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SUMMARY PLAN

FOR

EVALUATING PILOT TEST DATA AGAINST MPHRA

Pueblo Chemical Agent-Destruction Pilot Plant (PCAPP) Project

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Table of Contents

Page

1.0 PURPOSE 7
2.0 OVERVIEW OF PILOT TEST APPROACH 7
3.0 PILOT TEST DEMONSTRATION DATA QUALITY OBJECTIVES FOR EMISSIONS SAMPLING 10
4.0 SAMPLE DESIGN 13
4.1.1 SAMPLE LOCATIONS 13
4.1.2 JUSTIFICATION OF SAMPLE DESIGN 17
4.1.3 CONTINUOUS EMISSIONS MONITORING 19
4.1.4 CRITICALITY OF MEASUREMENTS 20
5.0 DATA COLLECTION, VERIFICATION, REDUCTION, AND REPORTING 24
5.1 DATA COLLECTION AND VERIFICATION 24
5.1.1 PCAPP PROCESS DATA 24
5.1.2 FIELD SAMPLING DOCUMENTATION AND SAMPLE TRACEABILITY DOCUMENTATION 24
5.1.3 ANALYTICAL DATA PACKAGES 24
5.2 DATA REDUCTION, ASSESSMENT AND REPORTING 25
5.2.1 ASSESSMENT AGAINST MPHRA THRESHOLDS 25
5.2.2 COMPARISON OF RESULTS FROM DIFFERENT MEASUREMENT SYSTEMS 27
6.0 EXECUTION 27
7.0 ATTACHMENTS 31
8.0 REFERENCES 31

List of Tables

Page

Table 1. PTDP DQOs associated with emissions sampling 12
Table 2. Evaluation of PAS Detection Limits for 1,2-DCA and vinyl chloride, ppbv 19
Table 3. Classification of Measurements as Critical (A), Significant (B), Non-critical (process measurement) (C), or not applicable (NA– no sample) 22
Table A-1. Sample Location and Associated Process Instruments A-4
Table B-1. Nominal COPC detection limits for selected PCAPP Emissions Sampling Methods A-2

List of Figures

Page

Figure A. Overview of Pilot Test Demonstration 11
Figure B. Simplified schematic of AFA sampling. 14
Figure C. Simplified schematic of 30-day OTS and BTS OTS sampling. 15
Figure D. Simplified schematic of WRS OTS and BRS OTS sampling. 16
Figure E. Decision diagram for assessment of sample design 18
Figure F. Execution of DQOs Associated with Controlling Emissions at the AFA 29
Figure G. Execution of DQOs Associated with Controlling Emissions at the BTA 30

ACRONYMS

AFA	Agent Filtration Area
AFU	Agent Filtration Unit
ANR	agent neutralization reactor
APB	Agent Processing Building
BCFT	brine concentrator feed tank
BOX	bulk oxidizer
BRS	Brine Reduction System
BTA	Biotreatment Area
BTS	Biotreatment System
CDPHE	Colorado Department of Public Health and Environment
COPC	chemical of potential concern
1,2-DCA	1,2-dichloroethane
demo	demonstration
DL	detection limit
DQO	data quality objective
DRE	destruction and removal efficiency
EDS	Explosive Destruction System
EPA	Environmental Protection Agency
ERB	Enhanced Reconfiguration Building
HAL	high agent loading
HEPA	high-efficiency particulate air
HRT	hydraulic residence time
IFD	Integrated Facility Demonstration
JTG	Joint Test Group
LQCP	Laboratory Quality Control Plan
LSAP	Laboratory Sampling and Analysis Plan for Pilot Test Phase Operations
MDL	method detection limit
MPHRA	Multiple Pathway Health Risk Assessment
MQO	measurement quality objective
MWS	Munitions Washout System
MTU	Munitions Treatment Unit
OMP	Odor Monitoring Plan for Pilot Test Phase Operations

OTS	Off-gas Treatment System
PCAPP	Pueblo Chemical Agent-Destruction Pilot Plant
PRRS	Paint Residue Removal System
PTD	Pilot Test Demonstration
PTDP	Pilot Test Demonstration Plan
RL	reporting limit
SVOC	semivolatile organic compound
TBD	to be determined
TDG	thiodiglycol
THC	total hydrocarbon
TIC	tentatively identified compound
VOC	volatile organic compounds
WRS	Water Recovery System

1.0 PURPOSE

In support of resolving the Notice of Deficiency issued by the Colorado Department of Public Health and Environment (CDPHE) on Permit Modification #51, *Pilot Test Demonstration Plan, CDRL H002*, this white paper:

- Provides the rationale and justification for the sampling design satisfying *Pilot Test Demonstration Plan*, 24852-GPP-GYPM-00006 (PTDP) Data Quality Objectives (DQOs) associated with emissions sampling
- Defines the calculations and procedures for assessing air sampling data in PTDP DQO decision rules (e.g., planned approach to non-detect analytes)
- Defines how pilot test data can be used to support continuous operations following execution of the integrated facility demonstration (IFD).
- Provides a definition of the MPHRA threshold criterion for the Pilot Test and Operations Plans

2.0 OVERVIEW OF PILOT TEST APPROACH

Because of the use of novel and/or first-of-a-kind technologies, PCAPP's Research, Development and Demonstration Resource Conservation and Recovery Act permit allows development and testing of operating conditions during an initial pilot test phase for incorporation into the Part B permit. The pilot test phase demonstrates process facilities and equipment operate as designed, validates the underlying assumptions incorporated into the *Multiple Pathway Health Risk Assessment Report, PCAPP with EDS*, 24852-3RC-000-V0007 (MPHRA) and establishes operating parameters for the Part B Permit. As such, the PTDP incorporates testing designed to maximize operational flexibility by assessing the impact on site emissions over a range of operating conditions.

Figure A and the following paragraphs provide an overview of planned pilot test demonstration (PTD) activities. Detailed descriptions of these activities are included within the PTDP.

- Initial system ramp-up and testing through the IFD are conducted under the existing MPHRA which incorporates conservative assumptions that demonstrate anticipated emissions from PCAPP design-rate operations for 24-hrs per day do not pose a risk to the public or workers. Initial ramp-up is complete when the facility is able to demonstrate continuous operations of process systems at the maximum sustained rate (to be determined during testing with goal of design rate) for a minimum of four hours (i.e., the period of time estimated to provide sufficient detection limits to satisfy the sample design). Four hours of continuous operations

at design rate corresponds to approximately 50% of expected average daily facility throughput.

- Following system ramp-up, system demonstrations (demos) are performed to collect preliminary emissions data. These demonstrations include the Munitions Washout System (MWS) and Munitions Treatment Unit (MTU) demo and the Agent Neutralization Reactor (ANR) demo to provide an assessment of the relative contribution of the MWS/MTU and the ANR to site emissions. Data collected from these demos will be compared against calculated emission rates (i.e., *MPHRA thresholds*) derived from the current MPHRA (Tables 2-2 and Table 2-3), to assess whether PCAPP emissions are within expected ranges for normal operations.

- The Off-gas Treatment System and Agent Filtration Area (OTS/AFA) demo provides initial AFA emissions for integrated operation of agent processing systems. These data will be assessed to establish initial comparisons with MPHRA calculated emission rates as found in Table 2-2 and Table 2-3 (i.e., *MPHRA thresholds).* If concentrations of all the COPCs are below the estimated emissions used in MPHRA calculations, it will be determined that emissions meet MPHRA threshold values. If any of the COPCs exceed the estimated emissions from the MPHRA, then the MPHRA will be updated (i.e., *MPHRA update*) based on actual measured concentrations. Because Biotreatment Area (BTA) emissions data will not be available, this assessment will include currently estimated BTA emissions. Carbon sampling to determine the butane activity of filter carbon using the standard American Society for Testing and Materials (ASTM) butane activity method is conducted immediately following emissions sampling during the OTS/AFA demo. This sampling will provide an initial data point to be used in determining a correlation between emission results and the change in carbon butane activity from baseline measured prior to operations.

- Emissions sampling during subsequent test sequences, which include High Agent Loading (HAL) Testing, MTU Heel Testing, and OTS without bulk oxidizer (BOX) testing, will be assessed against *MPHRA thresholds* to identify appropriate operating conditions to meet these thresholds. This testing is contingent on results of the OTS/AFA demo satisfying performance criteria to include agent destruction and removal efficiency (DRE) and *MPHRA thresholds*. Therefore, until OTS/AFA demo results are available, facility ramp-up and test activities that may result in potentially greater source emissions than demonstrated during OTS/AFA demo (e.g., loss of paint residue removal station [PRRS] testing) will not be executed. The MTU heel test is expected to correspond to worse-case emissions from the AFA. Therefore, MTU Heel Test emissions data will be used in a second MPHRA assessmentto support continued operations following completion of the IFD. Notably, the current MPHRA assumes feed of 5 wt% heel at full facility throughput (i.e., 46.8 lb/hr) and therefore is bounding of the MTU Heel test. Two more carbon samples are collected to support correlation of change in butane activity with

observed chemicals of potential concern (COPCs) during the MTU heel test and the OTS without BOX test.

- When one of the 30-day storage tanks reaches 50% full of hydrolysate, Module 1 of the Biotreatment System (BTS), which will be operating with surrogate feed, will be transitioned to hydrolysate feed. Following this transition and the initial demonstration period of two hydraulic residence times (HRTs), preliminary COPC emissions sampling of the BTA stacks (30-day storage tank vent, BTS module 1 OTS, Water Recovery System [WRS] OTS, and Brine Reduction System [BRS] OTS) will be performed, unless odor detections have already required sampling. This emissions data will be available at approximately the same time as the MTU heel test and can therefore allow a complete assessment of site emissions against *MPHRA thresholds* (with Module 1 emissions multiplied by four to account for the remaining 3 modules). While data are being processed facility ramp-up will continue. Carbon sampling of the BTA OTS will be performed immediately following emissions sampling to support evaluation of a correlation between change in butane activity and COPC emission data.

- The establishment of a baseline and standard deviation for 1,2-dichloroethane (1,2-DCA) requires operations at full daily throughput (i.e., 100%). This nine-day test is run before and during execution of the IFD with collection of volatile organic compound (VOC) samples between banks 4 and 5 of each of the eight operating Agent Filtration Units (AFUs).

- The IFD is the final pilot test activity. Emissions sampling performed at each OTS during the IFD provides data to confirm adherence to *MPHRA thresholds* at 100% throughput at the AFA and BTA. Carbon sampling is performed at all OTSs (i.e., AFA, BTS, BRS, 30-day storage tank vent, WRS). While awaiting this final data and evaluation, PCAPP may continue to operate, at a reduced rate of throughput approved by CDPHE.

- The screening-level MPHRA will be updated, prior to full-scale operations, based on the highest obtained emissions for each emission source obtained during the pilot test activities. The MPHRA will be updated based upon actual emissions from PCAPP and EDS operations, modeled air concentrations and deposition rates resulting from PCAPP and EDS emissions, and the selected exposure scenarios in order to obtain a conservative exposure estimate (i.e., reasonable maximum exposure [RME]) and the associated potential risk and hazard. Upon review and acceptance of the results of the MPHRA, and in concert with its review of the engineering design aspects of the PCAPP and EDS, CDPHE will establish operating conditions and requirements in a final Part B Permit for full-scale operation of the units.

3.0 PILOT TEST DEMONSTRATION OBJECTIVES FOR EMISSIONS SAMPLING

The PTDP objectives associated with emissions sampling are identified in Table 1. The complete DQOs (inputs, performance criteria, and decision rules) are provided in the PTDP. Table 1 identifies the sampling activities defined to satisfy the PTDP objective.

