

Prepared for:
Tronox LLC
Henderson, Nevada

Appendix E

Data Validation Summary Report

Revisions made by Ramboll Environ September 28, 2017 are shown in underline (text insertions) and strike-through (text deletions)

ENSR Corporation
September 2006
Document No.: 04020-023-152

Prepared for:
Tronox LLC
Henderson, Nevada

Appendix E

Data Validation Summary Report

Revisions made by Ramboll Environ September 28, 2017 are shown in underline (text insertions) and strike-through (text deletions)

Prepared By Robert Kennedy
Senior Project Chemist
ENSR International

Reviewed By

ENSR Corporation
September 2006
Document No.: 04020-023-152

Contents

1.0 INTRODUCTION	2
2.0 DATA VALIDATION PROCESS.....	4
3.0 DATA VALIDATION RESULTS	7
3.1 Holding Times and Sample Preservation	8
3.2 Instrument Calibration and Tuning.....	8
3.3 Interference Check Sample Results	9
3.4 Blank Contamination	10
3.5 Surrogate Recoveries.....	10
3.6 Laboratory Control Samples	11
3.7 Matrix Spikes	11
3.8 Internal Standards	12
3.9 Laboratory Duplicates.....	12
3.10 Field Duplicates	14
3.11 ICP Serial Dilution.....	14
3.12 Quantitation.....	14
3.13 Other Issues.....	15
3.14 Rejected Results.....	15
4.0 EVALUATION OF DATA QUALITY INDICATORS.....	16
4.1 Precision	16
4.2 Accuracy	17
4.3 Representativeness.....	18
4.4 Completeness.....	18
4.5 Comparability	19
4.6 Sensitivity	19
5.0 CONCLUSIONS	20
6.0 REFERENCES	21

1.0 INTRODUCTION

The purpose of formally validating the Upgradient Investigation laboratory results was to determine the suitability of the data for potential use in the conceptual site model, risk assessment, and other future on-site environmental assessments.

MWH Laboratories in Monrovia, CA was the primary lab contracted by Tronox for the Upgradient Investigation chemical analyses. MWH performed the analysis of selected parameters in groundwater samples only for this project and contracted the remaining analyses to the following laboratories:

- EMAX Laboratories Inc. in Torrance, CA ([hereafter abbreviated as EMAX](#)) conducted the majority of the soil analyses;
- General Engineering Laboratories, LLC in Charleston, SC (hereafter abbreviated as GEL) performed all the project radiochemical analyses;
- Severn Trent Laboratories facility in Sacramento, CA (hereafter abbreviated as STL) conducted the dioxin analyses;
- Frontier GeoSciences Inc. in Seattle, WA (hereafter abbreviated as FGS) performed the methylmercury analyses; and
- EMS Laboratories, Inc. in Pasadena, CA performed the asbestos analysis in soil.

The specific analyses performed by each laboratory are identified in Table 7 of the Upgradient Investigation Workplan Addendum (ENSR February 2006).

[The following analyses were performed, matrices, and number of samples included in this Data Validation Summary Report are as follows:](#)

Analytical Method	Matrix	Number of Samples Analyzed
ASTM D 2216	Soil	3
ASTM D 5174	Soil	20
ASTM D 5174	Water	19
DOE RP 280 mod	Soil	20
DOE RP 280 mod	Water	19
EPA 100.2	Water	1
EPA 160.1	Water	17
EPA 160.2	Water	1
EPA 1630	Soil	3
EPA 1630	Water	1
EPA 300.0	Soil	10
EPA 300.1B	Water	18
EPA 310.1	Soil	10

