or by Barr clients.

Applicability

This SOP applies to routine metals data validation for analysis by:

- ICP/AES (Methods EPA 200.7 or EPA 6010C)
- ICP/MS (Methods EPA 200.8 or EPA 6020A)
- Mercury (Methods EPA 245.1/245.5, EPA 7470A/7471B and EPA 1631E (including appendix))
- Any of the above in conjunction with TCLP procedure (EPA 1311)

Validation of Contract Laboratory Program (CLP) data should be performed in accordance with to the *USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (October 2004)*.

Definitions

AFS. Atomic Fluorescence Spectroscopy. A flame is used to solvate and atomize the sample, and a lamp emits light at a specific wavelength into the flame to excite the analyte atoms in the flame. The atoms of certain elements fluoresce and emit light in a different direction. The intensity of this fluorescing light is used for quantifying the amount of analyte element in the sample.

Blank. A sample designed to assess specific sources of contamination.

Duplicate. A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

Field Blank. Any sample that is submitted from the field and identified as a blank. A field blank is used to check for cross-contamination during sample collection, sample shipment, and in the Laboratory. A field blank includes trip blanks, equipment blanks, etc.

Holding Time. The maximum recommended amount of time samples may be held before they are processed.

HNO_3. Nitric acid. Used as a preservative.

Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD). A control sample of known composition. LCSs and LCSDs are processed using the same sample preparation, reagents, and analytical methods employed for samples received.

Matrix. The predominant material of which the sample to be analyzed is composed (e.g. water, soil, sediment, etc.)

Matrix Effect. In general, the effect of a particular matrix on the constituents with which it contacts. Matrix effects may prevent efficient purging/extraction of target analytes, and may affect DMC and surrogate recoveries. In addition, non-target analytes may be extracted from the matrix causing interferences.

Matrix Spike* (MS) *and Matrix Spike Duplicate (MSD). Introduction of a known concentration of analyte into a sample to provide information about the effect of the sample matrix on the digestion and measurement methodology.

Method Detection Limit (MDL). The concentration of a target parameter that, when a sample is processed through the complete method, produces a signal with 99% probability that it is different from the blank.

Method (Preparation) Blank. An analytical control that contains reagent water and reagents, which is carried through the entire preparation and analytical procedure.

Narrative. The portion of the data package which includes laboratory, contact, sample number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution.

NELAP. National Environmental Laboratory Accreditation Program. NELAP adopts standards (e.g. rules) that are based on the International Organization for Standardization (ISO) and are developed through a consensus process. Oversight is provided by the NELAP Board which consists of one representative and one alternate from each of the recognized accreditation bodies.

PE Sample. Performance Evaluation Sample. A reference sample provided to a laboratory for the purpose of demonstrating that the laboratory can successfully analyze the sample within limits of performance specified.

PT Sample. Proficiency Testing Sample. A sample, the composition of which is unknown to the laboratory and is provided to test whether a laboratory can produce analytical results within the specified acceptance criteria. Required for accreditation by MN Rules and NELAP.

QAPP. Quality Assurance Project Plan. A formal document describing in comprehensive detail the necessary quality assurance (QA), quality control (QC), and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria.

QA/QC. Quality Assurance/Quality Control.

Reporting Limit (RL). The RL is the lowest reported concentration, provided on the sample-analysis data report, after corrections have been made for sample dilution, sample weight, and (for soils and sediments) amount of moisture in the sample.

Sample Delivery Group (SDG). Identifies a group of samples for delivery, A sample delivery group is defined by the following, whichever is most frequent:

- Each set of field samples received; or
- Each 20 field samples within a sampling event; or
- Each 7 calendar day period (3 calendar day period for 7-day turnaround) during which field samples are received.

SAP. Sampling and Analysis Plan. The purpose of the SAP is to ensure that sampling data collection activities are comparable to and compatible with previous data collection activities performed at the site and to document the details of all field activities and laboratory analyses prior to the work being conducted.

TCLP. Toxicity Characteristic Leaching Procedure. A test designed to determine whether a waste is hazardous or requires treatment to become less hazardous; also can be used to monitor treatment techniques for effectiveness.

Equations

For % Recovery (%R or %Rec):

$$\%R = \frac{SSR - SR}{SA} \times 100$$

Where: %R = % recovery
SSR = spiked sample result
SR = sample result
SA = spike added to native sample

In the case of LCS and other laboratory-prepared samples, the sample result (SR) is zero.

For RPD:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where: RPD = relative percent difference
S = original sample result
D = duplicate sample result

References

This SOP is based on the recommendations of *USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (October 2004)* and quality control recommendations outlined in:

- **EPA Methods 200.7/6010C** – *"Determination of Metals in Waters and Wastes by ICP-AES"*, 1994/February 2007
- **EPA Methods 200.8/6020A –** *"Determination of Trace Elements in Waters and Wastes by ICP-MS"*, 1994/February 2007
- **EPA Methods 245.1/245.5** – *"Determination of Mercury in Water by CVAAS/ Automated Cold Vapor Technique"*, 1994/1974
- **EPA Method 1631E (including Appendix)** – *"Mercury in Water by Oxidation, Purge and Trap, and CVAAS"*, August 2002
- **EPA Methods 7470A/7471B** – *"Mercury in Liquid/Solid Waste (Manual Cold Vapor Technique)"*, September 1994/February 2007

Responsibilities

The laboratory is responsible for generating metals data from the samples submitted for analysis. In instances where QC criteria are not met for the analysis of samples, the laboratory is responsible for reanalysis of the samples, provided reanalysis is possible (considering matrix interference, holding times and sample volume, etc.).

The QA/QC officer is responsible for validating the metals data in accordance with this document, in addition to using professional judgment where necessary or appropriate.

Procedure

I. Hold Time and Preservation Evaluation

The purpose of hold time evaluation is to ascertain the validity of the analytical results based on the sample condition, proper preservation and the time elapsed between the date of sample collection and date of analysis.

The recommended hold time and preservation acceptance criteria are in *Table 1*.

Table 1 – Recommended Holding Times and Preservation

Compound	Matrix	Temperature	Preservative	Maximum Hold Time
Mercury	aqueous	< 6° C	HNO_3 < 2 pH	28 days
	aqueous (low level)	< 6° C	Pre-tested hydrochloric acid or bromium chloride	28 days
	sediment/soil	< 6° C	ice	28 days
	sediment/soil (low level)	< 6° C	Pre-tested hydrochloric acid or bromium chloride	28 days
All other metals	aqueous	< 6° C	HNO_3 < 2 pH	180 days
	sediment/soil	< 6° C	ice	180 days

If samples do not meet hold time, preservation and extraction/analysis recommendations in *Table 1*, consider qualification with an "**h**". Other matrices, such as product samples (e.g. oil) may not be necessarily be subjected to the same hold time recommendations.

It is noted that the temperature of sample upon laboratory receipt may exceed the recommended temperature if the sample was collected the same day or shortly before receipt by the laboratory. While Minnesota requires that samples are stored and received on ice this may have little impact on the temperature of samples collected within five (5) hours before submission to the laboratory. Other states may have additional or different requirements. Use professional judgment when evaluating the application of qualifiers in these cases.

Professional judgment should be applied (considering matrix and magnitude of exceedence, etc.) when evaluating the application of qualifiers when criteria are not met.

Low-level mercury considerations

Low-level mercury (Method 1631E) must be collected directly into a specially cleaned, pretested, fluoropolymer bottle using sample handling techniques specially designed for collection of mercury at trace levels and preserved with pre-tested hydrochloric acid (required for methyl mercury) or bromium chloride. Borosilicate glass bottles may be used if mercury is the only target analyte. Samples not collected in the correct type of container may be qualified with an "**h**". These samples may be shipped unpreserved provided:

- the sample is collected in a fluoropolymer bottle
- the bottle contains no headspace and is capped tightly
- sample temperature was maintained between 0-4°C, and
- the samples are acid-preserved within 48 hours of sampling.

II. Blanks

Blank evaluation is conducted to determine the existence and magnitude of target analyte contamination as a result of activities in the field during collection and transport or from inter-laboratory sources.

- For each matrix, at least one method blank should be prepared and analyzed with each sample delivery group, or each batch digested (whichever is more frequent).
- Field blank collection and analysis frequency is project-specific.
- Low-level mercury method requires *at least* three method blanks per run per analytical batch.