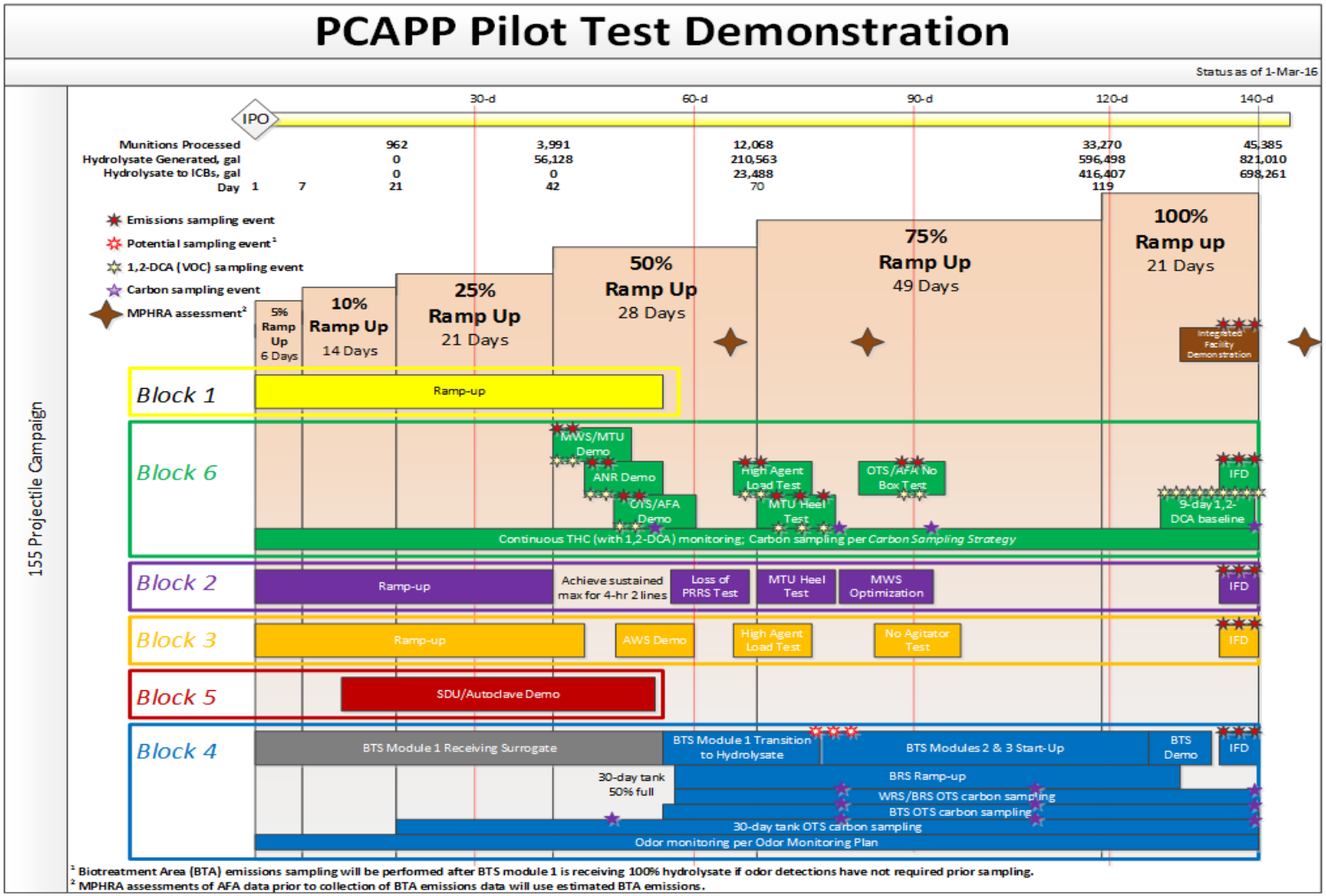


Figure A. Overview of Pilot Test Demonstration

Table 1. PTDP Emissions sampling Objectives

PTDP Block	Objective No.	Objective	Activity(ies)	Sampling Events
A2B, Munitions Treatment Unit [MTU]	A2B-1	Evaluate stack emissions under MWS process upset condition in which munitions bodies known to contain residual agent are fed to the MTU	MTU Heel Test	3 sampling events for tests at 25, 50, and 100% of 23.4 lbs/hr agent feed (i.e., ≈ 5wt% heel for 40 rounds/hr)
A4A, Biotreatment System [BTS] A4B, Brine Reduction System [BRS]	A4A-2 A4B-2	Verify the control of COPC emissions and assess odor emissions in air	Odor Monitoring and COPC sampling per *OMP* Carbon sampling per *Carbon Sampling Strategy*	Routine odor monitoring potential COPC sampling per property line odor detection or when module 1 is at 100% hydrolysate feed Carbon sampling every 30-days after on-line for first 120 days
A6, Off-gas Treatment System [OTS] and Agent Filtration Area [AFA]	A6-1	Evaluate contributions of individual systems on COPC emissions	MWS/MTU Demo ANR Demo HAL Test	2 sampling events per demo
A6, OTS and AFA	A6-2	Evaluate OTS and AFA performance with respect to agent destruction and removal efficiency (DRE) (i.e., 97% destruction and removal at the OTS and 99.9999% destruction and removal at the stack), and evaluate performance with respect to acid gases, particulates, and COPCs	OTS/AFA Demo	2 sampling events
A6, OTS and AFA	A6-3	Evaluate the role of B20 (OTS) in controlling COPC emissions	OTS/AFA without BOX	2 sampling events
A6, OTS and AFA	A6-4	Verify the Control COPC emissions	Carbon sampling Emissions sampling THC monitoring	Carbon sampling immediately following emissions sampling (e.g., OTS/AFA Demo, MTU heel test, OTS/AFA without BOX test, and IFD) THC monitoring (including 1,2-DCA and vinyl chloride) continuously
A6, OTS and AFA	A6-5	Establish baseline and standard deviation for 1,2-dichloroethane (1,2-DCA) in the filter units	9-day trial for 1,2-DCA at full daily munitions throughput	9 days, 4 hour sampling each day during sustained maximum throughput
A6, OTS and AFA	A6-7	Determine relationship of THC monitoring to emissions	Continuous THC monitoring Emissions sampling	Continuous during pilot
A7, Integrated Facility Demonstration (IFD)	A7-2	Generate and collect site-wide emissions data at the maximum achievable rate to support development of the RCRA Part B permit conditions	Integrated Facility Demonstration	3 sampling events

4.0 SAMPLE DESIGN

The Laboratory *Sampling and Analysis Plan for Pilot Test Phase Operations*, 24852-GPP-GGL-00013 (LSAP), defines the target analytes and selected sampling and analytical methods to be employed. The following paragraphs provide the rationale and justification for the proposed sampling design.

4.1.1 SAMPLE LOCATIONS

In support of the PTDP DQOs, sampling will be conducted before and after the carbon at each PCAPP emissions source (i.e., AFA, 30-day tank OTS, BTS OTS, Water Recovery System [WRS] OTS, BRS OTS). Additional sampling is planned between AFA carbon banks and between BTA lead and lag carbon adsorbers to support the DQOs. Sample locations are defined in 24852-GPP-GGI-NP001 *Environmental and Hazardous Waste Sampling*. Figures B, C and D provide an overview of the sampling design for the AFA, 30-day OTS and BTS OTS, and WRS OTS and BRS OTS, respectively.

Sample locations were selected to meet the PTDP DQOs. Although COPC sampling at the reheater would provide more concentrated results for process emissions, this location was not selected based on relative humidity and high agent content, which would complicate analysis.

Except in the case of the AFA stack where velocity will be determined in accordance with Environmental Protection Agency (EPA) Methods 1 and 2, plant instrumentation will be used to calculate total mass flow for conversion of analytical results to mass emission rates. Attachment A provides an overview of the calculations to be performed to convert measured analytical results into emission rates for evaluation within the MPHRA model.

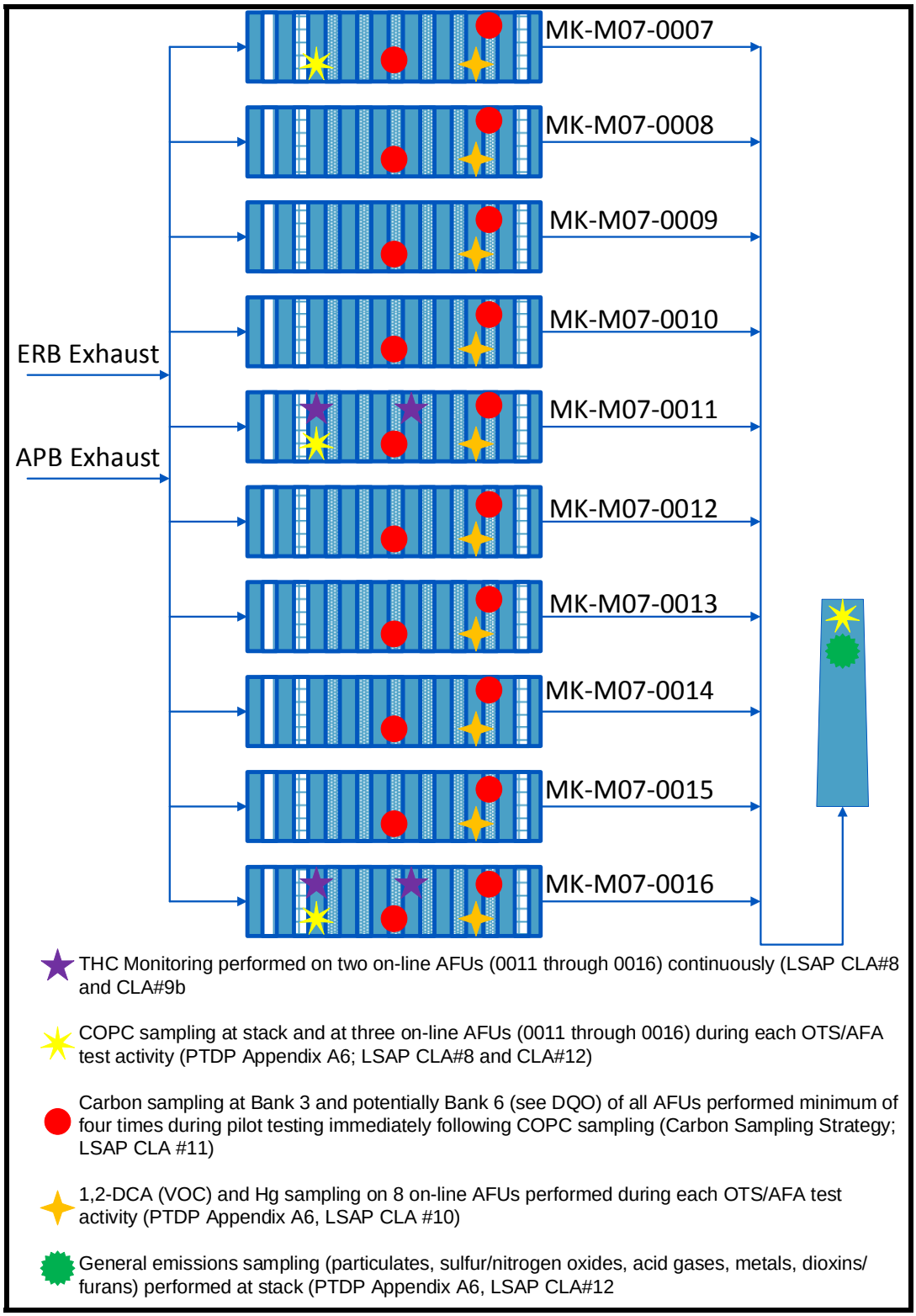


Figure B. Simplified schematic of AFA sampling.

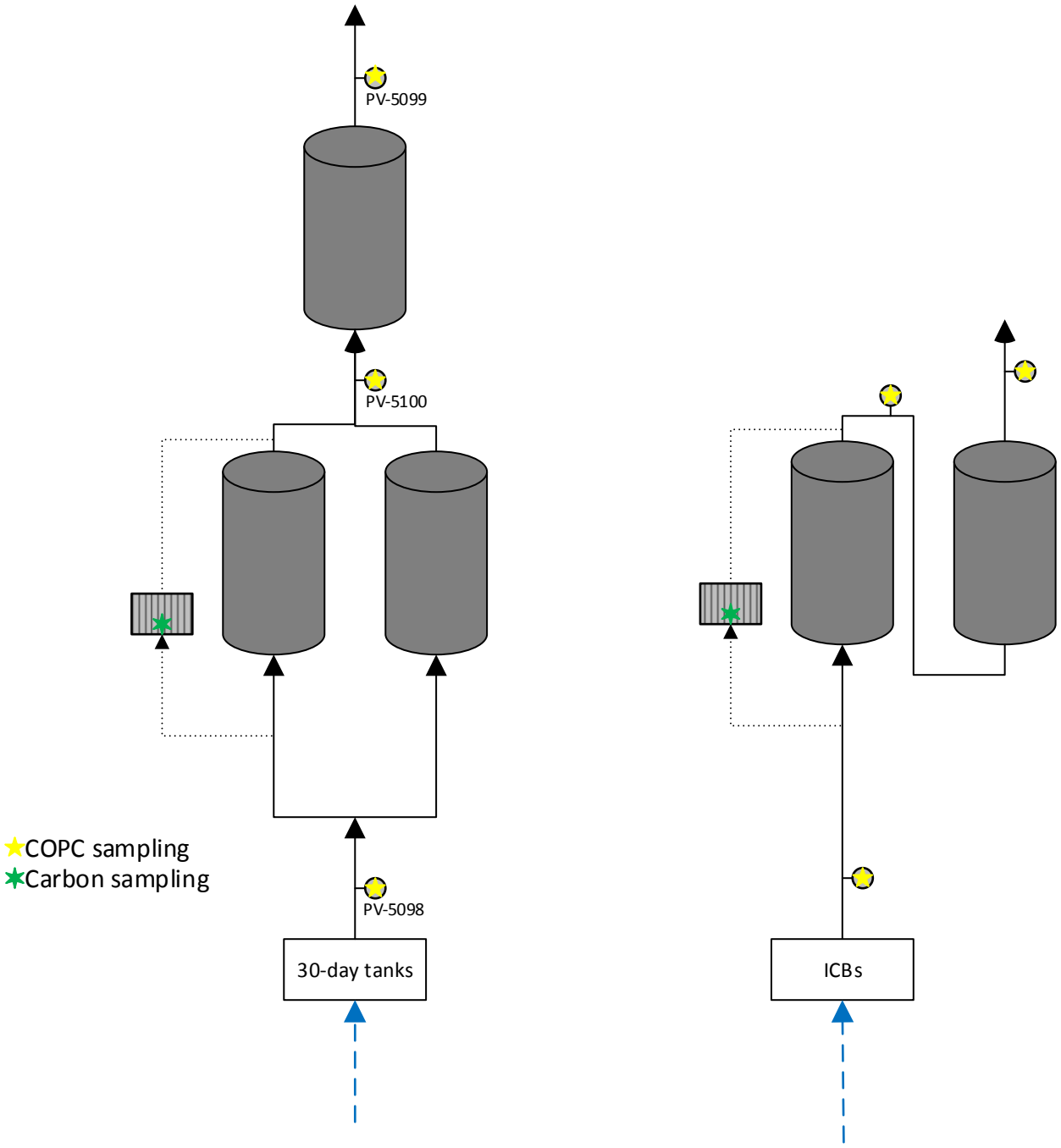


Figure C. Simplified schematic of 30-day OTS and BTS OTS sampling.