<u>Analytical Method</u>	<u>Matrix</u>	<u>Number of Samples Analyzed</u>
<u>EPA 314</u>	<u>Water</u>	<u>20</u>
<u>EPA 314.0</u>	<u>Soil</u>	<u>55</u>
<u>EPA 330.3</u>	<u>Soil</u>	<u>3</u>
<u>EPA 350.1</u>	<u>Water</u>	<u>1</u>
<u>EPA 350.2</u>	<u>Soil</u>	<u>3</u>
<u>EPA 365.1</u>	<u>Water</u>	<u>1</u>
<u>EPA 365.2</u>	<u>Soil</u>	<u>3</u>
<u>EPA 370.1</u>	<u>Soil</u>	<u>3</u>
<u>EPA 376.2</u>	<u>Soil</u>	<u>3</u>
<u>EPA 377.1</u>	<u>Soil</u>	<u>3</u>
<u>EPA 377.1</u>	<u>Water</u>	<u>1</u>
<u>EPA 425.1</u>	<u>Soil</u>	<u>3</u>
<u>EPA 900.0</u>	<u>Water</u>	<u>1</u>
<u>EPA 900.0 mod</u>	<u>Soil</u>	<u>3</u>
<u>EPA 901.1</u>	<u>Water</u>	<u>19</u>
<u>EPA 903.1 mod</u>	<u>Water</u>	<u>19</u>
<u>EPA 904.0 mod</u>	<u>Water</u>	<u>19</u>
<u>EPA600/R-93/116</u>	<u>Soil</u>	<u>3</u>
<u>HASL-300</u>	<u>Soil</u>	<u>20</u>
<u>HASL-300 Po mod</u>	<u>Soil</u>	<u>3</u>
<u>HASL-300 Po mod</u>	<u>Water</u>	<u>1</u>
<u>HASL-300 Th mod</u>	<u>Soil</u>	<u>20</u>
<u>HASL-300 Th mod</u>	<u>Water</u>	<u>19</u>
<u>HASL-300 U mod</u>	<u>Soil</u>	<u>20</u>
<u>HASL-300 U mod</u>	<u>Water</u>	<u>19</u>
<u>SM 2320B</u>	<u>Water</u>	<u>17</u>
<u>SM 2510B</u>	<u>Soil</u>	<u>10</u>
<u>SM 4500</u>	<u>Water</u>	<u>1</u>
<u>SM 4500P-E</u>	<u>Water</u>	<u>1</u>
<u>SM 5540C</u>	<u>Water</u>	<u>1</u>
<u>SM 7500RN</u>	<u>Water</u>	<u>1</u>
<u>SW 846 1010</u>	<u>Soil</u>	<u>3</u>
<u>SW 846 1010</u>	<u>Water</u>	<u>1</u>
<u>SW 846 6010B</u>	<u>Water</u>	<u>20</u>
<u>SW 846 6020</u>	<u>Water</u>	<u>20</u>
<u>SW 846 6020A</u>	<u>Soil</u>	<u>57</u>
<u>SW 846 7199</u>	<u>Soil</u>	<u>57</u>
<u>SW 846 7199</u>	<u>Water</u>	<u>19</u>
<u>SW 846 7470</u>	<u>Water</u>	<u>20</u>
<u>SW 846 7471A</u>	<u>Soil</u>	<u>57</u>
<u>SW 846 8015B</u>	<u>Soil</u>	<u>45</u>
<u>SW 846 8015B</u>	<u>Water</u>	<u>26</u>

<u>Analytical Method</u>	<u>Matrix</u>	<u>Number of Samples Analyzed</u>
<u>SW 846 8081A</u>	<u>Soil</u>	<u>3</u>
<u>SW 846 8081A</u>	<u>Water</u>	<u>2</u>
<u>SW 846 8082</u>	<u>Soil</u>	<u>3</u>
<u>SW 846 8082</u>	<u>Water</u>	<u>2</u>
<u>SW 846 8141A</u>	<u>Soil</u>	<u>3</u>
<u>SW 846 8141A</u>	<u>Water</u>	<u>2</u>
<u>SW 846 8260B</u>	<u>Soil</u>	<u>40</u>
<u>SW 846 8260B</u>	<u>Water</u>	<u>26</u>
<u>SW 846 8270C</u>	<u>Soil</u>	<u>3</u>
<u>SW 846 8270C</u>	<u>Water</u>	<u>2</u>
<u>SW 846 8270C SIM</u>	<u>Soil</u>	<u>3</u>
<u>SW 846 8270C SIM</u>	<u>Water</u>	<u>2</u>
<u>SW 846 8290</u>	<u>Soil</u>	<u>3</u>
<u>SW 846 8290</u>	<u>Water</u>	<u>1</u>
<u>SW 846 9012A</u>	<u>Water</u>	<u>17</u>
<u>SW 846 9014</u>	<u>Soil</u>	<u>10</u>
<u>SW 846 9030</u>	<u>Water</u>	<u>1</u>
<u>SW 846 9040B</u>	<u>Water</u>	<u>17</u>
<u>SW 846 9045C</u>	<u>Soil</u>	<u>10</u>
<u>SW 846 9050A</u>	<u>Water</u>	<u>17</u>
<u>SW 846 9056</u>	<u>Soil</u>	<u>10</u>
<u>SW 846 9056</u>	<u>Water</u>	<u>17</u>
<u>SW 846 9060</u>	<u>Water</u>	<u>1</u>
<u>SW 846 9214</u>	<u>Water</u>	<u>1</u>
<u>Walkley-Black</u>	<u>Soil</u>	<u>3</u>