Professional judgment regarding the usability of the data should be used in cases where gross detections of target analytes are found in the method blank. In such cases, it may be appropriate to qualify the affected data with "******" (usable value, QA/QC criteria not met).

Table 2 – Guidelines for the Evaluation of Blank Contamination	
Sample Result	**Recommended Action**
Non-detect	No action required
<5x blank concentration	Qualify with "b"
>5x blank concentration	Use professional judgment
Gross contamination	Qualify associated samples with "**"

Note: "**" indicates that the reported value is unusable and QA/QC criteria were not met;
"b" indicates the reported value may be a potential false positive based on blank data validation procedures.

III. Laboratory Control Samples (LCS) and Laboratory Control Sample Duplicates (LCSD)

The laboratory control sample is used to monitor the overall performance of each step during analysis, including sample preparation. LCSs should be analyzed:

- Once every preparation batch
- Once for each matrix
- For low-level mercury, ongoing precision and recovery (OPR) samples are run before and after each analytical batch. Quality control samples (QCS) should be from a different source and analyzed once per analytical batch.

Laboratory control samples contain a known amount of a prescribed number of target compounds (per MN Rules and NELAP; see Table 9) and the percent recoveries are evaluated based either on the laboratory's internally generated acceptance windows or default method criteria (as given in *Table 3*).

Table 3 – Guidelines for Laboratory Control Sample Recoveries		
Matrix	**Acceptance Criteria**	**Action**
aqueous	80% to 120% recovery	if LCS > upper limit and samples are non-detect, no action; if detections, qualify with "*"
		if LCS is between < lower limit, use professional judgment when considering qualifying with "*"
		if LCS is << lower limit and samples are non-detect, qualify with "**"; if detections, qualify with "*"
sediment/soil	70% to 130% recovery	if LCS > 130%, and samples are non-detect, no action; if detections, qualify with "**"**
		if LCS < 70% qualify detections with "*"; use professional judgment when considering non-detections with "**"

Note: "*"indicates the reported value is estimated and QA/QA criteria were not met.
"**" indicates the reported value is unusable and QA/QC criteria were not met.

IV. Laboratory Duplicates

Laboratory duplicates are separate aliquots of field samples analyzed to demonstrate acceptable method precision by the laboratory at the time of analysis. Field blanks and performance evaluation (PE) standards may not be used for duplicate analysis and duplicate RPDs are only evaluated for samples with concentrations greater than five times (>5x) the MDL. RPDs are calculated using the equation as provided in the *Equations* section found in the beginning of this SOP, and are not calculated where data is already qualified with b, U, < or **.

Duplicates should be analyzed (whichever is more frequent):

- One from each matrix (soil or water), or
- One from each SDG

MS/MSD duplicate pairs may be substituted for laboratory duplicates.

Duplicate results are compared to the associated native result for evaluation, using the equation for RPD defined above.

Use laboratory acceptance criteria to evaluate RPDs, where available. When acceptance criteria is not available, use the following:

Table 4 – Guidelines for Laboratory Duplicate RPDs	
% RPD	**Action**
RPD is < upper limit	no action is required
RPD is > upper limit	if both results are <5x RL, no action is required
RPD is > upper limit	if both results are >5x RL, consider qualifying with "***".**

Note: "*"indicates the reported value is estimated and QA/QA criteria were not met.

If both samples are non-detect, the RPD is not calculated.

It is noted that RPD results will be dependent on the heterogeneity of the samples. Higher RPDs are expected when results are at or near the reporting limits and are not always indicative of poor precision. Use professional judgment when considering qualification of associated results.

V. Field Duplicates

Field duplicates (also known as "masked or "blind" duplicates) are also used to demonstrate acceptable precision and reproducibility of results by the laboratory. Frequency of collection is project-specific. RPDs are calculated using the equation as provided in the *Equations* section found in the beginning of this SOP, and are not calculated where data is already qualified with b, U, < or **.

Acceptance criteria for field duplicates is subject to the professional judgment of the QC officer, but typically RPDs between 20-30% for aqueous samples and 30-40% for soil and sediment samples are considered acceptable. In cases where the either of samples (native or field duplicate) is non-detect for a parameter and the other corresponding sample is detected and greater than two times (>>2x) the RL, professional judgment should be used to determine if qualification is appropriate.

It is noted that RPD results will be dependent on the heterogeneity of the samples. Higher RPDs are expected when results are at or near the reporting limits and are not always indicative of poor precision. Use professional judgment when considering qualification of associated results.

VI. Matrix Spikes (MS) and Matrix Spike Duplicates (MSD)

Matrix spikes provide information about the effect of each samples' matrix may have on the sample preparation procedures and analytical results. Matrix spike and matrix spike duplicate samples contain a known amount of a prescribed number of target compounds (per MN Rules and NELAP; see Table 9).

Matrix spikes are typically analyzed at the following frequencies:

- 1 (MS/MSD pair) in every 20 samples
- 1 per preparation batch per matrix, or
- 1 per sample delivery group

However, the frequency may be project-specific and the QC officer should review the documents outlining the needs of the project (SAP, QAPP, etc.). In some cases, MS/MSD analysis is not required.

If a matrix spike does not meet acceptance criteria and is not associated with a project sample, no further action is required unless other systematic evidence warrants qualification.

If the native concentration of a spiked sample is significantly greater than the spike added (>4x), spike recovery can not be accurately evaluated, therefore the criteria do not apply. Professional judgment should be used for percent recoveries nominally outside laboratory acceptance criteria prior to qualifying data.

Percent recoveries of matrix spikes (and matrix spike duplicates) should be calculated using the appropriate equation for percent recovery provided in the *Equations* section in the beginning of this SOP.

If laboratory acceptance criteria are provided for the percent recoveries of matrix spikes, those criteria should be used for the evaluation of the data. If acceptance criteria are not provided, percent recoveries between 75-125% are generally considered acceptable for matrix spikes.

Solid samples may have highly variable concentrations of target analytes and percent recoveries (%R) may be influenced by the sampling precision and inherent sample homogeneity.

Table 5 – Guidance for Matrix Spike Evaluation	
Spike Result	**Recommended Action**
% recovery > upper acceptance limit	Non-detects, no qualification
	Detects, qualify with "*****"
% recovery meets acceptance limits	No qualification
% recovery is between 20% and lower acceptance limit	Non-detects, qualify with "*****"
	Detects, qualify with "*****"
% recovery is below 20%	Non-detects, use professional judgment; consider qualifying with "******"
	Detects, qualify with "*****"

While matrix spike duplicates are not required by all methods, if results for MSD analyses are reported, evaluate the RPD for MS and MSD pairs using the equation for RPD evaluation in the *Equations* section in the beginning of this document. Generally, acceptance criteria for MS/MSD are <20-30% RPD for aqueous samples and <30-40% for soils/sediments, but professional judgment should be used for difficult matrices and the acceptance criteria adjusted accordingly.

VII. Overall Assessment

The chain-of-custody should be reviewed to determine if the laboratory report matches the requested analyses and that project-specific parameters were analyzed as requested. The narrative and other supporting documentation should be evaluated to ensure that sample condition was appropriately documented by the laboratory upon receipt. If available, historical data should be used to assist with data evaluation. Any additional anomalies should be documented and evaluated, if necessary.

VIII. Documentation

The QC officer performing the validation should complete a Routine Level Quality Control Report as part of the validation process, making sure that all exceedances of acceptance criteria are documented in the appropriate sections. If revised reports are required, copies should be given to the appropriate data management personnel for record maintenance.

All qualifiers, added, removed or retained, should be documented on the Control Report.