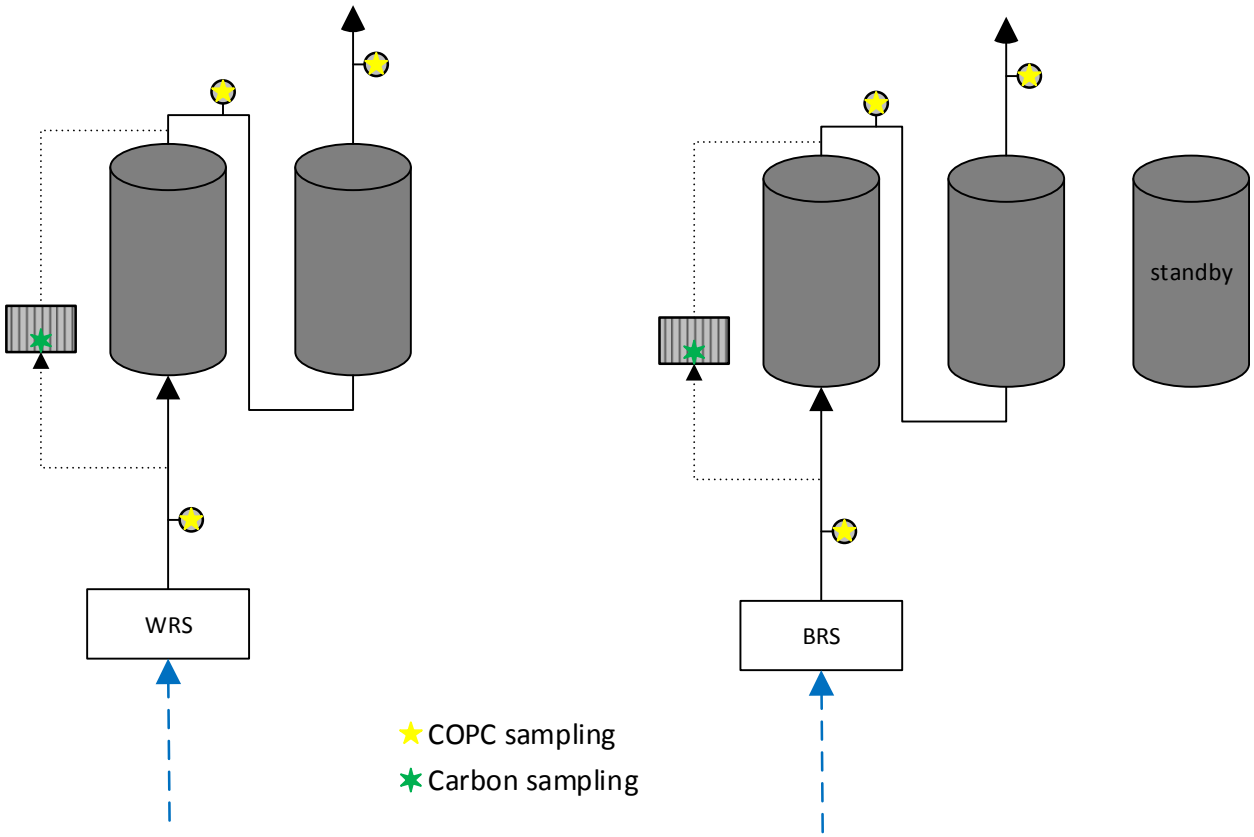


Figure D. Simplified schematic of WRS OTS and BRS OTS sampling.

4.1.2 JUSTIFICATION OF SAMPLE DESIGN

As defined in the *Multi-Pathway Health Risk Assessment Protocol for Pueblo Chemical Agent-Destruction Pilot Plant Project with Explosive Destruction System*, 24852-3RC-000-V0006, PCAPP COPCs have the following general characteristics based on the current design:

- Analytes for which high confidence of occurrence exists and emission rates are likely to be greater than their corresponding emission testing detection limit (DL)
- Analytes for which a reasonable confidence of occurrence exists and emission rates are likely to be less than their corresponding DL
- Analytes for which low confidence of occurrence exists and for which no reliable emission estimating methodology can be established.

Constituents with reasonable and high confidence of occurrence are those constituents incorporated into the MPHRA with estimated emissions calculated using observed air or liquid concentrations documented in historical programmatic data.

As discussed in Section 5, analytes for which there exists low confidence of occurrence will not be incorporated into the MPHRA assessment if they are not detected. Analytes with a reasonable confidence of occurrence which are not detected during emissions sampling will be incorporated into the MPHRA at the DL. The decision diagram included in Figure E was used to evaluate whether the nominal DLs for the selected methods (Attachment B) would provide sufficient resolution to satisfy PTDP DQOs. Results of this assessment indicated that the selected analytical methods are adequate to assess PTDP DQOs related to MPHRA thresholds (Tables 2-2, and 2-3).

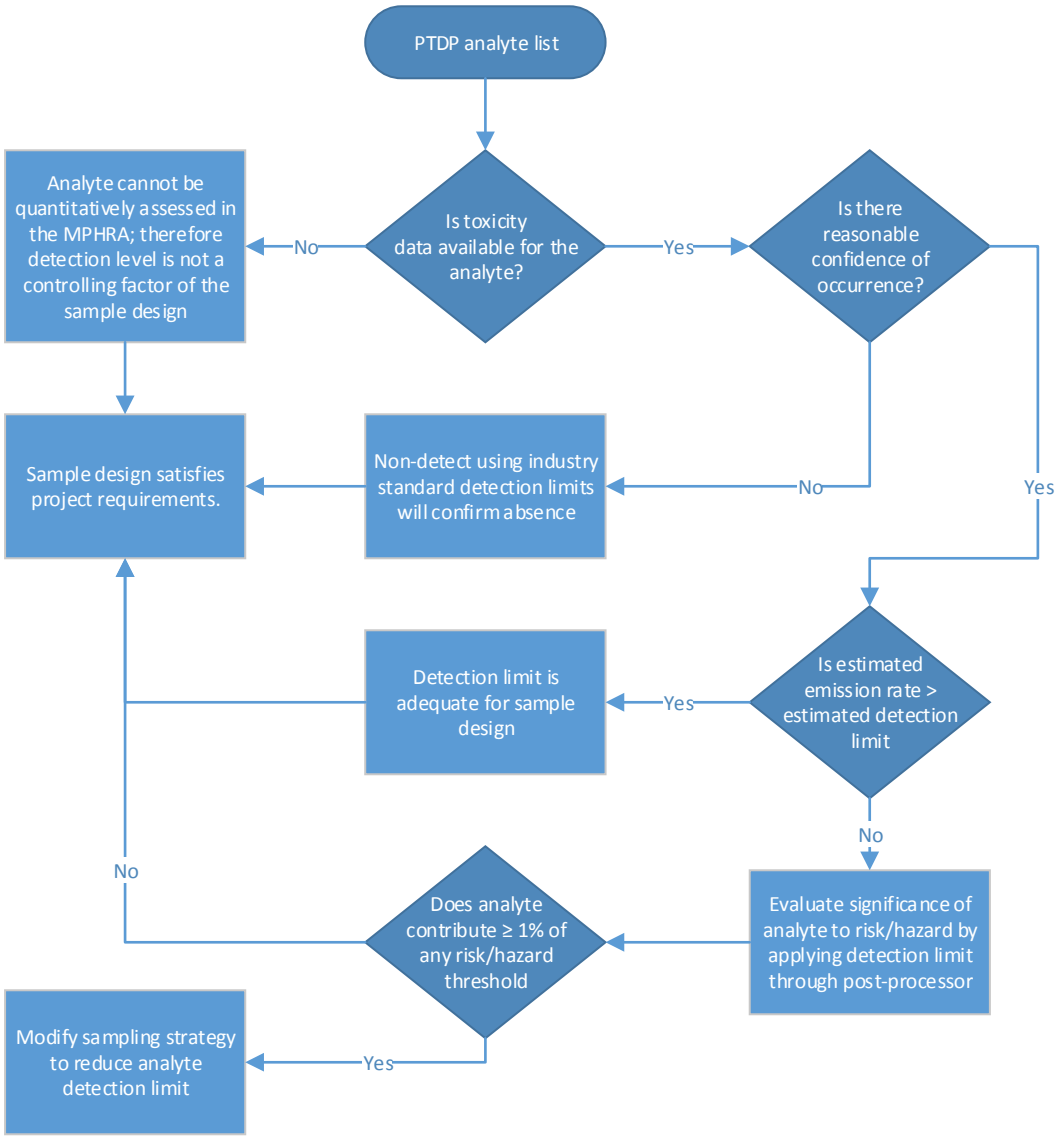


Figure E. Decision diagram for assessment of sample design

4.1.3 CONTINUOUS EMISSIONS MONITORING

Total hydrocarbon (THC) monitoring will be performed using photoacoustic spectrometry (PAS) in lieu of a conventional flame ionization detector. This technology will allow continuous emission monitoring of THC at a lower detection limit with correction for contributions from methane, water, and carbon dioxide and the potential to continuously monitor for 1,2-DCA and vinyl chloride. As summarized in Table 3, the estimated limit of detection for 1,2-DCA (approximately 100 ppbv with a 50 second integration time) and vinyl chloride (approximately 70 ppbv with a 50 second integration time) are insufficient to provide reliable data for expected emissions rates based on vapor-liquid equilibria calculations (i.e., 100 ppbv for 1,2-DCA and 0.7 ppbv for vinyl chloride as calculated from emission rates provided in Calculation 24852-RD-M5C-000-B0004, PCAPP Emissions Calculation). However, the instrument may be capable of reliably detecting 1,2-DCA and vinyl chloride at the concentrations applied in the MPHRA which used Aberdeen Chemical Agent Disposal Facility (ABCDF) emissions data (i.e., 130 ppbv for 1,2-DCA and 210 ppbv for vinyl chloride) and will be capable of providing reliable real-time monitoring of concentrations that could result in emissions exceeding a risk or hazard threshold (i.e., concentrations 28 times greater than MPHRA emissions for 1,2-DCA or 7 times greater than MPHRA emissions for vinyl chloride).

Table 2. Evaluation of PAS Detection Limits for 1,2-DCA and vinyl chloride, ppbv

	Estimated detection limit (5-s integration time)*	Estimated detection limit (50-s integration time)*	Calculated vapor-liquid emission concentration (Calc RD-M5C-000-B0004)	Concentration for emissions rate used in PCAPP MPHRA	Estimated concentration resulting in exceedance of risk/hazard threshold**
1,2-DCA	300	100	100	130	3,640
Vinyl chloride	200	70	0.7	210	1,470

* Estimated values provided during teleconference with Dr. Jason Midyett, California Analytical Instruments, Inc. regarding the Innova 1412i Photoacoustic Gas Analyzer. Estimated detection limits assume a 981 cm^{-1} optical filter for 1,2-DCA, a 977 cm^{-1} optical filter for vinyl chloride, and correction for water and carbon dioxide. However, the estimated detection limits do not consider potential matrix interferences.

** These estimated concentrations are derived by holding all other MPHRA COPCs constant at the levels estimated in the current MPHRA and iteratively increasing either 1,2-DCA or VC total emissions (all source groups) until a risk/hazard threshold is reached.

Analyzers will be installed in two positions (between the high efficiency particulate air [HEPA] filter and Carbon Bank #1 and between Carbon Bank #3 and Bank #4) within two of the ten AFUs (MK-M07-0011 through and MK-M07-0016). The analyzers will be moved as required during testing to ensure analyzers are installed in two on-line AFUs at all times during pilot testing (see *PCAPP Position Paper on Total Hydrocarbon Monitoring During Pilot Test Demonstration*, 24852-30H-000-V0003). The location of

THC monitors will allow evaluation of continuous THC monitoring for identification of potential facility upset conditions resulting in increased emissions and determination of carbon activity. The monitors are also expected to provide continuous monitoring demonstrating that 1,2-DCA and vinyl chloride emissions remain below levels that would result in exceeding a long-term risk/hazard threshold if maintained over the complete operating period.

Although a carbon dioxide monitor will be installed at the exhaust of the MTUs, this monitor is solely associated with identification of MWS process upsets and will not be used to satisfy PTDP DQOs associated with MPHRA thresholds.

4.1.4 CRITICALITY OF MEASUREMENTS

Although it is the intention of PCAPP to collect valid measurements for all data indicated in the PTDP and LSAP, loss of a single data point or test iteration for a specific activity may not warrant expenditure of resources to repeat the test iteration to satisfy PCAPP DQOs. Loss of a single data point or test iteration could result from a sample collection failure or if process conditions specified for the test iteration are not met during any particular test (e.g., throughput below target or site alarm in progress). In order to support rapid decision making during pilot test operations versus convening the JTG to determine whether the test will be repeated, PCAPP has defined the criticality of each emissions sampling measurement (see Table 3). For example, although the data collected during initial system demonstrations may be useful in defining final permit conditions, in the event site emissions result in exceeding an MPHRA threshold, these data are not necessarily essential for demonstrating PCAPP emissions are below MPHRA thresholds and therefore may not warrant repeating the testing. PCAPP understands that continuation of pilot test operations, without obtaining all “non-essential” anticipated data points, is conducted at risk and may impact CDPHE’s ability to fully assess PCAPP’s requested operational preferences. This may result in CDPHE approving more restrictive operational requirements to ensure for adequate protection of human health and the environment. Alternatively, data collected from the OTS/AFA demo are essential to demonstrate site emissions remain within MPHRA thresholds under normal design conditions and are required to proceed to subsequent off-normal testing (see Section 5). Table 2 uses the following classification:

- A = Critical Measurement: Test data is essential for satisfying a PTDP DQO and/or in supporting a decision required to proceed with pilot test activities. If data are not collected or if collected data do not meet measurement quality objectives (MQO), the test will be repeated.

- B = Significant measurement: Test data are required to satisfy a PTDP DQO; however, other collected measurements may be available to satisfy the DQO or the overall significance of the DQO does not support the potential project risk (e.g., to cost, schedule) for repeating the test activity. If data are not collected or if collected data do not meet MQO, evaluate other data collected and perform

analysis of potential risks and benefits to determine if test needs to be repeated to collect lost data.

- C = Process measurement: Test data are required to satisfy an operational DQO (i.e., not a DQO associated with permitting or Army requirements as defined in Table 2-1 of the PTDP) or are collected to support PCAPP Process understanding. If data are not collected or data do not meet MQO, the test need not be repeated to collect lost data.

This table will address only random errors resulting in loss of a measurement. Identification of systematic errors resulting in loss of multiple measurements will be addressed per site procedures before proceeding with testing.