2.0 DATA VALIDATION PROCESS

The laboratory results for the Upgradient Investigation were subjected to formal data validation as described in the Workplan Section 5.1 and following the guidance on data validation provided by [the Nevada Division of Environmental Protection \(NDEP\)](#) for the [Black Mountain Industrial \(BMI\) Plant Sites](#) (NDEP, 2006). The data from each laboratory were submitted as Contract Laboratory Program (CLP)-like data packages in pdf format and EQiS format electronic data deliverables (EDDs). The EDDs were imported into an EQiS database at Tronox specifically created for this project. ENSR validated the data using the hard copy data package and subsequently entered the qualifiers into the database. Results were compared to the goals stated in the Upgradient Investigation Workplan Addendum (ENSR February 2006), hereafter referred to as “the Workplan”,

and the Draft Quality Assurance Project Plan (ENSR November 2005, revised August 2006) hereafter referred to as “the QAPP”.

A comprehensive (“full”) data validation was performed on 9 of the 46 laboratory Sample Delivery Groups (SDGs) and the remainder underwent a more limited validation as described below. The goal of 10% full validation that was established for the project was exceeded by 10% in order to cover the complete set of samples analyzed for the extended [Site Related Chemical \(SRC\)](#) list. This ensured that some data for every analytical method utilized during the Upgradient Investigation were subjected to full data validation.

Limited validation consisted of reviewing the following data elements to the level of summary data forms.

- Agreement of analyses conducted with chain-of-custody (COC) requests
- Holding times and sample preservation
- Initial and continuing calibrations
- Laboratory blanks/equipment blanks/ field blanks
- Surrogate recoveries
- Laboratory control sample (LCS)/ laboratory control sample duplicate (LCSD) results
- Matrix spike/matrix spike duplicate (MS/MSD) results
- Laboratory duplicate results
- Field duplicate results
- Quantitation limits and sample results

Full validation consisted of reviewing to the level of raw data all of the elements covered in the limited validation plus the following elements where applicable as defined by the analytical methods.

- Mass spectrometer tuning
- GC/MS performance checks
- Interference check sample (ICS) results
- ICP serial dilution results
- Internal standard performance
- Compound or element identification
- Peak integration and mass spectral matches
- Chemical yield (tracers and carriers)
- Calculation and transcription verifications

Analytical data were evaluated with reference to the National Functional Guidelines (EPA, 1999 and 2004) and other method appropriate validation guidance documents, as well as the Region 9 Superfund Data Evaluation/Validation Guidance (EPA, 2001), the above mentioned NDEP Guidance on Data Validation (NDEP, 2006), the quality control (QC) criteria specified in the [Quality Assurance Project Plan \(QAPP\)](#), and Upgradient Investigation Work Plan Addendum (ENSR, 2006). The Regional and National Functional

Guidelines were modified to accommodate the non-CLP methodologies. The specific guidelines used for the various methods were as follows:

- Inorganic analytical data were evaluated with reference to "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" (EPA, 2004)
- Organic analytical data were evaluated with reference to the "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review" (EPA, 1999)
- Dioxin data were evaluated with reference to "USEPA Analytical Services Branch (ASB) National Functional Guidelines for Chlorinated Dibenzo-p-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs) Data Review", EPA-540-R-05-001 (EPA, 2005)
- Radiochemical analytical data were evaluated with reference to the Department of Energy "Evaluation of Radiochemical Data Usability" (DOE, 1997) and the "Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)", (NUREG, 2004).

In general, the validation qualifiers and definitions employed were based on those used by EPA in the documents mentioned above. The "B" and "JB" qualifiers used exclusively for the radiochemical data were based on the radiochemical documents (DOE, 1997 and EPA, 2004) cited above and professional judgment. An additional qualifier Z was added to denote probable false positive results in the fuel alcohol data. Validation qualifiers and definitions are listed in **Table E-1**. A reason code was assigned to all the applications of validation qualifiers for this project. The reason codes and their explanations are listed in **Table E-2**. These codes were entered in the project database for each application of a validation qualifier that changed a lab qualifier or result value to indicate the primary reason(s) for data qualification. Conversions of the laboratory reported "ND" for not detected to the U flag in the database and the laboratory-applied "J" qualifier to indicate results less than the reporting limit but greater than the method detection limit are not discussed in this report. [A reason code of "sp" was applied for laboratory-applied "J" qualifiers.](#)