IX. Additional Tables

Table 9 – Number of Target Compounds Required by NELAP and MN Rules for LCS/LCSD and MS/MSD samples	
Number of Target Parameters	**Required Number of Spiked Compounds**
1-10 analytes	Spike *all* compounds
11-20 analytes	*At least* 10 compounds or 80% of all analytes, whichever is greater
More than 20 analytes	Spike *at least* 16 compounds

X. Attachments

Attachment 1: Routine Level Quality Control Report
Attachment 2: Barr Qualifiers/Footnotes
Attachment 3: Revisions to SOP

Attachment 1
Routine Level Quality Control Report

Barr Project # _____	***Project Name:*** _____		
Laboratory: _____	***Sample ID Event or COC#*** _____		
Lab Report # _____	***Matrix:*** ***Soil*** _____	***Required Analysis:*** ***VOC***	_____
Report Date: _____	***Water*** _____	***SVOC***	_____
Review By: _____ ***Date:*** _____	***Air*** _____	***Metal***	_____
	Other _____	***GenChem***	_____
	Holding Times Met: ☐ ***Yes*** ☐ ***No***		
	Comments:		

Accuracy Data:	MS/MSD % Recovery Yes / No Sample ID_____	LCS/LCSD % Recovery
VOC		
SVOC		
Metals		
Other		

Precision Data:	MS/MSD RPDs, % Yes / No Sample ID_____	LCS/LCSD RPDs, %
VOC		
SVOC		
Metals		
Other		

Surrogate Standards Data		
Organics:		Inorganic Sample Dups:
VOC		Frequency: ____
SVOC		Results:

Blank Data:	Field Blank	Trip Blank (VOC Only)	Laboratory/Method Blank
VOC			
SVOC			
Metals			
Other			

Completeness Check: 100% Yes / No Comments:	**Historical Comparison:** N/A ____ Comments:

Masked/Blind Duplicate Results: **N/A**____ **Sample**_____

	Native Result	Duplicate Result	Native Result	Duplicate Result
VOC				
SVOC				
Metals				
Other				

Qualifiers/Qualifier Summary: **Yes / No** **(Note any TB, FB and MB affected)**

Sample Parameter	Add Qualifier	Remove Qualifier	Retain Qualifier

Other Actions Taken: Revised Report Requested _____	Lab Exception Report Completed: _____
Summary:	

Attachment 2
Barr Qualifiers/Footnotes

Data Qualifiers/Footnotes

--	Not analyzed/not available.
DLND	Not detected, detection limit not determined.
ND	Not detected.
AT	Sample chromatogram is noted to be atypical of a petroleum product.
a	Estimated value, calculated using some or all values that are estimates.
B	The reported value is less that the Contract Required Detection Limit (CRDL) but greater than or equal to the Instrument Detection Limit (IDL).
b	Potential false positive value based on blank data validation procedures.
c	Coeluting compound.
e	Estimated value, exceeded the instrument calibration range.
h	EPA recommended sample preservation, extraction or analysis holding time was exceeded.
I	Indeterminate value based on failure of blind duplicate data to meet quality assurance criteria.
J	Associated value is an estimate.
j	Reported value is less than the stated laboratory quantitation limit and is considered an estimated value.
p	Small peak in chromatogram below method detection limit.
r	The presence of the compound is suspect based on the ID criteria of the retention time and relative retention time obtained from the examination of the chromatograms.
s	Potential false positive value based on statistical analysis of blank sample data.
U	Not detected.
*	Estimated value, QA/QC criteria not met.
**	Unusable value, QA/QC criteria not met.

Attachment 3:
Revisions to PCDOCS No.: 248176

Revision Number	Date of Revision	Section	Revision Made
3.1	02/2009	Document Wide	Edits to references, formatting; minor language additions and corrections;
		IX	Changed to Section X
		Attachments	Added Attachment 3
		IX (new)	Added Table 9.

STANDARD OPERATING PROCEDURE

for Routine Level General Chemistry Data Validation

PCDOCS No.: 248821

Revision 2.1

March 16, 2009

Approved By: MICHAEL DUPAY _____ 03-16-09

Print QA Manager(s) Signature Date

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Annual Review of the SOP has been performed
and the SOP still reflects current practice.

Initials: _____ Date: _____

Initials: _____ Date: _____

Initials: _____ Date: _____

Initials: _____ Date: _____

Initials: _____ Date: _____

Standard Operating Procedures for Routine Level General Chemistry Data Validation

Purpose

This SOP is intended as a guidance document for the routine level validation of general chemistry data provided by laboratories to be used in Barr Engineering Company (Barr) projects or by Barr clients.

Applicability

This SOP applies to routine general chemistry data validation including a variety of approved methods not limited to the following analyses:

Chromium VI (Hexavalent Chromium)	Nitrate (or Nitrite) only
Alkalinity as $CaCO_3$	Nitrate + Nitrite
Ammonia	pH – *in lab*
BOD (Biological Oxygen Demand)	Phosphorus, total
COD (Chemical Oxygen Demand)	Sulfate
Chloride	Sulfide
Conductance, Specific – *in lab*	Total Dissolved Solids (TDS)
Cyanide (CN^- as HCN)	Total Kjeldahl Nitrogen (TKN)
Fluoride	Total Organic Carbon (TOC)
Hardness	Total Suspended Solids (TSS)
HEM (Oil and Grease)	

In the case of specific analyses not listed above, the guidelines within this document will provide the basis upon which to make adequate professional judgment in the evaluation of data submitted for review.

Definitions

Blank. A sample designed to assess specific sources of contamination.

BOD. Biological Oxygen Demand. The BOD test is an empirical bioassay-type test which measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing organic matter in a sample.

COD. Chemical Oxygen Demand. The COD test determines the quantity of oxygen required to oxidize organic matter in a waste sample.

Contamination. A component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

Duplicate. A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

Field Blank. Any sample that is submitted from the field and identified as a blank. A field blank is used to check for cross-contamination during sample collection, sample shipment, and in the Laboratory. A field blank includes trip blanks, equipment blanks, etc.

Field Duplicate. A duplicate sample generated in the field, not in the Laboratory.

HCl. Hydrochloric acid. Used as a sample preservative in some analyses.

HNO_3. Nitric acid. Used as a sample preservative in some analyses.

H_2SO_4. Sulfuric acid. Used as a sample preservative for some analyses.

Initial Calibration. Analysis of analytical standards at different concentrations to define the linear range of an analytical instrument.

Instrument Blank. A blank designed to determine the level of contamination either associated with the analytical instruments, or resulting from carryover.

Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD). A control sample of known composition. LCSs and LCSDs are processed using the same sample preparation, reagents, and analytical methods employed for samples received. Sometimes referred to as a LFB (Laboratory Fortified Blank).

LFB. Laboratory Fortified Blank. See *Laboratory Control Sample*.

Matrix. The predominant material of which the sample to be analyzed is composed (e.g. water, soil, sediment, etc.)

Matrix Effect. In general, the effect of a particular matrix on the constituents with which it contacts. Matrix effects may prevent efficient purging/extraction of target analytes, and may affect DMC and surrogate recoveries. In addition, non-target analytes may be extracted from the matrix causing interferences.

Matrix Spike (MS). Aliquot of the sample fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

Matrix Spike Duplicate (MSD). A second aliquot of the same as the MS sample that is fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to determine precision of the method.

Method Detection Limit (MDL). The concentration of a target parameter that, when a sample is processed through the complete method, produces a signal with 99% probability that it is different from the blank. MDL studies performed by the laboratory should be consistent with SW-846, Ch. 1.

Method Blank. An analytical control that contains reagent water and reagents, which is carried through the entire preparation and analytical procedure. The method blank is used to define the level of contamination associated with the processing and analysis of samples.

NaOH. Sodium hydroxide. Used as a preservative in some analyses.

Narrative. Portion of the data package which includes laboratory, contact, sample number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution.

NELAP. National Environmental Laboratory Accreditation Program. NELAP adopts standards (e.g. rules) that are based on the International Organization for Standardization (ISO) and are developed through a consensus process. Oversight is provided by the NELAP Board which consists of one representative and one alternate from each of the recognized accreditation bodies.

PE Sample. Performance Evaluation Sample. A reference sample provided to a laboratory for the purpose of demonstrating that the laboratory can successfully analyze the sample within limits of performance specified.

PT Sample. Proficiency Testing Sample. A sample, the composition of which is unknown to the laboratory and is provided to test whether a laboratory can produce analytical results within the specified acceptance criteria. Required for accreditation by MN Rules and NELAP.

QAPP. Quality Assurance Project Plan. A formal document describing in comprehensive detail the necessary quality assurance (QA), quality control (QC), and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria.

QA/QC. Quality Assurance/Quality Control.

Retention Time (RT). The time a target analyte is retained on a Gas Chromatograph (GC) column before elution. The identification of a target analyte is dependent on a target compound's RT falling within the specified RT Window established for that compound. The RT is dependent on the nature of the column's stationary phase, column diameter, temperature, flow rate, and other parameters.