Table 3. Classification of Measurements as Critical (A), Significant (B), Non-critical (process measurement) (C), or not applicable (NA– no sample)

Sample Location	Analyte Group	PTDP DQO	Criticality Category										
			Activity	Background	OTS/AFA-MWS/MTU Demo	OTS/AFA-ANR Demo	OTS/AFA-OTS/AFA Demo	HAL Test	MTU Heel Test	BTA Start-up**	No-Box Test	9-day baseline	IFD
			Iterations	3	2	2	2	3	2	3	2	9	3
Upstream of Preheater	HD	A6-2		C	C	C	A	C	NA	NA	B	NA	A
Between Box and Venturi	HD	NA		C	C	C	C	C	NA	NA	C	NA	C
Between OTS Reheater and Blowers	HD	A6-2		C	C	C	A	C	NA	NA	B	NA	A
AFA - HEPA/Bank 1	HD	NA		B	C	C	B	B	B	NA	B	B	B
	COPCs*	A2B-1, A6-1, A6-2, A6-3, A6-4, A6-7		B	C	C	A	B	A	NA	A	NA	A
	THC	A6-4, A6-7		A	C	C	A	A	A	NA	NA	B	A
AFA - Bank 1/2	HD	NA		C	A	A	A	A	A	NA	A	A	A
AFA - Bank 2/3	HD	NA		C	B	B	B	B	B	NA	B	B	B
AFA - Bank 3	butane activity	A6-4		A	NA	NA	A	NA	A	NA	NA	NA	A
AFA - Bank 3/4	THC	A6-4		A	C	C	A	A	A	NA	A	B	A
AFA - Bank 5/6	1,2-DCA (VOC)	A6-5		C	C	C	A	B	A	NA	A	A	A
	mercury –vapor	A6-2		B	C	C	B	B	A	NA	B	NA	A
	mercury - particulate	A6-2		C	C	C	C	C	C	NA	C	NA	C
AFA - Bank 6	butane activity	A6-4		B	NA	NA	B	NA	NA	NA	B	NA	B
AFA Stack	HD	A6-2		C	C	C	A	B	A	NA	A	B	A
	COPCs*	A2B-1, A6-1, A6-2, A6-3, A6-4, A6-7, A7-2		A	C	C	A	B	A	NA	A	A (VOC)	A
	Dioxins/Furans	A6-4, A7-2		A	C	C	A	B	A	NA	A	NA	A
	Metals	A6-4, A7-2		A	C	C	A	B	A	NA	B	NA	A
	mercury	A6-4, A7-2		A	C	C	A	B	A	NA	B	NA	A

*COPCs correspond to the analytes defined in the LSAP for each sampling location. For the 9-day baseline, COPC sampling at the stack will be limited to VOCs.
** Prior to the IFD, BTA emissions sampling will be performed in response to odor detections (see OMP) or after BTS Module 1 is transitioned to hydrolysate.

Sample Location	Analyte Group	PTDP DQO	Criticality Category										
			Activity	Background	OTS/AFA-MWS/MTU Demo	OTS/AFA-ANR Demo	OTS/AFA-OTS/AFA Demo	HAL Test	MTU Heel Test	BTA Start-up**	No-Box Test	9-day baseline	IFD
			Iterations	3	2	2	2	3	2	3	2	9	3
AFA Stack (cont.)	sulfur/nitrogen oxides, particulates	A6-4, A7-2		A	C	C	A	B	A	NA	B	NA	A
30-day tanks - Pre-carbon	COPCs*	A4A-2		B	NA	NA	NA	NA	NA	A	NA	NA	A
30-day tank - carbon	butane activity	A4A-2		A	NA	NA	NA	NA	NA	A	NA	NA	A
30-day tank – between carbon	COPCs*	A4A-2		C	NA	NA	NA	NA	NA	C	NA	NA	C
30-day tanks - Post-carbon	COPCs*	A4A-2, A7-2		A	NA	NA	NA	NA	NA	A	NA	NA	A
BTS (each module) - Pre-carbon	COPCs*	A4A-2		B	NA	NA	NA	NA	NA	A	NA	NA	A
BTS (each module) - carbon	butane activity	A4A-2		A	NA	NA	NA	NA	NA	A	NA	NA	A
BTS (each module) – between carbon	COPCs*	A4A-2		C	NA	NA	NA	NA	NA	C	NA	NA	C
BTS (each module) - post-carbon	COPCs*	A4A-2, A7-2		A	NA	NA	NA	NA	NA	A	NA	NA	A
WRS - Pre-carbon	COPCs*	A4B-2		B	NA	NA	NA	NA	NA	A	NA	NA	A
WRS carbon	butane activity	A4B-2		A	NA	NA	NA	NA	NA	A	NA	NA	A
WRS – between carbon	COPCs*	A4B-2		C	NA	NA	NA	NA	NA	C	NA	NA	C
WRS - Post-carbon	COPCs*	A4B-2, A7-2		A	NA	NA	NA	NA	NA	A	NA	NA	A
BRS - Pre-carbon	COPCs*	A4B-2		B	NA	NA	NA	NA	NA	A	NA	NA	A
BRS carbon	butane activity	A4B-2		A	NA	NA	NA	NA	NA	A	NA	NA	A
BRS – between carbon	COPCs*	A4B-2		C	NA	NA	NA	NA	NA	C	NA	NA	C
BRS - Post-carbon	COPCs*	A4B-2, A7-2		A	NA	NA	NA	NA	NA	A	NA	NA	A

*COPCs correspond to the analytes defined in the LSAP for each sampling location. For the 9-day baseline, COPC sampling at the stack will be limited to VOCs.
** Prior to the IFD, BTA emissions sampling will be performed in response to odor detections (see OMP) or after BTS Module 1 is transitioned to hydrolysate.

5.0 DATA COLLECTION, VERIFICATION, REDUCTION, AND REPORTING

The following paragraphs define the data collection, reduction, verification, validation and reporting to be completed for emissions sampling.

5.1 DATA COLLECTION AND VERIFICATION

Data collection will include PCAPP process data, field sampling documentation, sample traceability documentation, and analytical data packages. Each of these must be collected, compiled, and assessed for subsequent data reduction.

5.1.1 PCAPP PROCESS DATA

PCAPP process data will include stack parameter data, process parameters identified in Attachment A, and site operating conditions (i.e., systems operational, throughput, and key operating parameters defined in the PTDP). These data are required for proper evaluation of the data collected. If site operating conditions required for execution of testing are not maintained during sample collection it may be necessary to repeat the test (see Table 3). Stack parameter data and process parameters are required to assess the analytical data against the MPHRA (Attachment A).

Process parameters will be collected immediately following testing for the sample collection period and averaged to provide values to be used in subsequent calculations (Attachment A). Data outliers (as defined by an appropriate statistical test such as the Grubbs test, also known as the maximum normed residual test) will be excluded from the average. Process data outliers will be assessed separately for each test phase rather than against the cumulative pilot test operating record.

5.1.2 FIELD SAMPLING DOCUMENTATION AND SAMPLE TRACEABILITY DOCUMENTATION

Field sampling documentation will be collected immediately following sampling and reviewed for omissions and/or errors. If errors are identified, it may be necessary to repeat the test (see Table 3).

5.1.3 ANALYTICAL DATA PACKAGES

The analytical data packages submitted by the lab will incorporate raw data for specific samples to allow independent verification of the reported results. Results will provide the relevant reporting limits (e.g., DL, method detection limit [MDL], and/or reporting limit [RL]) for each sample. Data packages will also identify data failing to meet MQOs. These failures will be evaluated against Table 3 to determine whether testing needs to be repeated. Final validation of data will consider evidence of field or laboratory contamination.

5.2 DATA REDUCTION, ASSESSMENT AND REPORTING

The compiled data in Section 5.1 must be assessed against the established PTDP DQO. This will include two primary assessments:

1) Assessment against *MPHRA thresholds*

2) Comparison of results from different measurement systems.

Each is addressed further in the following paragraphs.

5.2.1 ASSESSMENT AGAINST MPHRA THRESHOLDS AND CDPHE MPHRA BENCHMARK

Assessment of PCAPP pilot test data against the MPHRA will follow three distinct testing events during Pilot Test Demonstrations. A hold point will be employed at each MPHRA evaluation, until it can be verified by PCAPP, and approved in writing by CDPHE, that it is safe to proceed with the next phase of test demonstrations. MPHRA evaluations will occur after the OTS/AFA Demonstration, the MTU Heel Test, and following the Integrated Facility Demonstration (IFD). Preliminary MPHRA comparisons may not include updated stack parameters and may include estimated BTA emissions as opposed to measured emissions.

Following the OTS/AFA demonstration and the MTU Heel Test, test data will be compared against the estimated MPHRA calculated emission rates found in Table 2-2 and Table 2-3 of the MPHRA (i.e., MPHRA thresholds). If concentrations of all the COPCs are below the estimated emissions used in MPHRA calculations, it will be determined that emissions meet MPHRA threshold values. If any of the COPCs exceed the estimated emissions from the MPHRA, then the MPHRA will be updated (i.e., MPHRA Assessment) based on actual measured concentrations. The assessment against MPHRA thresholds will involve the incorporation of stack parameters and emission rates calculated from the analytical data (Attachment A) into the MPHRA model.

Following the IFD, the MPHRA will be updated based on the highest observed emissions for each COPC at each emission source from all testing phases. The MPHRA will be updated (i.e., MPHRA Assessment) based upon actual emissions from PCAPP and EDS operations, modeled air concentrations and deposition rates resulting from PCAPP and EDS emissions, and the selected exposure scenarios in order to obtain a conservative exposure estimate (i.e., reasonable maximum exposure [RME]) and the associated potential risk and hazard.

Results from the MPHRA assessments will be compared against the acceptable CDPHE risk and hazard benchmarks identified within the MPHRA. (CDPHE MPHRA benchmark). The “CDPHE MPHRA benchmark” is a maximum estimated lifetime cancer risk to any human receptor of a risk level of 1 in a million (i.e., 1.0 E-06), a maximum

estimated combined Hazard Index (HI) to any human receptor of 0.25, or a total acute HI for any receptor of 1.0. The following rules will be applied for all data collected:

- Non-Detects: If there was reasonable confidence of occurrence (see Section 4.1.2) the non-detected analyte will be incorporated into the MPHRA at an emission rate corresponding to the DL. If there was no reasonable confidence of occurrence, a non-detected analyte will not be incorporated into the MPHRA.

- Tentatively Identified Compounds (TICs): If the TIC is likely to be related to PCAPP operations per 24852-GPP-GGL-LP012 *Data Review and Qualification*, and toxicity data are available, it will be incorporated into the MPHRA assessment at the estimated concentration.

- Blanks: If analytes are detected in samples at less than the concentration detected in the field or laboratory blanks, and the analytes are not considered to be associated with PCAPP operations they will be excluded from assessment in the MPHRA.

- J-flags: J-flagged data will be incorporated into the MPHRA assessment unless invalidated by a prior rule (i.e., TIC, blank)

Each test activity includes a minimum of two sampling iterations to attempt to bracket process variability and allow identification of potential spurious results. If two sampling iterations conducted under the same underlying process conditions return results for the same analyte that differ by more than an order of magnitude, the Joint Test Group (JTG) will be convened with participation from the Colorado Department of Public Health and Environment to review the data and determine whether the test iteration is repeated and/or the data is discarded or used as generated. Where both sampling events detect the analyte, the maximum observed concentration will be used to calculate the emission rate. Where one event detects an analyte and the second does not, the concentration observed when detected will be used to calculate an emission rate for the MPHRA assessment.

The emission rate calculated for the 4-hour processing period will be conservatively assumed to occur continuously over a 24 hour period when evaluating emissions against the CDPHE MPHRA benchmark (Attachment A). This conservative assumption will provide a safety margin for continued operations pending final results of subsequent test activities.

Toxicity data applied in the assessment of risk and hazard will be the same as applied in the current MPHRA for the preliminary MPHRA updates, unless an analyte is observed that is not incorporated into the current model. In this case, the most current toxicity data will be acquired for that analyte. Following IFD, the MPHRA update (i.e. post MPHRA) will include updated toxicity data, as applicable.

Upon review and acceptance of the MPHRA update, and in concert with its review of the engineering design aspects of the PCAPP and EDS, CDPHE will establish operating conditions and requirements in a final Part B Permit for full-scale operation of the units.

5.2.2 COMPARISON OF RESULTS FROM DIFFERENT MEASUREMENT SYSTEMS

Execution of DQOs requires evaluation of data collected from different measurement systems, for example evaluation of near-real-time THC data against 4-hr emissions data. Evaluation methods are discussed in *PCAPP Position Paper on Total Hydrocarbon Monitoring During Pilot Test Demonstration*, 24852-30H-000-V0003.

6.0 EXECUTION

Figure F provides an illustrative overview of the anticipated process for pilot test evaluations of DQOs associated with controlling emissions from the AFA. Execution and evaluation of DQOs, and associated operational decision rules, are more fully developed in the Pilot Plan and LSAP. As shown, initial demonstration data are collected and errors/omissions evaluated against its relative criticality (Table 3). Ramp-up operations will continue pending results of emissions sample analyses, comparison against MPHRA thresholds, and MPHRA update. Following receipt, verification and conversion of analytical data to emission rates (Attachment A), results will be evaluated within the MPHRA model (see Section 5.2.1). If following IFD, it can be demonstrated that pre- and post-carbon emissions remain below MPHRA thresholds during both normal and off-normal operating conditions, PCAPP may request that carbon changeout, during operations be based on agent breakthrough. If, however, pre and/or post-carbon emissions samples are not within MPHRA thresholds, the site will evaluate (1) whether the key contributors to risk/hazard have an affinity for carbon, and if so, (2) the strategy for assessing carbon performance in controlling emissions. If PCAPP determines that the key contributors to risk/hazard do not have an affinity for carbon, the JTG will be convened to determine appropriate actions. Such actions could include a temporary pause in facility ramp-up pending evaluation of process or design changes to reduce emissions to acceptable levels.

PCAPP will evaluate three strategies for assessing carbon performance:

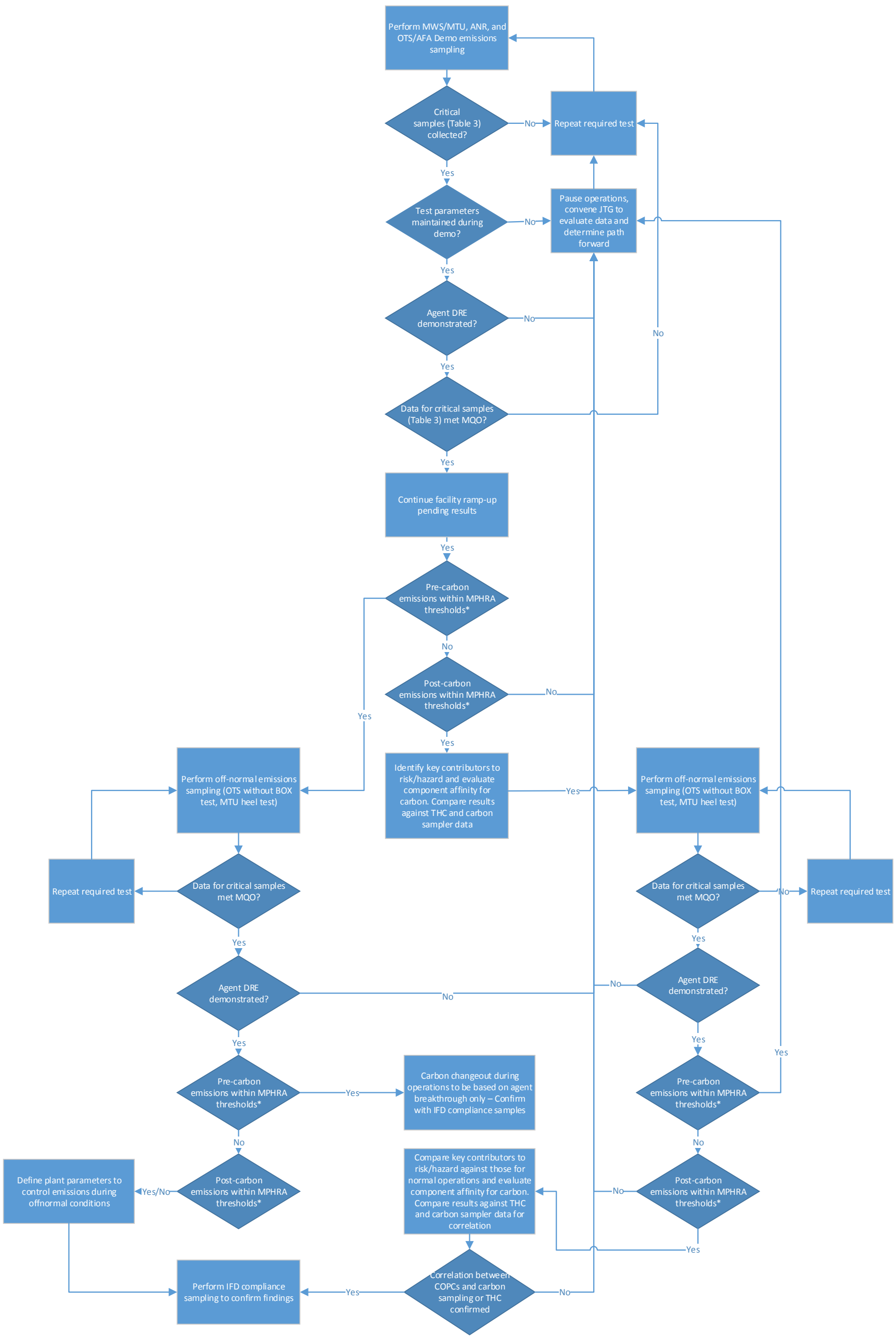
1) COPC sampling (e.g., 1,2-DCA)

2) THC monitoring

3) Carbon sampling

These evaluations are described in *PCAPP Position Paper on Total Hydrocarbon Monitoring During Pilot Test Demonstration*, 24852-30H-000-V0003.

Figure G provides an overview of the anticipated process for pilot test execution of DQOs associated with controlling emissions from the BTA. As shown, following start-up/transition of Module 1 to hydrolysate feed, preliminary BTA emissions sampling (at the 30-day tank vent, BTS Module 1 OTS, WRS OTS, and BRS OTS) will be performed if not already performed in response to odor detections per the OMP. Errors/omissions in emissions data collected will be evaluated to determine if repeat sampling needs to be conducted (Table 3). BTA ramp-up will continue pending results of emissions sample analysis and MPHRA assessment. Calculated emission rates for BTA sources with AFA emission rates observed during MTU heel testing will be evaluated within the MPHRA model (see Section 5.2.1). If pre- and post-carbon emissions are within MPHRA thresholds, and the MPHRA update demonstrates acceptable risks, results will be documented to support any recommendations for continued operations following the IFD. If, however, pre and/or post-carbon emissions samples are not within MPHRA thresholds, the site will evaluate (1) whether the key contributors to risk/hazard have an affinity for carbon, and if so, (2) the strategy for assessing carbon performance in controlling emissions. If PCAPP determines that the key contributors to risk/hazard do not have an affinity for carbon, the JTG will be convened to determine appropriate actions. Such actions could include pausing BTA ramp-up and reducing feed to the BTS pending evaluation of process or design changes to reduce emissions to acceptable levels.



* Initial evaluation of AFA data will involve processing emissions data through current post-processor. Emissions for other source stacks will be consistent with MPHRA report. Additionally, because other stack data may not be available, this may not incorporate updated AERMOD processing.

Figure F. Execution of DQOs Associated with Controlling Emissions at the AFA

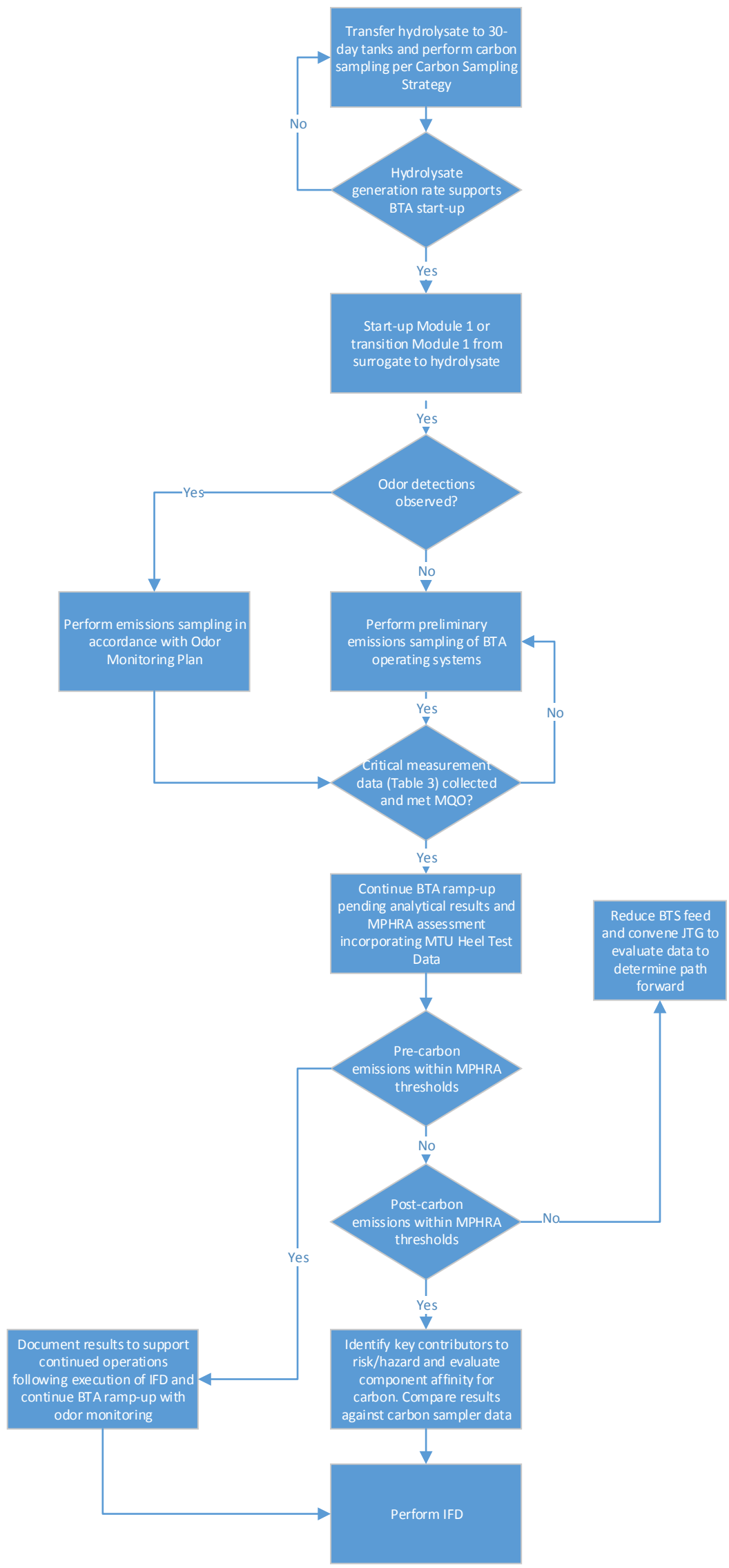


Figure G. Execution of DQOs Associated with Controlling Emissions at the BTA

7.0 ATTACHMENTS

- A. Calculations
- B Nominal Detection Limits

8.0 REFERENCES

White Paper on Carbon Sampling Strategy, 24852-30H-000-W0004

Multiple Pathway Health Risk Assessment Report, PCAPP with EDS, 24852-3RC-000-V0007

Pilot Test Demonstration Plan, 24852-GPP-GYPM-00006

Laboratory Sampling and Analysis Plan for Pilot Test Phase Operations, 24852-GPP-GGL-00013

Odor monitoring Plan for Pilot Test Phase operations, 24852-GPP-GGG-v0018 OMP

PCAPP Position Paper on Total Hydrocarbon Monitoring During Pilot Test Demonstration, 24852-30H-000-V0003

24852-GPP-GGI-NP001 Environmental and Hazardous Waste Sampling

24852-GPP-GGL-LP012 Data Review and Qualification

PCAPP Calculation 24852-RD-M5C-000-B0004*, PCAPP Emissions Calculation*

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ATTACHMENT A. CALCULATIONS

Emissions data collected must be converted to appropriate emission rates for assessment within the MPHRA model. Different sampling approaches will be used which need to be reconciled to ensure appropriate decisions are made. For specific sampling locations, process instruments will be used to support these calculations (Table A-1). The following paragraphs summarize the calculations, assumptions, and potential errors for each sampling location that will be employed in evaluation of emissions sample data.

A-1 AFA

Sampling at the AFA includes stack measurements performed by a third-party stack testing firm using isokinetic sampling in accordance with EPA Methods 1 and 2. Additionally, sampling includes non-isokinetic sampling within the agent filtration units. Data from these two locations must be compared to satisfy DQOs. As such, potential discrepancies must be understood.

A-1-1AFA Stack

The stack measurement provides a composite analysis for flow through the 8 operating AFUs. Emission rates will be calculated from submitted analytical data in µg/dscm as follows:

$$E_i = Q_{AFA} \times C_i \times K$$

where:

E_i = emission rate for constituent i in g/s
Q_{AFA} = measured AFA stack flow, dscfm
C_i = measured concentration of constituent i, µg/dscm
K = conversion factor, 35.31 dscm/dscf x 10^{-6} g/ µg x 0.0167 min/s

A-1-1AFA Filter Units

As documented in the LSAP, COPC sample data will be collected at three on-line AFUs (two outermost and one central) to balance out potential discrepancies associated with flow from the APB (approximately 2/3 flow) and ERB (approximately 1/3 flow). The observed concentrations from these three units will be averaged to provide a composite for comparison with stack COPC data.

COPC or mercury sample data collected at any location within an AFU will be converted to an emission rate. For each AFU the actual volumetric flow at the suction side of the AFU internal ID fan is measured for the air flow rate (FIT 4734, see Table A-1). The temperature, relative humidity and pressure within the AFU are required to convert this measurement to mass flow rate using the following:

$$scfm = acfm\ [\ (P_{act} - P_{sat}\ \Phi) / P_{std}\ ]*(T_{std} / T_{act}\ )$$

where:

acfm = actual volumetric flow rate, ft^3/min
dscfm = mass flow rate (dry basis), ft^3/min
P_{act} = line pressure in absolute, lbs/in^2
P_{sat} = saturation pressure of water, lbs/in^2
P_{std} = standard pressure (14.7 psia) per EPA method 2.4, lbs/in^2
Φ = relative humidity, %
T_{act} = line temperature, R
T_{std} = standard temperature (537 R) per EPA method 2.4, R

Variations in atmospheric conditions can impact the conversion of acfm to dscfm. The following meteorological data was measured at PCD between 2008 and 2012:

Parameter	Units	Min	Avg	Max
Temperature	(°F)	-16.6	53.6	109.4
Barometric Pressure	(psia)	11.98	12.35	12.64
Dew Point	(°F)	-40.0	30.2	82.4

Since the temperature and relative humidity are controlled in the ERB and APB, only the variations in barometric pressure impact this calculation. The above measured variations in barometric pressure lead to a ± 3 percent uncertainty. The building temperature varies from a low of 73 °F in winter to a high of 86 °F in summer. The variation of line pressure (± 0.1) psi results from loading of the particulate filters in the AFU. At a maximum 70% RH, the combined variations in temperature, pressure and humidity gives a ± 2½% uncertainty in the mass flow in the AFUs.

Sample flow rates will be measured at the start and end of sampling and the minimum flowrate will be used to estimate concentrations (thereby resulting in a conservative estimate of actual concentration). This process could result in a maximum error of approximately 10%. This error, the above conversion errors, and the differential flow between the APB and ERB must be considered when comparing AFA and AFA stack concentrations.

B-2 30-day tank vents

The 30-day tanks do not have forced ventilation and therefore the determination of emission rate will be based on the displacement associated with hydrolysate transfer to the 30-day tanks. No credit will be taken for transfer out of the 30-day tanks to the BTS.

B-3 BTS OTS

The air flow rate for each module in the biotreatment system is measured after the air compressors. While the flow instrument provides volumetric flow, nearby temperature and line pressure are available to establish the corresponding mass flow rate. However

the humidity is not measured prior to the ICBs. The uncertainty in determining the mass flow is a result of the variability in barometric pressure (11.98 to 12.64 psia) and in atmospheric humidity (dew point range of -40 to 82 °F). This leads to a combined uncertainty of ± 1½ %.

B-4 WRS OTS

The WRS volumetric air flow rate is measured prior to the brine concentrator feed tanks (BCFT) along with temperature and pressure. However the humidity is not measured prior to the BCFT. The uncertainty in determining the mass flow is a result of the variability in barometric pressure (11.98 to 12.64 psia) and in atmospheric humidity (dew point range of -40 to 82 °F).The variation in barometric pressure and humidity produces a ± 1½ % uncertainty in mass flow determination for the WRS.