SAP. Sampling and Analysis Plan. The purpose of the SAP is to ensure that sampling data collection activities are comparable to and compatible with previous data collection activities performed at the site and to document the details of all field activities and laboratory analyses prior to the work being conducted.

Sample Delivery Group (SDG). Identifies a group of samples for delivery, A sample delivery group is defined by the following, whichever is most frequent:

- Each set of field samples received; or
- Each 20 field samples within a sampling event; or

- Each 7 calendar day period (3 calendar day period for 7-day turnaround) during which field samples are received.

TDS. Total Dissolved Solids. The amount of filterable residue in a given water sample.

TKN. Total Kjeldahl Nitrogen. The combination of organically bound nitrogen and ammonia (NH_3 and NH_4^+) in biological wastewater.

TOC. Total Organic Carbon. The carbon bound in an organic compound in waters and used as an indicator of water quality. Source of nutrients for undesirable biological growth.

TSS. Total Suspended Solids. The amount of non-filterable residue in a given water sample.

ZnAc + NaOH. Zinc acetate and sodium hydroxide. Used as a preservative of samples in the analysis for sulfide.

Equations

For % Recovery (%R or %Rec):

$$\%R = \frac{SSR - SR}{SA} \times 100$$

Where,

%R = % recovery
SSR = spiked sample result
SR = sample result
SA = spike added to native sample
In the case of LCS and other laboratory-prepared samples, the sample result (SR) is zero.

For RPD:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where,

RPD = relative percent difference
S = original sample result
D = duplicate sample result

References

This SOP is based on the recommendations of the associated approved analytical methods (EPA, ASTM, NPDS, etc.) and *Standard Methods for the Examination of Water and Wastewater*, 20th Ed. (Parts 1020A and 1020B).

Responsibilities

The laboratory is responsible for generating data from the samples submitted for analysis. In instances where QC criteria are not met for the analysis of samples, the laboratory is responsible for reanalysis of the samples, provided reanalysis is possible (considering matrix interference, holding times and sample volume, etc.).

The QA/QC officer is responsible for validating the data in accordance with this document, in addition to using professional judgment where necessary or appropriate.

Procedure

I. Hold Time and Preservation Evaluation

The purpose of hold time evaluation is to ascertain the validity of the analytical results based on the sample condition, proper preservation and the time elapsed between the date of sample collection and date of analysis.

All samples should meet acceptance criteria for their respective analyses (and matrices) in the charts attached to the end of this SOP

If samples do not meet hold time, preservation and extraction/analysis recommendations in *Attachments 1* and *2*, consider qualification with an "**h**".

It is noted that the temperature of sample upon laboratory receipt may exceed the recommended temperature if the sample was collected the same day or shortly before (receipt). While Minnesota requires that samples are stored and received on ice this may have little impact on the temperature of samples collected within five (5) hours before submission to the laboratory. Other states may have additional or different requirements. Use professional judgment when evaluating the application of qualifiers in these cases.

Professional judgment should be applied (considering matrix and magnitude of exceedence, etc.) when evaluating the application of qualifiers when criteria are not met.

It is understood that the method recommends that pH is a parameter that should be measured in the field. However, for conformational measurements in the laboratory, a recommended maximum holding time of 7 days from sample collection will be used for as a guideline for qualification. QAPP and SAP requirements may differ from this recommendation and professional judgment should be applied before qualifying any data.

II. Blanks

Blank evaluation is conducted to determine the existence and magnitude of target analyte contamination as a result of activities in the field during collection and transport or from inter-laboratory sources.

While not required for all methods, method blanks are recommended for all but pH analyses. Refer to *Attachments 1 and 2* at the end of this SOP for individual method requirements for method blank evaluation.

Professional judgment regarding the usability of the data should be used in cases where gross detections of target analytes are found in the method blank. In such cases, it may be appropriate to qualify the affected data with "******" (usable value, QA/QC criteria not met).

Table 1 – Guidelines for the Evaluation of Blank Contamination

Sample Result	Recommended Action
Non-detect	No action required
<5x blank concentration	Qualify with "**b**"
>5x blank concentration	Use professional judgment
Gross contamination	Qualify associated samples with "******"

Note: "******" indicates that the reported value is unusable and QA/QC criteria were not met;
"b" indicates the reported value may be a potential false positive based on blank data validation procedures.

III. Laboratory Control Samples (LCS) and Laboratory Control Sample Duplicates (LCSD)

The laboratory control sample is used to monitor the overall performance of each step during analysis, including sample preparation. Per method (laboratories may have developed other acceptable QC measures), LCSs should be analyzed:

- Once every preparation batch
- Once for each matrix

Not all methods require an LCS (or equivalent, such as a LFB). *Attachments 1 and 2* should be consulted to determine those analyses that require an LCS.

Laboratory control samples contain a known amount of each target compound and the percent recoveries are evaluated based either on the laboratory's internally-generated acceptance windows or default acceptance criteria when laboratory limits are not assigned generally fall between 75-125% recovery. *Table 2* presents the recommended guidelines for evaluating LCS/LCSD recoveries and qualification of samples from the associated batch.

Table 2 – LCS/LCSD Recovery Guidelines		
Spike Recovery	**Sample Concentration**	**Recommended Action**
< Lower Limit	Non-detect	Qualify with "*****" If LCS recovery is < 10%, consider "******"
	Detected	Qualify with "*****"
Between Lower and Upper Limits	Non-detect or Detected	Acceptable, no qualification.
> Upper Limit	Non-detect	No qualification required.
	Detected	Qualify with "*****"; If LCS recovery is >> upper limit, use professional judgment

Note: "*****"indicates that the reported value is estimated and QA/QA criteria were not met;
"******" indicates that the reported value is unusable and QA/QC criteria were not met.

IV. Laboratory Duplicates

Laboratory duplicates are analyzed to demonstrate acceptable method precision by the laboratory at the time of analysis. Field blanks and performance evaluation (PE) standards may not be used for duplicate analysis and are only evaluated for samples with concentrations greater than five times (>5x) the MDL. When methods require duplicates, they should be analyzed for each matrix.

In general, laboratory duplicates should be analyzed 1 duplicate in every 20 sample (where required). In some cases, a matrix spike duplicate may be considered an acceptable laboratory duplicate for methods requiring a matrix spike.

Duplicate results are compared to the associated native result for evaluation, using the equation for RPD defined in the *Equations* section in the beginning of this SOP.

RPD values are calculated only for results above the reporting limit and only if the following qualifiers do not apply: b, U, < and **.

Use laboratory acceptance criteria to evaluate RPDs, when available. The guidelines in *Table 3* may be used when laboratory acceptance criteria is not available.

Table 3 – Duplicate RPD Guidelines	
Matrix	**Recommended Action**
aqueous	if RPD is <20%, no action is required
	if RPD is >20%, but both results are <5x RL, no action is required
	if RPD is >20% and both results are >5x RL, qualify with *****
soil/sediment	if RPD is <35%, no action is required
	if RPD is >35%, but both results are <5x RL, no action is required
	if RPD is >35% and both results are >5x RL, qualify with *****

If both samples are non-detect, the RPD is not calculated.

V. Field Duplicates

Field duplicates (also known as "masked or "blind" duplicates) are also used to demonstrate acceptable precision and reproducibility of results by the laboratory. Frequency of collection is project-specific. RPDs are calculated using the same equation as found in the *Equations* section in the beginning of this SOP, and are not calculated where data is already qualified with b, U, < or **.

Acceptance criteria for field duplicates is subject to the professional judgment of the QC officer, but typically RPDs of <20-30% for aqueous samples and <30-40% for soil or sediment samples are considered acceptable. In cases where the either of samples (native or field duplicate) is non-detect for a parameter and the other corresponding sample is detected and greater than two times (>>2x) the RL, professional judgment should be used to determine if qualification is appropriate.

It is noted that RPD results will be dependent on the heterogeneity of the samples. Higher RPDs are expected when results are at or near the reporting limits and are not always indicative of poor precision. Use professional judgment when considering qualification of associated results based on field duplicate RPDs.

VI. Matrix Spikes (MS) and Matrix Spike Duplicates (MSD)

Matrix spikes provide information about the effect of each samples' matrix may have on the sample preparation procedures and analytical results. While not required by every method, matrix spikes are typically analyzed 1 in 20 samples where required.