B-5 BRS OTS

The BRS air flow is not directly measured. With a design flow rate of 1,000 scfm and a negligible COPC content, the BRS off-gas is a minor contributor to the MPHRA. Therefore, the design flow rate will be used to estimate the BRS contribution to the MPHRA.

Table A-1. Sample Location and Associated Process Instruments

Filtration System	Sample location		Instrument			
			Flow (F)	Moisture (M)	Temperature (T)	Pressure (P)
AFA	Mass Flow Measurement	Suction side of AFU ID Fan	FIT 4734 G/H/J/K/L/M/N/P/Q/R	None	None	None
	Pre-carbon	3 AFUs between HEPA bed 1 (see GPP-GGI-NP001)	FIT4734 G/H/J/K/L/M/N/P/Q/R	None	None	None
	Between carbon	each AFU between beds 3/4 (see GPP-GGI-NP001)		None	None	None
	Post-carbon	Stack (see GPP-GGI-NP001)	EPA Method 1 and 2			
30-day tanks	Pre-carbon	PV-5098	Calculated flow based on hydrolysate transfer			
	Post-carbon	PV-5099				
BTS - Modules 1/2/3/4*	Mass Flow Measurement	Between Compressors and ICB	FIT 1363 A/B/C/D FIT 1364 A/B/C/D FIT 1365 A/B/C/D FIT 1366 A/B/C/D	None	TIT 1361 A/B/C/D	PIT 1362 A/B/C/D
	Pre-carbon	see 24852-GPP-GGI-NP001	None	MT1782A/B/C/D	TIT1782A/B/C/D	PIT1505A/B/C/D
	Post-carbon	see 24852-GPP-GGI-NP001	None		TIT1755A/B/C/D	PIT1749A/B/C/D
WRS	Mass Flow Measurement	Between Compressors and BCFT	FIT 2302 FIT 2304 FIT 2305	None	TIT 2299	PIT 2300
	Pre-carbon	see 24852-GPP-GGI-NP001	None	MT2293	TIT2230CB	PIT2296
	Post-carbon	see 24852-GPP-GGI-NP001	None		TIT2230A	PIT2292
BRS	Pre-carbon	see 24852-GPP-GGI-NP001	None	MT2046C	TIT2046B	PIT2045
	Post-carbon	see 24852-GPP-GGI-NP001	None			

* BTS Modules 1, 2, 3, 4 correspond to A, B, C, D, respectively.

ATTACHMENT B. NOMINAL DETECTION LIMITS

Table B-1. Nominal COPC detection limits for selected PCAPP Emissions Sampling Methods.

COPC	CAS Number	PCAPP Classification		Sampling Method	Analytical Method	Method DL	Units
1,1,1,2-tetrachloroethane	630-20-6	VOC	Target	TO-15	8260	0.206	µg/m³
1,1,1-trichloroethane	71-55-6	VOC	Target	TO-15	8260	0.355	µg/m³
1,1,2,2-tetrachloroethane	79-34-5	VOC	Target	TO-15	8260	0.474	µg/m³
1,1-dichloroethane	75-34-3	VOC	Target	TO-15	8260	0.291	µg/m³
1,1-dichloroethene	75-35-4	VOC	Target	TO-15	8260	0.511	µg/m³
1,2,3-trichlorobenzene	87-61-6	VOC	Target	TO-15	8260	4.58	µg/m³
1,2,4-trichlorobenzene	120-82-1	VOC	Target	TO-15	8260	3.21	µg/m³
1,2,4-trimethyl benzene	95-63-6	VOC	Target	TO-15	8260	0.796	µg/m³
1,2-bis(ethylthio)-ethene	13105-10-7	SVOC	TIC*	TO-13	8270	NA	
1,2-bis(vinylthio)-ethane	63938-34-1	SVOC	TIC*	TO-13	8270	NA	
1,2-dichlorobutane	616-21-7	VOC	TIC*	TO-15	8260	NA	
1,2-dichloroethane	107-06-2	VOC	Target	TO-15	8260	0.356	µg/m³
1,2-dichloropropane	78-87-5	VOC	Target	TO-15	8260	1.11	µg/m³
1,4-dioxane	123-91-1	VOC	Target	TO-15	8260	0.364	µg/m³
1,4-dithiane	505-29-3	SVOC	Target	TO-13(A)	8270	1.8	µg/sample
1,4-oxathiane	15980-15-1	SVOC	Target	TO-13(A)	8270	1.8	µg/sample
1-chlorobutane	109-69-3	VOC	TIC*	TO-15	8260	NA	
1-hexene	592-41-6	VOC	TIC*	TO-15	8260	NA	
2,2-dimethyl-trans-thiirane	3772-13-2	VOC	TIC*	TO-15	8260	NA	
2,3-dimethyl-thiophene	632-16-6	VOC	TIC*	TO-15	8260	NA	
2-butanone	78-93-3	VOC	Target	TO-15	8260	0.587	µg/m³
2-chlorobutane	78-86-4	VOC	TIC*	TO-15	8260	NA	
2-chloroethoxyethane	112-26-5	VOC	TIC*	TO-15	8260	NA	
2-ethyl 1,3-butadiene	3404-63-5	VOC	TIC*	TO-15	8260	NA	
2-hexanone	591-78-6	VOC	Target	TO-15	8260	0.357	µg/m³
2-methyl-1,3-dithiacyclopentane	5616-51-3	SVOC	TIC*	TO-13	8270	NA	
2-methyl-1,3-dithiane	6007-26-7	SVOC	TIC*	TO-13	8270	NA	
2-methyl-1,3-oxathiolane	17642-74-9	SVOC	TIC*	TO-13	8270	NA	
3-methyl phenol	108-39-4	SVOC	Target	TO-13(A)	8270	25	µg/sample
4-methyl phenol	106-44-5	SVOC	Target	TO-13(A)	8270	25	µg/sample
4-methyl-2-pentanone	108-10-1	VOC	Target	TO-15	8260	0.553	µg/m³
acetaldehyde	75-07-0	VOC	TIC*	TO-15	8260	NA	
acetone	67-64-1	VOC	Target	TO-15	8260	0.423	µg/m³

COPC	CAS Number	PCAPP Classification		Sampling Method	Analytical Method	Method DL	Units
acrolein	107-02-8	VOC	Target	TO-15	8260	0.507	µg/m³
alpha-methylstyrene	98-83-9	VOC	TIC*	TO-15	8260	NA	
benzene	71-43-2	VOC	Target	TO-15	8260	0.252	µg/m³
carbon disulfide	75-15-0	VOC	Target	TO-15	8260	0.243	µg/m³
chloroethane	75-00-3	VOC	Target	TO-15	8260	0.813	µg/m³
chloroform	67-66-3	VOC	Target	TO-15	8260	0.464	µg/m³
chloromethane	74-87-3	VOC	Target	TO-15	8260	0.407	µg/m³
chloromethoxyethane	3188-13-4	VOC	TIC*	TO-15	8260	NA	
diethyl ether	60-29-7	VOC	TIC*	TO-15	8260	NA	
ethane	74-84-0	VOC	Target	TO-15	ASTM D1946	0.0000107	% v/v
ethene	74-85-1	VOC	Target	TO-15	ASTM D1946	0.0000114	% v/v
ethylbenzene	100-41-4	VOC	Target	TO-15	8260	0.274	µg/m³
hexachlorobutadiene	87-68-3	VOC	Target	TO-15	8260	4.61	µg/m³
hexachloroethane	67-72-1	SVOC	Target	TO-13(A)	8270	1.2	µg/sample
hexane	110-54-3	VOC	Target	TO-15	8260	0.264	µg/m³
methane	74-82-8	VOC	Target	TO-15	ASTM D1946	0.00002	%v/v
methyl tert-butyl ether	1634-04-4	VOC	Target	TO-15	8260	0.180	µg/m³
methylene chloride	75-09-2	VOC	Target	TO-15	8260	0.250	µg/m³
naphthalene	91-20-3	VOC	Target	TO-15	8260	2.95	µg/m³
octane	111-65-9	VOC	Target	TO-15	8260	0.257	µg/m³
pentane	109-66-0	VOC	Target	TO-15	8260	0.770	µg/m³
propene	115-07-1	VOC	TIC*	TO-15	8260	NA	
tert-butyl alcohol	75-65-0	VOC	Target	TO-15	8260	0.321	µg/m³
tetrachloroethene	127-18-4	VOC	Target	TO-15	8260	0.346	µg/m³
thiirane	420-12-2	VOC	TIC*	TO-15	8260	NA	
thiodiglycol	111-48-8	SVOC	Target	TO-13(A)	8270	4	µg/sample
toluene	108-88-3	VOC	Target	TO-15	8260	0.192	µg/m³
trichloroethene	79-01-6	VOC	Target	TO-15	8260	0.564	µg/m³
vinyl chloride	75-01-4	VOC	Target	TO-15	8260	0.307	µg/m³
xylenes	1330-20-7	VOC	Target	TO-15	8260	0.321	µg/m³
ammonia	7664-41-7	Cation		EPA 350.3	OSHA ID-188	25	µg/sample
chlorine	7782-50-5	Acid Gas		EPA EMC 26A		0.250	mg/sample
hydrogen chloride	7647-01-0	Acid Gas		EPA EMC 26A		0.257	mg/sample

NA – not available

* Tentatively identified compounds (TICs) will be analyzed per the procedures defined in 24852-GPP-GGL-LP012 *Data Review and Qualification*. For evaluation, volatile organic compounds (VOCs) were assumed to have a detection limit of 5 µg/m^3 and semivolatile organics (SVOCs) were assumed to have a detection limit of 10 µg/sample.

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Pueblo Chemical Agent-Destruction Pilot Plant

PCAPP

PUEBLO CHEMICAL AGENT-DESTRUCTION PILOT PLANT PROJECT

24852-GPP-GGL-00011
Revision 003

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Brine Reduction System (BRS) Recovered Water Sampling and Analysis Plan

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Contract No. W52P1J-09-C-0012

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Revision History

Rev. No.	Description of Revision	Approval/Date
000	Initial Issue	07/09/2014
001	Clarified volatile organic chemical limits in Table 1. Clarified sampling locations, techniques, and quality control sample sections.	04/20/2015
002	Revised volatile organic chemicals, semi-volatile organic chemicals and limits in Tables 1 and 2. Clarified sampling locations, frequencies, and collection sections.	06/26/2015
003	Complete revision of document. Clarified document based on CDPHE comments; removed DQOs.	

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TABLE OF CONTENTS

Page

ACRONYMS AND ABBREVIATIONS IX

1.0 INTRODUCTION 11
2.0 SCOPE 12
3.0 RESPONSIBILITIES 13
3.1 CHIEF SCIENTIST 13
3.2 LABORATORY MANAGER 13
3.3 LABORATORY OPERATIONS BRANCH 13
3.4 LABORATORY MONITORING BRANCH 13
3.5 LABORATORY QUALITY ASSURANCE/QUALITY CONTROL BRANCH ... 13
3.6 PROJECT MANAGER 14
3.7 QUALITY AND PERFORMANCE MANAGEMENT MANAGER 14
3.8 SAFETY AND HEALTH MANAGER 14
3.9 OPERATIONS 14
3.10 ENVIRONMENTAL 14
3.11 WASTE MANAGEMENT 15
4.0 INITIAL SOURCE OF WATER FOR PUEBLO CHEMICAL AGENT-DESTRUCTION PILOT PLANT SYSTEMS 15
5.0 PROPOSED ALTERNATIVE LIST OF BRINE REDUCTION SYSTEM RECOVERED WATER CONSTITUENTS 15
5.1 PROPOSED CONSTITUENTS 15
5.2 BASIS AND JUSTIFICATION 17
6.0 SAMPLING DESIGN FOR RECOVERED WATER ANALYSIS 18
6.1 DATA QUALITY OBJECTIVES 19
6.2 SAMPLING LOCATIONS AND FREQUENCIES 19
6.3 SAMPLE COLLECTION 20
6.4 SAMPLE CHAIN OF CUSTODY 20
6.5 QUALITY ASSURANCE AND CONTROL 20
6.5.1 Personnel and Instrument Certification Requirements 20
6.5.2 Methods and Instrumentation 20
6.5.3 Quality Control Samples 21
6.5.3.1 Data Quality Indicators 21
6.5.3.2 Tentatively Identified Compounds (TICs) Analysis 21
6.5.3.3 Validation of Analytical Results 22
6.5.4 Data Collection, Review, and Evaluation 22
6.5.5 Nonconformance and Corrective Action Process 22
6.6 GENERAL HAZARD ASSESSMENT 22
6.7 WASTE GENERATION AND MANAGEMENT 22
6.8 THIRD-PARTY LABORATORY TESTING 23
6.8.1 Quality Assurance and Control Process 23
6.8.2 Nonconformance and Corrective Action Process 23
7.0 REFERENCES 23
7.1 DOCUMENTS CITED 23

7.2 CODES, STANDARDS, REGULATIONS, AND PROCEDURES 26
7.3 DRAWINGS 26
7.4 DATA 26

LIST OF TABLES

Page

Table 1. Proposed Organic Constituent List for PCAPP Recovered Water 16
Table 2. Proposed Inorganic Constituent List for PCAPP Recovered Water 17
Table 4. Summary of Recovered Water Sampling Valves 19
Table 5. Summary of BRS Recovered Water Analyses 21
Table 6. Types of Quality Samples 21
Table 7. EPA-Based Methods for Potential Third-Party Analysis 23

ACRONYMS AND ABBREVIATIONS

ABCDF	Aberdeen Chemical Agent Disposal Facility
ACWA	Assembled Chemical Weapons Alternatives
BC	brine concentrator
BRS	brine reduction system
CCR	Code of Colorado Regulations
CDPHE	Colorado Department of Public Health and Environment
DQI	data quality indicator
DQO	data quality objective
EPA	Environmental Protection Agency
GC/MSD	gas chromatograph/mass selective detector
LAMP	Laboratory Analysis and Monitoring Plan
LIMS	laboratory information management system
LQCP	Laboratory Quality Control Plan
mg/L	milligram per liter
PCAPP	Pueblo Chemical Agent-Destruction Pilot Plant
PCD	Pueblo Chemical Depot
QA	quality assurance
QC	quality control
RCRA	Resource Conservation and Recovery Act
RCRA RD&D permit	*State of Colorado RCRA Research, Development, and Demonstration Permit*
RO	reverse osmosis
S&H	Safety and Health
SVOC	semi-volatile organic compound
VOC	volatile organic compound
WAP	Waste Analysis Plan

Abbreviations

Division	CDPHE Hazardous Materials and Waste Management Division
NP001	*Environmental and Hazardous Waste Sampling*, 24582-GPP-GGL-NP001
SW-846	EPA *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*
TDG	Thiodiglycol

1.0 INTRODUCTION

The Pueblo Chemical Agent-Destruction Pilot Plant (PCAPP) is an Assembled Chemical Weapons Alternatives (ACWA) chemical demilitarization facility located at Pueblo Chemical Depot (PCD). PCAPP has been designed and constructed to safely destroy 2,611 tons of mustard agent in mortar and artillery projectiles stored at PCD. The PCAPP facility will access and drain the mustard agent contained in the 155-mm and 105-mm projectiles and 4.2-inch mortar rounds. The mustard agent will be destroyed using a neutralization process followed by biotreatment. The PCAPP team consists of Bechtel National, Inc. (BNI), AECOM, and Battelle Memorial Institute. The team is charged with the construction, systemization, demonstration, operation, and closure of the PCAPP facility.

This document serves to meet permit conditions I.J.1.w.vii and III.F.6 in the *State of Colorado Resource Conservation and Recovery Act (RCRA) Research, Development, and Demonstration Permit* (RCRA RD&D permit), CO-04-07-01-01 (PCAPP internal document number 24852-30L-H01-00017V01), which is administered by the Colorado Department of Public Health and Environment (CDPHE) Hazardous Materials and Waste Management Division (Division). The permit conditions require the development of a Brine Reduction System (BRS) Recovered Water Sampling and Analysis Plan that describes sample collection and analysis methods used for measuring the concentrations of constituents in this plan. Analyses will be conducted using PCAPP analytical methods that are based on U.S. Environmental Protection Agency (EPA) SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. EPA SW-846 methods have been evaluated and approved for use in complying with the RCRA regulations.

Permit condition III.F.6 also requires that PCAPP obtains a sample of BRS effluent during pilot testing to assess BRS performance. During pilot testing, PCAPP will conduct the required sampling and analysis of the recovered water to demonstrate that the quality of the recovered water is acceptable for use as an effective substitute for commercially-available water for PCAPP processes, as defined in Tables 1 and 2 for initial water recovery analysis during pilot testing. The design and function of the BRS is described in *System Design Description for Brine Reduction System (BRS)*, 24852-RD-3YD-B12-B0001 and *Engineering Specification for Brine Reduction System*, 24852-RD-3PS-000-M0086. The BRS is designed to treat a blended wastewater stream comprised of the following:

- Biologically treated hydrolysate from the immobilized cell bioreactors
- Cooling tower blowdown
- Boiler blowdown
- Reverse osmosis (RO) reject water

The effluent streams are blended and stored in three aerated brine concentrator (BC) feed tanks upstream of the BRS equipment. The blended stream is processed in the BRS to produce recovered water for reuse in upstream processes. Since the recovered

water is expected to contain some volatile organic compounds, an activated carbon adsorption treatment is utilized to satisfy water quality requirements. Until the recovered water is sampled and analyzed during pilot testing and demonstrated to be an effective substitute for commercially-available water (as defined in Tables 1 and 2 for initial water recovery analysis during pilot testing), it shall be managed as a hazardous waste.

Once the quality of the recovered water is ascertained, and PCAPP receives approval from the Division to use the recovered water as process water, recovered water will then be used as indicated in the flow diagrams for the Process Water System (drawings 24852-RD-M5-M16-M0001 and M0002). The Process Water System supplies process water to the following systems, as described in *System Design Description for Process Water*, 24852-RD-3YD-M16-M0001:

- Agent collection and neutralization (mechanical seals)
- Biotreatment (immobilized cell bioreactor feed tanks)
- Off-gas treatment system
- Munitions treatment unit (water seals)
- Autoclave (vacuum pump)
- RO system
- Munitions washout system utility stations
- Hot process water system (which supplies process water to the agent hydrolyzers)
- Spent decon storage system (mechanical seals)
- BRS
- Boiler blowdown tank
- Cooling towers

2.0 SCOPE

The PCAPP Laboratory has the scope to collect and analyze recovered water to establish that it is of sufficient quality for use as a substitute for commercially-available water. The PCAPP Laboratory proposes to test the recovered water initially during pilot testing for volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), anions/cations, and metals using the alternative list of constituents identified in Tables 1 and 2 in Section 5.0 and the current, approved methods for these analyses. The PCAPP Laboratory proposes to 1) reduce the list of constituents in Section 5.0

based on the results from pilot testing and 2) analyze for the reduced list thereafter to assess BRS performance.

3.0 RESPONSIBILITIES

Detailed position descriptions for PCAPP Laboratory personnel can be found in the *Laboratory Analysis and Monitoring Plan* (LAMP), 24852-GPP-GGL-00002 and *Laboratory Quality Control Plan* (LQCP), 24852-GPP-GGL-00003.

3.1 CHIEF SCIENTIST

The PCAPP chief scientist functionally reports to the PCAPP project manager and is responsible for approving all aspects of Laboratory operations during pilot testing and operations, including changes to air monitoring methods, analytical methods, and Laboratory-specific plans. The PCAPP chief scientist will also provide oversight for pilot testing, as described in the *Pilot Test Demonstration Plan*, 24852-GPP-GYPM-00006.

3.2 LABORATORY MANAGER

The PCAPP Laboratory manager is responsible for all aspects of Laboratory operations, which includes documentation (i.e., plans, procedures, desktop instructions, and methods), sample collection, analysis, reporting, quality, safety, training, monitoring, and maintenance.

3.3 LABORATORY OPERATIONS BRANCH

The PCAPP Laboratory Operations Branch is responsible for the analysis of recovered water samples using certified/validated methods. Analytical results are collected and stored via the in-house designed laboratory information management system (LIMS) database.

3.4 LABORATORY MONITORING BRANCH

The PCAPP Laboratory Monitoring Branch is responsible for the collection of recovered water samples.

3.5 LABORATORY QUALITY ASSURANCE/QUALITY CONTROL BRANCH

The PCAPP Laboratory Quality Assurance (QA)/Quality Control (QC) Branch functionally reports to the Quality & Performance Management manager and has the responsibility to:

- Review, audit, and perform surveillances on analytical and air monitoring operations to ensure they meet the quality objectives established by the LQCP
- Conduct audits of subcontractor laboratories

- Review a representative sample set of subcontractor laboratory data before final release of data to ensure completeness, accuracy, and traceability

3.6 PROJECT MANAGER

Along with general management responsibilities, the PCAPP project manager has the responsibility for coordinating Safety, Security, Environmental, Quality, and Plant Management for the safe, secure, and efficient execution of the pilot testing and operations.

3.7 QUALITY AND PERFORMANCE MANAGEMENT MANAGER

The Quality and Performance Management manager functionally reports to the PCAPP Project Manager for project-related quality matters and is responsible for conducting audits and surveillances through pilot testing and operations to verify effective implementation of test procedures and compliance with objectives and criteria.

3.8 SAFETY AND HEALTH MANAGER

The Safety and Health (S&H) manager functionally reports to the PCAPP project manager for project-related safety matters and is responsible for ensuring safe execution of plant operations. The S&H manager will ensure performance of industrial hygiene monitoring as required during pilot testing and normal operations to ensure any potential worker exposure conditions are identified, tested, and quantified to establish personal protective equipment or stay-time requirements for continued operations. The S&H manager will also be responsible for performing any required risk assessments and developing hazard analyses for execution of plant operations.

3.9 OPERATIONS

PCAPP Operations is responsible for the operation and maintenance of the BRS. The Operations manager is responsible for coordinating all plant activities and ensuring they are conducted in a safe, environmentally-sound, effective, and consistent manner in accordance with plant operating procedures and applicable permit and regulatory requirements. Plant shift personnel receive direction from plant management regarding goals and objectives for the shift-to-shift operation of the plant. They are responsible for conducting operations, including recovered water sample collection, safely, and in accordance with approved procedures and work orders.

3.10 ENVIRONMENTAL

PCAPP Environmental is responsible for 1) developing and administering PCAPP's environmental programs and the implementation of environmental plans and procedures and 2) performing assessments during pilot testing and operations to monitor compliance with established permit requirements. Each process, procedure, and operation is subject to inspection and audit for compliance with the intent of

continuously improving the environmental compliance of the project. The Environmental manager is responsible for transmitting analytical results to CDPHE.

3.11 WASTE MANAGEMENT

PCAPP Waste Management functionally reports to Environmental and is responsible for developing and implementing procedures and prescribing activities to ensure proper minimization, management, storage, and off-site transportation of PCAPP waste. The PCAPP Waste Management manager is responsible for overseeing waste management operations, for providing waste management compliance reporting, and for ensuring that newly generated waste is properly characterized, containerized, and labeled.

4.0 INITIAL SOURCE OF WATER FOR PUEBLO CHEMICAL AGENT-DESTRUCTION PILOT PLANT SYSTEMS

During the initial stages of pilot testing, potable water (site well water) will be used as the source of water throughout the plant. Once PCAPP recovered water is determined to be an effective substitute for commercially-available water (as defined in Tables 1 and 2 for initial water recovery analysis during pilot testing), recovered water can be used as described in *System Design Description for Process Water*, 24852-RD-3YD-M16-M0001.

5.0 PROPOSED ALTERNATIVE LIST OF BRINE REDUCTION SYSTEM RECOVERED WATER CONSTITUENTS

5.1 PROPOSED CONSTITUENTS

In accordance with permit conditions I.J.1.w.vii and III.F.6, this section provides an alternative list of constituents to be analyzed for during recovered water analysis. Table 1 and Table 2 compares the proposed alternative list of target organic and inorganic constituents to hydrolysate data, and identifies which PCAPP methods will be used for the analysis.

Table 1. Proposed Organic Constituent List for PCAPP Recovered Water

Applicable and Relevant Organic Constituents	CAS Number	Concentration Limits, µg/L	Detected in PCD HD/HT Hydrolysate Samples, mg/L[1]	Present in PCAPP Bench Scale Hydrolysate Data, mg/L[2]	Detected in ABCDF Hydrolysate Samples, mg/L[3]	PCAPP Method (24852-GPP-GGL-00###)
Vinyl chloride	75-01-4	2	Yes	Yes	Yes	115
Benzene	71-43-2	5	No	Yes	Yes	115
Carbon tetrachloride	56-23-5	5	No	Yes	No	115
1,2-Dichloroethane	107-06-2	5	Yes	Yes	Yes	115
Trichloroethylene	79-01-6	5	No	Yes	Yes	115
1,1,1-Trichloroethane	71-55-6	200	No	Yes	Yes	115
Cis-1,2-dichloroethylene	156-59-2	70	No	Yes	No	115
Monochlorobenzene	108-90-7	100	No	Yes	No	115
Tetrachloroethylene	127-18-4	5	No	Yes	Yes	115
Xylenes (total)	1330-20-7	10,000	No	Yes	Yes	115
Dichloromethane	75-09-2	5	No	Yes	No	115
1,1,2-Trichloroethane	79-00-5	5	No	Yes	No	115
Chloroform	67-66-3	70	No	Yes	No	115
1,1-Dichloethylene	75-35-4	7	No	No	No	115
Methyl ethyl ketone	78-93-3	10	No	No	Yes	115
Pentachlorophenol	87-86-5	10	No	Yes	No	116
Hexachlorethane	67-72-1	10	No	No	Yes	116
Hexchlorobutadiene	87-68-3	10	No	No	Yes	116
TDG	111-48-8	1000	Yes	Yes	Yes	114
1,4-Dithiane	505-29-3	1000	Yes	Yes	Yes	205
1,4-Oxathiane	15980-15-1	1000	Yes	Yes	Yes	205

CAS = Chemical Abstracts Service; µg/L = microgram per liter; ABCDF = Aberdeen Chemical Agent Disposal Facility

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[1] Battelle Memorial Institute Sample No. HD-16 of PCD HD Hydrolysate, Sample 3/9/2011; Analysis 8/3/2011. Battelle Memorial Institute Sample No. HT-15 of PCD HT Hydrolysate, Sample 2/14/2011; Analysis 7/30/2011.

[2] *Test Report for Bench-Scale Evaluation of HT, HD, and Energetics Hydrolysis and Biotreatment, Appendix F Analytical*, 24852-3TS-000T-L0001A006. *Test Report for Bench-Scale Evaluation of HT, HD, and Energetics Hydrolysis and Biotreatment*, 24852-3TS-000T-L0001.

[3] *SR for Immobilized Cell Bioreactors (ICBs) for the Treatment of agent Hydrolysate*. 24852-SRA-MS00-00001. Based on Aberdeen Chemical Agent Disposal Facility (ABCDF) hydrolysate analyses.

Table 2. Proposed Inorganic Constituent List for PCAPP Recovered Water

Applicable and Relevant Inorganic Constituents	Concentration Limits, µg/L	Detected in PCD HD/HT Hydrolysate Samples, mg/L[1]	Present in PCAPP Bench Scale Hydrolysate Data, mg/L[2]	Detected in ABCDF Hydrolysate Samples, mg/L[3]	PCAPP Method (24852-GPP-GGL-00###)
Antimony	6	Yes	Yes	No	103
Arsenic	10	Yes	Yes	Yes	103
Barium	200	Yes	Yes	Yes	103
Beryllium	4	No	Yes	No	103
Cadmium	5	Yes	Yes	No	103
Chromium	100	Yes	Yes	Yes	103
Lead	15	Yes	Yes	Yes	103
Mercury	2	No	Yes	Yes	103 and/or 119
Nickel	100	Yes	Yes	Yes	103
Selenium	50	Yes	Yes	Not tested	103
Silver	10	Yes	Yes	Not tested	103
Thallium	2	Not tested	Yes	Not tested	103
Fluoride	400	Yes	Yes	Yes	104

MCL = maximum contaminant level; µg/L = microgram per liter; ABCDF = Aberdeen Chemical Agent Disposal Facility

Recovered water samples will be analyzed using SW-846-based VOC and SVOC methods, which have standard analyte panels (see PCAPP methods 24852-GPP-GGL-00115 and 24852-GPP-GGL-00116). The range of compounds identified in the PCAPP methods will be analyzed for and reported if detected. The tentatively identified compounds process described in Section 6.5.3.2 will be used in accordance with *Data Review and Qualification*, 24852-GPP-GGL-LP012.