However, the frequency may also be project-specific and the QC officer should review the documents outlining the needs of the project (SAP, QAPP, etc.).

If a matrix spike does not meet acceptance criteria and is not associated with the specific project sample, no further action is required unless other systematic evidence warrants qualification.

If the native concentration of a spiked sample is significantly greater than the spike added (greater than 4 times the native concentration (>4x)), spike recovery cannot be accurately evaluated, therefore the criteria do not apply. Professional judgment should be used for percent recoveries nominally outside laboratory acceptance criteria prior to qualifying data.

Percent recoveries of matrix spikes (and matrix spike duplicates) should be calculated using the appropriate equation for percent recovery defined in the *Equations* section in the beginning of this SOP.

If laboratory or QAPP acceptance criteria are provided for the percent recoveries of matrix spikes, those criteria should be used for the evaluation of the data. If acceptance criteria are not provided, percent recoveries between 75-125% are generally acceptable for matrix spikes.

Solid samples may have highly variable concentrations of target analytes and percent recoveries (%R) may be influenced by the sampling precision and inherent sample homogeneity.

In general, matrix spikes and matrix spike duplicates may be evaluated as follows:

Table 4 – MS/MSD Recovery Guidelines

% Recovery of MS/MSD	Native Concentration	Recommended Action
<< Lower Limit (e.g. < 20%)	Non-detect	Consider qualifying with "**"
	Detected	Qualify with "*"
< Lower Limit	Non-detect	Qualify with "*"
	Detected	Qualify with "*"
Between Lower and Upper Limits	Non-detect or Detected	No qualification required
> Upper Limit	Non-detect	No qualification required
	Detected	Qualify with "*"

While matrix spike duplicates are not required by all methods, if results for MSD analyses are reported, evaluate the RPD for MS/MSD pairs using the equation for RPD evaluation in the *Equations* section in the beginning of this document. Generally, acceptance criteria for MS/MSD are <20-30% RPD for aqueous samples and <30-40% for soils/sediments, but professional judgment should be used for difficult matrices and the acceptance criteria adjusted accordingly.

VII. Overall Assessment

The chain-of-custody should be reviewed to determine if the laboratory report matches the requested analyses and that project-specific parameters were analyzed as requested. The narrative and other supporting documentation should be evaluated to ensure that sample condition was appropriately documented by the laboratory upon receipt. If available, historical data should be used to assist with data evaluation. Any additional anomalies should be documented and evaluated, if necessary.

VIII. Documentation

The QC officer performing the validation should complete a Routine Level Quality Control Report as part of the validation process, making sure that all exceedances of acceptance criteria are documented in the appropriate sections. If revised reports are required, copies should be given to the appropriate data management personnel for record maintenance.

All qualifiers, added, removed or retained, should be documented on the Control Report.

IX. Attachments

Attachment 1: QC/QA Recommendations and Requirements Chart for Water Samples
Attachment 2: QC/QA Recommendations and Requirements Chart for Soil Samples
Attachment 3: Routine Level Quality Control Report
Attachment 4: Barr Qualifiers/Footnotes
Attachment 5: Revisions to SOP

Attachment 1
QC/QA Recommendations and Requirements Chart for Water Samples

Parameter (*Alternate Name*)	Recommended Hold Time						Required Preservation						QC Requirements					
	24 Hours (or ASAP)	48 Hours	7 Day	14 Day	28 Day	180 Day	Ice Only (or ≤ 6°C)	HCl	HNO_3	H_2SO_4	NaOH	ZnAc + NaOH	Method Blank	LCS	LSCD	Duplicate	MS	MSD
Chromium VI (*Hexavalent Chromium*)	X						X						X	X				
Alkalinity, as $CaCO_3$				X			X						R	R		R	R	
Ammonia					X					X			X	X		R	X	
BOD (*Biological Oxygen Demand*)		X					X						R			R		
COD (*Chemical Oxygen Demand*)					X					X			X			R		
Chloride					X		B						X	X	O	O	X	O
Conductance, specific – *in lab*					X		X						R	R		R		
Cyanide (*CN^- as HCN*)				X							X		X	X			X	
Fluoride					X		B						X	X	O	O	X	O
Hardness						X			X				R	R		R		
Nitrate (or Nitrite) only		X					X						X	X		O	X	O
Nitrate + Nitrite					X					X			X	X			X	
Oil and Grease (HEM)					X			X[b]		X[b]			X	X			X	R
pH[a] – *in lab*			X				X							R		R		
Phosphorus, total					X					X			R	R		R	R	
Sulfate					X		X						X	X	O	O	X	O
Sulfide			X									X	R	R		R	X	
Total Dissolved Solids (*TDS*)			X				X						R	R	R	R		
Total Kjeldahl Nitrogen (*TKN*)					X					X			R	R		R	R	
Total Organic Carbon (*TOC*)					X			X[b]		X[b]			X	R		R	X	
Total Suspended Solids (*TSS*)			X				X						R	R	R	R		

a Preferably in the field, otherwise 7 days
b Either preservative may be used (to pH <2)
R Recommended QA/QC test, not method requirement
X Method requirement
O Optional requirement (one must be used)
B No preservation is required, but ice is recommended for all samples

Attachment 2
QC/QA Recommendations and Requirements Chart for Soil Samples

Parameter (*Alternate Name*)	Recommended Hold Time					Required Preservation					QC Requirements					
	24 Hours (or ASAP)	48 Hours	7 Day	14 Day	28 Day	Ice Only (or ≤ 6°C)	HCl	H_2SO_4	NaOH	ZnAc + NaOH	Method Blank	LCS	LSCD	Duplicate	MS	MSD
Chromium VI (*Hexavalent Chromium*)					X	X					X	X		O	O	
Ammonia					X			X			X	X		R	X	
Chloride					X	X					X	X	O	O	X	O
Cyanide (*CN^- as HCN*)				X					X		X	X			X	
Fluoride					X	X					X	X	O	O	X	O
Nitrate (or Nitrite) only		X				X					X	X		O	X	O
Nitrate + Nitrite					X			X			X	X			X	
pH[a] – *in lab*			X			X						R		R		
Phosphorus, total					X			X			R	R		R	R	
Sulfate					X	X					X	X	O	O	X	O
Sulfide			X							X	R	R		R	X	
Total Kjeldahl Nitrogen (*TKN*)					X			X			R	R		R	R	
Total Organic Carbon (*TOC*)					X		X[b]	X[b]			X	R		R	X	

a Preferably in the field, otherwise 7 days
b Either preservative may be used (to pH <2)
R Recommended QA/QC test, not method requirement
X Method requirement
O Optional requirement (one must be used)

Attachment 3
Routine Level Quality Control Report

Barr Project # _____	***Project Name:*** _____		
Laboratory: _____	***Sample ID Event or COC#*** _____		
Lab Report # _____	***Matrix:*** ***Soil*** _____	***Required Analysis:*** ***VOC***	_____
Report Date: _____	***Water*** _____	***SVOC***	_____
Review By: _____ ***Date:*** _____	***Air*** _____	***Metal***	_____
	Other _____	***GenChem***	_____
	Holding Times Met: ☐ ***Yes*** ☐ ***No***		
	Comments:		

Accuracy Data:	MS/MSD % Recovery Yes / No Sample ID_____	LCS/LCSD % Recovery
VOC		
SVOC		
Metals		
Other		

Precision Data:	MS/MSD RPDs, % Yes / No Sample ID_____	LCS/LCSD RPDs, %
VOC		
SVOC		
Metals		
Other		

Surrogate Standards Data		
Organics:		Inorganic Sample Dups:
VOC		Frequency: ____
SVOC		Results:

Blank Data:	Field Blank	Trip Blank (VOC Only)	Laboratory/Method Blank
VOC			
SVOC			
Metals			
Other			

Completeness Check: 100% Yes / No Comments:	**Historical Comparison:** N/A ____ Comments:

Masked/Blind Duplicate Results: **N/A**____ **Sample**_____

	Native Result	Duplicate Result	Native Result	Duplicate Result
VOC				
SVOC				
Metals				
Other				

Qualifiers/Qualifier Summary: **Yes / No** **(Note any TB, FB and MB affected)**

Sample Parameter	Add Qualifier	Remove Qualifier	Retain Qualifier

Other Actions Taken: Revised Report Requested _____	Lab Exception Report Completed: _____
Summary:	

Attachment 4
Barr Qualifiers/Footnotes

Data Qualifiers/Footnotes

--	Not analyzed/not available.
DLND	Not detected, detection limit not determined.
ND	Not detected.
AT	Sample chromatogram is noted to be atypical of a petroleum product.
a	Estimated value, calculated using some or all values that are estimates.
B	The reported value is less that the Contract Required Detection Limit (CRDL) but greater than or equal to the Instrument Detection Limit (IDL).
b	Potential false positive value based on blank data validation procedures.
c	Coeluting compound.
e	Estimated value, exceeded the instrument calibration range.
h	EPA recommended sample preservation, extraction or analysis holding time was exceeded.
I	Indeterminate value based on failure of blind duplicate data to meet quality assurance criteria.
J	Associated value is an estimate.
j	Reported value is less than the stated laboratory quantitation limit and is considered an estimated value.
p	Small peak in chromatogram below method detection limit.
r	The presence of the compound is suspect based on the ID criteria of the retention time and relative retention time obtained from the examination of the chromatograms.
s	Potential false positive value based on statistical analysis of blank sample data.
U	Not detected.
*	Estimated value, QA/QC criteria not met.
**	Unusable value, QA/QC criteria not met.

Attachment 5
Revisions to PCDOCS No.: 248821

Revision Number	Date of Revision	Section	Revision Made
2.1	02/2009	Document Wide	Edits to references, formatting; minor language additions and corrections
		Attachments	Added Attachment 5
		Attachment 1	Corrections to hold times and preservation requirements
		Attachment 2	Corrections to hold time requirements

STANDARD OPERATING PROCEDURE

for Routine Level Polychlorinated Biphenyls (PCB), Aroclor™, Pesticide and Herbicide Data Validation

PCDOCS No.: 248817

Revision 1.1

March 16, 2009

Approved By:	Michael Dupay		03-16-09
	Print QA Manager(s)	Signature	Date

Barr Engineering Company
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Annual Review of the SOP has been performed
and the SOP still reflects current practice.

Initials:	_____	Date:	_____
Initials:	_____	Date:	_____
Initials:	_____	Date:	_____
Initials:	_____	Date:	_____
Initials:	_____	Date:	_____

Standard Operating Procedures for Routine Level Polychlorinated Biphenyls (PCB), Aroclor™, Pesticide and Herbicide Data Validation

Purpose

This SOP is intended as a guidance document for the routine level validation of polychlorinated biphenyls (PCBs), Aroclor™, herbicide and pesticide data provided by laboratories to be used in Barr Engineering Company (Barr) projects or by Barr clients.

Applicability

This SOP applies to routine level PCB, Aroclor™, herbicide and pesticide data validation by the analytical methods including, but not limited to:

- GC/ECD for Pesticides (EPA Methods 608/8081B)
- GC/ECD or GC/ELCD for PCBs/Aroclor™ (EPA Method 8082A)
- GC/FPD or GC/NPD for Organophosphorous Compounds (EPA Method 8141B)
- GC/ECD for Herbicides (EPA Method 8151A)

Validation of Contract Laboratory Program (CLP) data should be performed in accordance with to the *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (June 2008)*.

Definitions

Aroclor™. A trademarked name for a mixture of polychlorinated biphenyls (PCBs) used in a variety of applications including additives in lubricants, heat transfer dielectric fluids, adhesives, etc.

Blank. An analytical sample designed to assess specific sources of contamination. See individual definitions for types of blanks.

Contamination. A component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

Field Blank. A blank used to provide information about contaminants that may be introduced during sample collection.

Herbicide. Any substance, or mixture of substances, intended to prevent the growth of or to destroy terrestrial or aquatic weeds. Weeds are any woody or non-woody undesirable vegetation.

GC/ECD. Gas Chromatography/Electron Capture Detector. Measures electron capturing compounds (usually halogenated) by creating an electrical field in which molecules exiting a GC column can be detected by the drop in current in the field. Identifies potential compounds based on retention time in a GC column, but the identification of the compound is not selective with one detector. Additional conformational analyses must be performed (either GC/MS or a separate GC/ECD with a different stationary phase on the column).

GC/FPD. Gas Chromatography/Flame Photometric Detector. The flame photometric detector (FPD) measures sulfur and phosphorus containing compounds, measuring chemiluminescent reactions from these compounds in a hydrogen / air flame.

GC/MS. Gas Chromatography/Mass Spectrometry (sometimes Mass Selective Detector (MSD)). An analytical technique used to measure the mass-to-charge ratio of ions. A MS detector can selectively identify a compound based on the compound's mass-to-charge ratio and generally does not require secondary confirmation.

GC/NPD. Gas Chromatography/Nitrogen-Phosphorus Detector. The nitrogen phosphorus detector (NPD) is a highly sensitive but specific detector similar to an FID. It gives a strong response to organic compounds containing nitrogen and/or phosphorus.

GC/PID. Gas Chromatography/Photoionization Detector. Uses ultraviolet light to ionize analyte exiting from a GC column. The resultant electrical charge produces a measurable current on a detector.

Initial Calibration. Analysis of analytical standards at different concentrations to define the linear range of an analytical instrument.

Instrument Blank. A blank designed to determine the level of contamination either associated with the analytical instruments, or resulting from carryover.

Laboratory Control Sample (LCS). The LCS is an internal laboratory Quality Control (QC) sample designed to assess the capability of the laboratory to perform the analytical method.

Matrix. The predominant material of which the sample to be analyzed is composed.

Matrix Effect. In general, the effect of a particular matrix on the constituents with which it contacts. Matrix effects may prevent efficient purging/extraction of target analytes, and may affect DMC and surrogate recoveries. In addition, non-target analytes may be extracted from the matrix causing interferences.

Matrix Spike (MS). Aliquot of the sample fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

Matrix Spike Duplicate (MSD). A second aliquot of the same sample that is fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to determine precision of the method.

Method Blank. A reagent aqueous sample spiked with internal standards, and surrogate standards (or DMCs), that is carried throughout the entire analytical procedure. The method blank is used to define the level of contamination associated with the processing and analysis of samples.

Narrative. The portion of the data package which includes laboratory, contact person, sample number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution.

NELAP. National Environmental Laboratory Accreditation Program. NELAP adopts standards (e.g. rules) that are based on the International Organization for Standardization (ISO) and are developed through a consensus process. Oversight is provided by the NELAP Board which consists of one representative and one alternate from each of the recognized accreditation bodies.

PE Sample. Performance Evaluation Sample. A reference sample provided to a laboratory for the purpose of demonstrating that the laboratory can successfully analyze the sample within limits of performance specified.

PT Sample. Proficiency Testing Sample. A sample, the composition of which is unknown to the laboratory and is provided to test whether a laboratory can produce analytical results within the specified acceptance criteria. Required for accreditation by MN Rules and NELAP.

Pesticide. Any substance or mixture of substances intended for preventing, destroying, repelling, or lessening the damage of any pest.

Polychlorinated Biphenyls (PCBs). A group of toxic, persistent chemicals used in electrical transformers and capacitors for insulating purposes, and in gas pipeline systems as a lubricant. The sale and new use of PCBs were banned by law in 1979.

QAPP. Quality Assurance Project Plan. A formal document describing in comprehensive detail the necessary quality assurance (QA), quality control (QC), and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria.

QA/QC. Quality Assurance/Quality Control.

Retention Time (RT). The time a target analyte is retained on a Gas Chromatograph (GC) column before elution. The identification of a target analyte is dependent on a target compound's RT falling within the specified RT Window established for that compound. The RT is dependent on the nature of the column's stationary phase, column diameter, temperature, flow rate, and other parameters.

SAP. Sampling and Analysis Plan. The purpose of the SAP is to ensure that sampling data collection activities are comparable to and compatible with previous data collection activities performed at the site and to document the details of all field activities and laboratory analyses prior to the work being conducted.

Sample Delivery Group (SDG). Identifies a group of samples for delivery, A sample delivery group is defined by the following, whichever is most frequent:

- Each set of field samples received; or
- Each 20 field samples within a sampling event; or
- Each 7 calendar day period (3 calendar day period for 7-day turnaround) during which field samples are received.