5.2 BASIS AND JUSTIFICATION

To generate the alternative list of constituents, the guidance in a memo entitled "*Update of Proposed Approach to Characterization of HD & HT Hydrolysate Prepared for PCAPP Laboratory Systemization*" was followed.[4] The basis for elimination of the

[4] Memo entitled "*Update of Proposed Approach to Characterization of HD & HT Hydrolysate Prepared for PCAPP Laboratory Systemization*" dated 2 November 2010 Final_Rev 2. To: Vicki Strause/ACWA-RMD, From: Robert O'Neil/SAIC.

various constituents was the reported analyzed composition of munitions grade HD, HD degradation products, and HD manufacturing impurities. The following compounds were eliminated from analysis and a justification and bases was provided in the memo:

- Pesticides
- Dioxins and furans
- Poly-aromatic hydrocarbons
- Non-chlorine organo-halogen compounds
- Cyanide
- Nitrosamines
- Other nitrogen-containing compounds
- Gases
- Arsenic compounds
- Organometallics and metal salts
- Pharmaceutical/medicinal compounds
- Miscellaneous compounds (including benzal chloride, cyclohexanone, isosafrole, osmium tetroxide, phosgene, phthalic anhydride, 1,1,2-trichloro-1,2,2-trifluoroethane, hexane, and hydrochloric acid)

Disinfection byproducts, including total trihalomethanes and haloacetic acids, are excluded because the disinfectants that produce these byproducts are not used by PCD to treat well water. Note: chloroform, which is a trichloromethane, is in the constituent list in Table 1 because chloroform may be formed as a byproduct of the treatment of mustard agent with water – not as a disinfectant. Halogen-type disinfectants, including chlorine, bromine, and iodine, are not used at PCD or PCAPP.

The analytical results from the sampling and analysis effort will be submitted to CDPHE as required by the RCRA RD&D permit. PCAPP may propose, based on operational experience and analytical results, a reduced list of constituents for subsequent sampling and analytical efforts associated with monitoring BRS performance.

6.0 SAMPLING DESIGN FOR RECOVERED WATER ANALYSIS

This section describes the design, techniques, and quality related to collection and analysis of PCAPP recovered water samples. The LQCP implements a program to ensure defensibility, accuracy, and precision of all methods used to collect and analyze

samples. The PCAPP Laboratory anticipates that some analyses may be performed by a qualified third-party laboratory, if necessary, as discussed in Section 6.8.

6.1 DATA QUALITY OBJECTIVES

Data quality objectives (DQOs) are developed at the project-level and are qualitative and quantitative statements developed to define the purpose of the data collection effort, to clarify what the data should represent to satisfy this purpose, and to specify the performance requirements for the quality of information to be obtained from the data (EPA 2000, 2006). The purpose of the DQO process is to collect a sufficient quantity of data with sufficient quality so that a project-specific decision can be made, such as determining if the recovered water is a suitable substitute for commercially-available water.

6.2 SAMPLING LOCATIONS AND FREQUENCIES

Recovered water will be collected after the water has been processed through the distillate carbon adsorption system. Design engineers and original equipment manufacturers utilized professional judgment and generator knowledge to determine the best representative sampling points within the system to sample for recovered water (judgmental sampling design). There are three distillate carbon filters, and two will be operational (i.e., the lead and lag filters), while the third will be in standby or maintenance. Sampling frequency at the locations in Table 3 includes:

- Collect samples upstream, between, and downstream of the operating distillate carbon filters every three days during BRS ramp up until CDPHE agrees that adequate operating experience and data have been acquired to establish carbon changeout frequency.
- Then, once CDPHE concurs, collect samples upstream, between, and downstream of the operating distillate carbon filters weekly through pilot test demonstration.
- PCAPP shall provide sampling after the lag carbon adsorbers when the carbon adsorbers are water bumped or backwashed above designed flow parameters to ensure that turnover of the carbon bed is not impacting the water quality objectives.

Recovered water will be sampled from the valves identified in Table 3, as shown in *Piping & Instrument Diagram Brine Reduction System Distillate Carbon Filters*, 24852-RD-M6-B12-M0015. The system inlet valve will be used to collect samples upstream of the lead filter. A valve on the outlet of the lead filter will be used to sample between the lead and lag filters. Downstream samples will be at the system outlet valve.

Table 3. Summary of Recovered Water Sampling Valves

Distillate Carbon Filters	Location	Valve Numbers
System inlet	Upstream of lead filter	PV-0765
0002A outlet	Between lead and lag filters	Primary: PV-0735 OR secondary: PV-0741
0002B outlet	Between lead and lag filters	Primary: PV-0736 OR secondary: PV-0742
0002C outlet	Between lead and lag filters	Primary: PV-0737 OR secondary: PV-0743
System outlet	Downstream of lag filter	PV-0793

6.3 SAMPLE COLLECTION

Grab sampling will be used to collect recovered water samples. A job plan will define the sampling process (sampling plan), including the number of samples to collect, what sample container(s) to use, how to physically collect the sample(s), and how to preserve the collected sample(s), in accordance with *Environmental and Hazardous Waste Sampling* (NP001), 24582-GPP-GGL-NP001. Samples are received by the Laboratory as described in *Receipt, Storage, Transfer, and Disposal of Analytical and Environmental Samples*, 24852-GPP-GGL-LP005.

6.4 SAMPLE CHAIN OF CUSTODY

Samples collected during pilot testing will be handled using chain of custody procedures as defined in the LQCP, NP001, and *Receipt, Storage, Transfer, and Disposal of Analytical and Environmental Samples*, 24852-GPP-GGL-LP005.

6.5 QUALITY ASSURANCE AND CONTROL

6.5.1 Personnel and Instrument Certification Requirements

Personnel will be trained and certified to perform sample collection, sample preparation and extraction, and instrument operations as described in the *Laboratory Training Plan,* 24852-GPP-GGL-00007 and the LQCP prior to collecting and/or analyzing any samples. Instruments will be calibrated as described in the LQCP prior to analyzing any samples.

6.5.2 Methods and Instrumentation

A variety of methods and instruments will be used to perform recovered water analyses, as summarized in Table 4. The range of compounds identified in the PCAPP methods will be analyzed for and reported if detected. The tentatively identified compounds process described in Section 6.5.3.2 will be used in accordance with *Data Review and Qualification*, 24852-GPP-GGL-LP012.

Method certification, validation, performance, and configuration control are accomplished as described in the LQCP. Detailed instrument descriptions are provided in the LAMP.

Table 4. Summary of BRS Recovered Water Analyses

Constituents	PCAPP Method(s)	Analysis Technique
TDG	24852-GPP-GGL-00114	High Performance Liquid Chromatography
1,4-Dithiane and 1,4-Oxathiane	24852-GPP-GGL-00205	GC/MSD
VOCs	24852-GPP-GGL-00115	Purge and Trap GC/MSD
SVOCs	24852-GPP-GGL-00116	GC/MSD
Anions/cations	24852-GPP-GGL-00104	Ion Chromatography/Conductance Detection
Metals (including mercury)	24852-GPP-GGL-00103	Inductively Coupled Plasma/Mass Spectrometry
Mercury	24852-GPP-GGL-00119	Cold Vapor Atomic Absorption

GC = Gas Chromatography; MSD = Mass Selective Detector; SVOCs = semi-volatile organic compounds; TDG = Thiodiglycol; VOCs = volatile organic compounds; SVOCs = semi-volatile organic compounds

6.5.3 Quality Control Samples

Instruments used for recovered water analysis shall be calibrated and challenged with various QC samples to ensure system performance from sample collection through analysis. QC sampling includes, but is not limited to, those identified in Table 5 to quantify and qualify analyses, based on requirements from the LQCP.

Table 5. Types of Quality Samples

QC Sample Types			
GC/MSD Tune	Initial Calibration Verification	Laboratory Control Sample	Matrix Spike
GC/MSD Tune Verification	Continuing Calibration Verification	Method Blank	Matrix Spike Duplicate

GC = Gas Chromatography; MSD = Mass Selective Detector

Each method/instrument will be calibrated and challenged for constituent(s), and each certified/validated analytical method defines QC sampling requirements for sample collection and analysis. The following list is an example of a typical SW-846 analytical batch for up to 20 samples: initial calibration verification after calibration, method blank, laboratory control sample, matrix spike, matrix spike duplicate, samples (1 – 20), and continuing calibration verification.

6.5.3.1 Data Quality Indicators

Data quality indicators (DQIs) include precision, accuracy, bias, representativeness, completeness, comparability, and sensitivity (EPA 2002). As opposed to DQOs, DQIs are implemented at the analysis-level and are documented within each analytical method. Further guidance is provided in the LQCP and analytical methods.

6.5.3.2 Tentatively Identified Compounds (TICs) Analysis

TICs, or non-target compounds, are compounds not associated with the calibration or challenge standards. *Data Review and Calculation*, 24852-GPP-GGL-LP012 will be followed for VOC and SVOC analysis by GC/MSD for samples containing TIC(s).

6.5.3.3 Validation of Analytical Results

The quality sampling that accompanies recovered water samples provides validation of the instrument response. Additional sampling and analysis may be requested by plant managers in the event of a result that exceeds the corresponding MCL. The PCAPP Decision Tree Regulatory Status of BRS Effluent in permit condition III.F.6 will be followed.

6.5.4 Data Collection, Review, and Evaluation

Analytical data will be collected, reviewed, and evaluated as described in analytical methods, *Data Review and Qualification*, 24852-GPP-GGL-LP012 and the LQCP. Quality records will be developed and managed as described in *Completing Quality Records*, 24852-GPP-GAM-00016.

6.5.5 Nonconformance and Corrective Action Process

The PCAPP Laboratory will operate in compliance with the LQCP in regards to non-conforming samples and data. Corrective and preventive actions will be implemented as described in the LQCP. In the event PCAPP organizations outside of the Laboratory are affected, the PCAPP process identified in *Condition Reporting and Corrective Action Process*, 24852-GPP-GAM-00023 will be followed.

6.6 GENERAL HAZARD ASSESSMENT

A hazard assessment and mitigation scheme is provided in each PCAPP Laboratory method and procedure, as described in *System Safety Program Plan for the Pueblo Chemical Agent-Destruction Pilot Plant (PCAPP) Project*, 24852-RD-30G-GHX-00001. This ensures that specific hazards are addressed for each activity performed by personnel.

6.7 WASTE GENERATION AND MANAGEMENT

Any waste generated during the conduct of laboratory sample collection and analysis will be managed as described in the *Waste Analysis Plan* (WAP), 24852-30L-H01-00017v02, *Laboratory Waste Management Plan,* 24852-GPP-GGL-00005 and *Laboratory Hazardous Waste Handling* Procedure, 24852-GPP-GGL-NP002.

6.8 THIRD-PARTY LABORATORY TESTING

6.8.1 Quality Assurance and Control Process

The PCAPP Laboratory anticipates performing the sampling and analyses identified in this plan. However, it is possible that some analyses may be analyzed ba a qualified third-party laboratory, as shown in Table 6. EPA SW-846-based methods shall be used to the extent possible for sample analysis. The Laboratory QA/QC Branch is responsible for conducting audits of subcontractor laboratories. Third party methods will not be validated by PCAPP.

Table 6. EPA-Based Methods for Potential Third-Party Analysis

Constituents	Corresponding EPA SW-846 Method(s)	Analysis Technique
TDG	8321	High Performance Liquid Chromatography
1,4-Dithiane and 1,4-Oxathiane	8270	GC/MSD
VOCs	8260	Purge and Trap GC/MSD
SVOCs	8270	GC/MSD
Anions/cations	9056	Ion Chromatography/Conductance Detection
Metals	6020	Inductively Coupled Plasma/Mass Spectrometry
Mercury	7470	Cold Vapor Atomic Absorption

GC = Gas Chromatography; MSD = Mass Selective Detector; SVOCs = semi-volatile organic compounds; TDG = Thiodiglycol; VOCs = volatile organic compounds

6.8.2 Nonconformance and Corrective Action Process

Should the third-party laboratory identify an issue, documentation and resolution of the issue will be managed as described in their quality management system. Should the PCAPP Laboratory identify an issue, documentation and resolution will be managed under the PCAPP Laboratory quality management system.

7.0 REFERENCES

7.1 DOCUMENTS CITED

Battelle Memorial Institute Sample No. HT-15 of PCD HT Hydrolysate, Sample 2/14/2011; Analysis 7/30/2011

Battelle Memorial Institute Sample No. HD-16 of PCD HD Hydrolysate, Sample 3/9/2011; Analysis 8/3/2011

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Laboratory Sampling and Analysis Plan for Pilot Test Phase Operations, 24852-GPP-GGL-00013

Laboratory Training Plan, 24852-GPP-GGL-00007

Laboratory Waste Management Plan, 24852-GPP-GGL-00005

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Pilot Test Demonstration Plan, 24852-GPP-GYPM-00006

Piping & Instrument Diagram Brine Reduction System Distillate Carbon Filters, 24852-RD-M6-B12-M0015

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System Design Description for Process Water, 24852-RD-3YD-M16-M0001

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7.2 CODES, STANDARDS, REGULATIONS, AND PROCEDURES

ACWA. 2012. *Chemical Agent Laboratory and Monitoring Quality Assurance Plan*

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7.3 DRAWINGS

Piping and Instrument Diagram Brine Reduction System Distillate Carbon Filters, 24852-RD-M6-B12-M0015

Flow Diagram Process Water System Storage & Distribution, 24852-RD-M5-M16-M0001

Flow Diagram Process Water System Hot Process Water Tank & Heater, 24852-RD-M5-M16-M0002

7.4 DATA

Battelle Memorial Institute Sample No. HT-15 of PCD HT Hydrolysate, Sample 2/14/2011; Analysis 7/30/2011

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