Semi-Volatile Organic Compounds (SVOC). An organic compound which has a boiling point higher than water and which may vaporize when exposed to temperatures above room temperature. Semi-volatile organic compounds include phenols and polynuclear aromatic hydrocarbons (PAH).

Surrogates (Surrogate Standard). Compounds added to every blank, sample, including Laboratory Control Sample (LCS/LCSD), Matrix Spike/Matrix Spike Duplicate (MS/MSD), and standards; used to evaluate analytical efficiency by measuring recovery. Surrogates are not expected to be detected in environmental media.

TCLP. Toxicity Characteristic Leaching Procedure. A test designed to determine whether a waste is hazardous or requires treatment to become less hazardous; also can be used to monitor treatment techniques for effectiveness.

Equations

For % Recovery (%R or %Rec):

$$\%R = \frac{SSR - SR}{SA} \times 100$$

Where,

%R = % recovery
SSR = spiked sample result
SR = sample result
SA = spike added to native sample
In the case of LCS and other laboratory-prepared samples, the sample result (SR) is zero.

For RPD:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where,

RPD = relative percent difference
S = original sample result
D = duplicate sample result

References

This SOP is based on the recommendations of *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (June 2008)*, and quality control recommendations outlined in:

- **EPA Methods 608** – *"Organochlorine Pesticides and PCBs"*
- **EPA Method 8081B** – "Organochlorine Pesticides by Gas Chromatography", February 2007.
- **EPA Method 8082A –** *"Polychlorinated Biphenyls (PCBs) by Gas Chromatography"*, February 2007.
- **EPA Method 8141B –** *"Organophosphorus Compounds by Gas Chromatography: Capillary Column Technique"*, February 2007.
- **EPA Method 8151A** – *"Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization"*, December 1996.
- **EPA Method 1311** – *"Toxicity Characteristic Leaching Procedure"* July 1992.

Responsibilities

The laboratory is responsible for generating data from the samples submitted for analysis. In instances where QC criteria are not met for the analysis of samples, the laboratory is responsible for reanalysis of the samples, provided reanalysis is possible (considering matrix interference, holding times and sample volume, etc.).

The QA/QC officer is responsible for validating the data in accordance with this SOP, in addition to using professional judgment where necessary or appropriate.

Procedure

I. Hold Time and Preservation Evaluation

The purpose of hold time evaluation is to ascertain the validity of the analytical results based on the sample condition, proper preservation and the time elapsed between the date of sample collection and date of analysis.

The recommended hold time and preservation acceptance criteria are in *Table 1*.

Table 1 – Recommended Hold Times and Preservation

Compound	Matrix	Temp.	Preservative	Maximum Hold Time
PCBs/Aroclor™/ Pesticides (EPA 8081/8082)	aqueous	< 6° C	ice	7 days extraction/ addl. 40 days analysis
	sediment/ soil	< 6° C	ice	14 days extraction/ addl. 40 days analysis
PCBs/Pesticides (EPA 608)	aqueous	< 6° C	ice (if >72 hrs to extraction, preserve to pH 5-9 with NaOH and/or H_2SO_4)	72 hours extraction unpreserved/ 7 day extraction preserved/ addl. 40 days analysis
Herbicides (EPA 8151)	all matrices	< 6° C	ice	7 day extraction/ addl. 40 days analysis

If samples do not meet hold time, preservation and extraction/analysis recommendations in *Table 1*, consider qualification with an "**h**". Other matrices, such as product samples (e.g. oil) may not be necessarily be subjected to the same hold time recommendations.

It is noted that the temperature of sample upon laboratory receipt may exceed the recommended temperature if the sample was collected the same day or shortly before receipt by the laboratory. While Minnesota requires that samples are stored and received on ice this may have little impact on the temperature of samples collected within five (5) hours before submission to the laboratory. Other states may have additional or different requirements. Use professional judgment when evaluating the application of qualifiers in these cases.

Professional judgment should be applied (considering matrix and magnitude of exceedence, etc.) when evaluating the application of qualifiers when criteria are not met.

II. Blanks

Blank evaluation is conducted to determine the existence and magnitude of target analyte contamination as a result of activities in the field during collection and transport or from inter-laboratory sources.

- For each matrix, at least one method blank should be prepared and analyzed with each sample delivery group, or each batch digested (whichever is more frequent).
- The laboratory should analyze a method blanks at least once every 20 samples.
- Field blank collection and analysis frequency is project-specific.

Professional judgment regarding the usability of the data should be used in cases where gross detections of target analytes are found in the method blank. In such cases, it may be appropriate to qualify the affected data with "******" (usable value, QA/QC criteria not met).

Table 2 – Guidelines for the Evaluation of Blank Contamination

Sample Result	Recommended Action
Non-detect	No action required
<5x blank concentration	Qualify with "**b**"
>5x blank concentration	Use professional judgment
Gross contamination	Qualify associated samples with "******"

Note: "******" indicates that the reported value is unusable and QA/QC criteria were not met;
"b" indicates the reported value may be a potential false positive based on blank data validation procedures.

III. Surrogates Standards

Recovery limit guidelines are presented in the table below. Keep in mind that the laboratory may have different limits and compounds than those recommended. Recommended surrogate compounds are in *Tables 6 and 7* in ***Section IX*****.** Laboratory or QAPP assigned limits should be used where provided.

All samples (blanks, spiked samples, project samples, QC samples) should contain surrogates. If a sample does not contain surrogates, professional judgment should be used to determine if the reported results are useable or not. Acceptable evaluation of surrogate spikes may not be applicable if dilution of the sample was required.

Table 3 – Guidelines for Surrogate Standard Recoveries			
Analysis	**Sample Concentration**	**Surrogate recovery**	**Recommended Action**
PCB/ Aroclor™/ Pesticides/ Herbicides	Non-detect	< 10% recovery	Qualify associated compounds with "**"
		< lower recovery limit	Qualify associated compounds with "*"
		Within or > acceptance criteria	No action
	Detections above reporting limits	< lower recovery limit	Qualify associated compounds with "*"
		Within acceptance criteria	No action
		> upper recovery limit	Qualify associated compounds with "*"

Note: "*"indicates that the reported value is estimated and QA/QA criteria were not met;
"**" indicates that the reported value is unusable and QA/QC criteria were not met.

In instances where surrogate recoveries are marginally outside acceptance criteria (within 10% of recovery limits), additional consideration should be given to historical results (where available) and general recovery trends in related samples of the same report before qualifying the sample.

IV. Laboratory Control Samples (LCS)

The laboratory control sample is used to monitor the overall performance of each step during analysis, including sample preparation. Per method (laboratories may have developed other acceptable QC measures), LCSs should be analyzed:

- Once every preparation batch
- Once for each matrix

Laboratory control samples contain a known amount of each target compound and the percent recoveries are evaluated based either on the laboratory's internally generated acceptance windows or default method criteria (as presented in *Table 4*). Herbicides do not currently have EPA-recommended recovery acceptance criteria. For the purposes of this SOP, use the recommended guidelines for LCS spike recoveries of PCBs/Aroclor™ to evaluate data (50-150% recoveries are acceptable).

Table 4 – Guidelines for Laboratory Control Sample Recoveries		
Analysis	**Acceptance Criteria**	**Recommended Action**
PCBs/Aroclor™	50-150% recovery (Aroclor™ 1016 and Aroclor™ 1260 are the recommended spike compounds)	if LCS > 150% & samples are non-detect, no action; if detections, qualify with "*"
		if LCS < 50%, qualify samples with "*****"
		if LCS < 10%, qualify detects with "*****" qualify non-detects with "******"
Pesticides	See Table 6 in **Section IX** for EPA-recommended compounds and recoveries	if LCS > upper limit & samples are non-detect, no action; if detections, qualify with "*"
		if LCS < lower limit, qualify samples with "*****"
		if LCS < 10%, qualify detects with "*****" qualify non-detects with "******"

Note: "*****"indicates that the reported value is estimated and QA/QA criteria were not met;
"******" indicates that the reported value is unusable and QA/QC criteria were not met.

V. Field Duplicates

Field duplicates (also known as "masked or "blind" duplicates) are used to demonstrate acceptable precision and reproducibility of results by the laboratory. Frequency of collection is project-specific. RPDs are calculated using the equation as provided in the *Equations* section found in the beginning of this SOP, and are not calculated where data is already qualified with b, U, < or **.

Acceptance criteria for field duplicates is subject to the professional judgment of the QC officer, but typically RPDs of <20-30% for aqueous samples and <30-40% for soil or sediment samples are considered acceptable. In cases where the either of samples (native or field duplicate) is non-detect for a parameter and the other corresponding sample has detectable concentrations much greater than two times (>>2x) the RL, professional judgment should be used to determine if qualification is appropriate.

It is noted that RPD results are dependent on the heterogeneity of the samples. Higher RPDs are expected when results are at or near the reporting limits and are not always indicative of poor precision. Use professional judgment when considering qualification of associated results.

VI. Matrix Spikes (MS) and Matrix Spike Duplicates (MSD)

Matrix spikes provide information about the effect of each samples' matrix may have on the sample preparation procedures and analytical results. Matrix spikes are typically analyzed at the following frequencies:

- 1 (MS/MSD pair) in every 20 samples
- 1 per preparation batch per matrix, or
- 1 per sample delivery group

However, the frequency may be project-specific and the QC officer should review the documents outlining the needs of the project (SAP, QAPP, etc.). In some cases, MS/MSD analysis is not required.

If a matrix spike does not meet acceptance criteria and is not associated with a project sample, no further action is required unless other systematic evidence warrants qualification.

If the native concentration of a spiked sample is significantly greater than the spike added (greater than 4 times (>4x)), spike recovery criteria do not apply. Professional judgment should be used for percent recoveries nominally outside laboratory acceptance criteria prior to qualifying data.

Percent recoveries of matrix spikes (and matrix spike duplicates) should be calculated using the appropriate equation for percent recovery provided in the *Equations* section in the beginning of this SOP.

Solid samples may have highly variable concentrations of target analytes and percent recoveries (%R) may be influenced by the sampling precision and inherent sample homogeneity.

In general, matrix spikes and matrix spike duplicates may be evaluated as follows:

Table 5 – Guidelines for Matrix Spike Evaluation	
Spike Result	**Recommended Action**
% recovery > upper acceptance limit	Non-detects, no qualification
	Detects, qualify with "*****"
between upper and lower limits	No qualification
% recovery is between 20% and lower acceptance limit	Non-detects, qualify with "*****"
	Detects, qualify with "*****"
% recovery is below 20%	Non-detects, use professional judgment; consider qualifying with "******"
	Detects, qualify with "*****"

While matrix spike duplicates are not required by all methods, if results for MSD analyses are reported, evaluate the RPD for MS/MSD pairs using the equation for RPD evaluation provided in the *Equations* section in the beginning of this SOP. Generally, acceptance criteria for MS/MSD are <20-30% RPD for aqueous samples and <30-40% for soils or sediments, but professional judgment should be used for difficult matrices and the acceptance criteria adjusted accordingly.

VII. Overall Assessment

The chain-of-custody should be reviewed to determine if the laboratory report matches the requested analyses and that project-specific parameters were analyzed as requested. The narrative and other supporting documentation should be evaluated to ensure that sample condition was appropriately documented by the laboratory upon receipt. If available, historical data should be used to assist with data evaluation. Any additional anomalies should be documented and evaluated, if necessary.

Note: Pesticides, herbicides, PCBs and Aroclors™ **require** additional ECD or GC/MS confirmation of tentatively identified compounds (TIC), using a separate column. This may occur at the same time as the initial analysis using a dual-column GC with an additional detector; or a second, separate analysis via EPA 8270 (See Barr SOP for SVOC Data Validation if positive detections occur). Herbicides are sufficiently identified by a single column if a GC/MS is used for analysis. If there is indication that confirmational analysis was not performed for the remaining parameters, professional judgment should be used to critically evaluate the usability of the data as reported.

VIII. Documentation

The QC officer performing the validation should complete a Routine Level Quality Control Report as part of the validation process, making sure that all exceedances of acceptance criteria are documented in the appropriate sections. If revised reports are required, copies should be given to the appropriate data management personnel for record maintenance.

All qualifiers, added, removed or retained, should be documented on the Control Report.

IX. Additional Tables

The following tables should be used for guidance purposes *only*. Priority should be given to laboratory limits and associated target compounds when provided by the laboratory. Use professional judgment before applying any of the data in the following tables to the validation process.

Table 6 – Recommended Guidance for LCS Compounds and Recovery for Pesticides

Compound	Recovery limits (%)
4,4'-DDE	50-150
Dieldrin	30-130
Endosulfan sulfate	50-120
Endrin	50-120
gamma-BHC	50-120
gamma-Chlordane	30-130
Heptachlor epoxide	50-150

Table 7 – Recommended Surrogates

Analysis	Recommend Surrogate
PCBs/Aroclor™/Pesticides	Tetrachloro-m-xylene (TCX)
	Decachlorobiphenyl (DCB)
Herbicides	2,4-Dichlorophenylacetic acid (DCAA)

X. Attachments

Attachment 1: Routine Level Quality Control Report
Attachment 2: Barr Qualifiers/Footnotes
Attachment 3: Revisions to SOP

Attachment 1
Routine Level Quality Control Report

Barr Project # _____	***Project Name:*** _____		
Laboratory: _____	***Sample ID Event or COC#*** _____		
Lab Report # _____	***Matrix:*** ***Soil*** _____	***Required Analysis:*** ***VOC***	_____
Report Date: _____	***Water*** _____	***SVOC***	_____
Review By: _____ ***Date:*** _____	***Air*** _____	***Metal***	_____
	Other _____	***GenChem***	_____
	Holding Times Met: ☐ ***Yes*** ☐ ***No***		
	Comments:		

Accuracy Data:	MS/MSD % Recovery Yes / No Sample ID_____	LCS/LCSD % Recovery
VOC		
SVOC		
Metals		
Other		

Precision Data:	MS/MSD RPDs, % Yes / No Sample ID_____	LCS/LCSD RPDs, %
VOC		
SVOC		
Metals		
Other		

Surrogate Standards Data		
Organics:		Inorganic Sample Dups:
VOC		Frequency: ____
SVOC		Results:

Blank Data:	Field Blank	Trip Blank (VOC Only)	Laboratory/Method Blank
VOC			
SVOC			
Metals			
Other			

Completeness Check: 100% Yes / No Comments:	**Historical Comparison:** N/A ____ Comments:

Masked/Blind Duplicate Results: **N/A**____ **Sample**_____

	Native Result	Duplicate Result	Native Result	Duplicate Result
VOC				
SVOC				
Metals				
Other				

Qualifiers/Qualifier Summary: **Yes / No** **(Note any TB, FB and MB affected)**

Sample Parameter	Add Qualifier	Remove Qualifier	Retain Qualifier

Other Actions Taken: Revised Report Requested _____	Lab Exception Report Completed: _____
Summary:	

Attachment 2
Barr Qualifiers/Footnotes

Data Qualifiers/Footnotes

--	Not analyzed/not available.
DLND	Not detected, detection limit not determined.
ND	Not detected.
AT	Sample chromatogram is noted to be atypical of a petroleum product.
a	Estimated value, calculated using some or all values that are estimates.
B	The reported value is less that the Contract Required Detection Limit (CRDL) but greater than or equal to the Instrument Detection Limit (IDL).
b	Potential false positive value based on blank data validation procedures.
c	Coeluting compound.
e	Estimated value, exceeded the instrument calibration range.
h	EPA recommended sample preservation, extraction or analysis holding time was exceeded.
I	Indeterminate value based on failure of blind duplicate data to meet quality assurance criteria.
J	Associated value is an estimate.
j	Reported value is less than the stated laboratory quantitation limit and is considered an estimated value.
p	Small peak in chromatogram below method detection limit.
r	The presence of the compound is suspect based on the ID criteria of the retention time and relative retention time obtained from the examination of the chromatograms.
s	Potential false positive value based on statistical analysis of blank sample data.
U	Not detected.
*	Estimated value, QA/QC criteria not met.
**	Unusable value, QA/QC criteria not met.

Attachment 3:
Revisions to PCDOCS No.: 248817

Revision Number	Date of Revision	Section	Revision Made
1.1	02/2009	Document Wide	Edits to references, formatting; minor language additions and corrections
		Attachments	Added Attachment 3