Data validation was organized by laboratory report SDG and analytical fraction. For each separate SDG/fraction combination a data validation memorandum was written by a validator and reviewed by a peer at ENSR's Westford office. These memoranda are included on CD-ROM as pdf documents and sorted by ENSR Identification (ID) which is correlated with the laboratory SDGs listed in **Table E-4**. Table E-4 specifies data validation memo number (ENSR ID) the number of samples in each analysis group by analytical fraction, the laboratory that performed the analyses, and indicates for the metals, wet chemistry, and radiochemical groups whether the analytical list was long or short. The long and short lists of analytes are defined in Table 3-1 and the Work Plan. The relationship between sample ID, matrix, collection date, laboratory ID, SDG numbers, and the level of validation performed is described in **Table E-3** and sorted by

sample ID. Table E-3 and Table E-4 are Excel spreadsheets which can be resorted to assist the data user in locating validation information for any particular sample, SDG, or analysis fraction.

3.0 DATA VALIDATION RESULTS

The data validation qualifiers and reason codes were used to select all the data in the database where results were qualified as a result of validation and this information was sorted by the ~~quality control (QC)~~ review elements listed below:

- Holding times and sample preservation
- Initial and continuing calibrations
- Mass spectrometer tuning
- ICS results
- Laboratory blanks/equipment blanks/ field blanks
- Surrogate recoveries
- ~~Laboratory control sample (LCS)/ laboratory control sample duplicate (LCSD) results~~
- ~~Matrix spike/matrix spike duplicate (MS/MSD) results~~
- Internal standard performance
- Laboratory duplicate results
- Field duplicate results
- ICP serial dilution results
- Quantitation limits and sample results
- GC/MS performance checks
- Compound or element identification
- Peak integration and mass spectral matches
- Chemical Yield (Tracers and Carriers)
- Calculation and transcription verifications

Tables E-5 through E-16 list all the results qualified based on quality control problems identified with regard to holding times, calibrations, interference check sample results, blanks, laboratory control samples results, matrix spike results, internal standard performance, laboratory duplicates, field duplicates, dioxin quantitation, probable false positives, and rejected data points. No QC problems were identified that resulted in qualification of results based on mass spectrometer tuning, surrogate spike recoveries, serial dilution results, compound identification, peak integration, or chemical yield of tracers and carriers. The data validation summary results table contents are sorted by ENSR ID to assist the data user in locating the

associated data validation memo. The data validation memos discuss the application of qualifiers in more detail. The results in each table will be summarized separately in sections below.

3.1 Holding Times and Sample Preservation

Holding times were derived from the EPA methods utilized and listed in the QAPP and Work Plan and were calculated beginning at the time of sample collection. The majority of analyses were performed within the method-specified holding times. Exceptions are summarized below and listed in Table E-5. No data were rejected on the basis of holding time exceedances.

The laboratory results for all 17 water samples analyzed for pH were qualified as estimated (J) because the pH was not determined immediately after collection.

The sulfide analysis for water sample M-120 was analyzed outside the method specified holding time of 7 days, but did not grossly exceed the holding time (defined as twice the holding time). Therefore the non-detect result reporting limit was qualified as estimated (UJ).

The nitrate and nitrite analyses of water sample M-121 were reported from diluted reanalyses acquired outside the holding time for these analytes, therefore the results were qualified as estimated with a possible low bias (J-) and an estimated non-detect (UJ), respectively.

Required holding times for hexavalent chromium in soil are not clearly specified in EPA methods 3060A, 7196A, and 7199. After correspondence with NDEP in January 2006, a holding time of 28 days for soil and 24 hours for soil digestates was agreed upon for this project. EMAX was notified of this decision, but exceeded the 24 hour digestate holding time by more than a factor of two (but less than four days) for twenty soil samples from borings M-120 and M-118. After discussion with NDEP about the proper treatment of these data points it was decided that rejecting the data was not necessary and that the suggested 168 hour (seven days) stability of digestates mentioned in EPA 3060A, combined with the good matrix spike recovery data for Cr(VI) in these samples (indicating reduction of any Cr(VI) over time was unlikely), was justification for accepting the non-detect data without qualification.

No data required qualification on the basis of sample preservation issues.

3.2 Instrument Calibration and Tuning

Table E-6 lists the sample results that were qualified based on exceeded calibration criteria. No data required qualification on the basis of instrument tuning.

Calibration criteria for validation were derived from both the analytical methods and the validation references listed in Section 2. In some cases calibration data met the method QC requirements but results were qualified based on professional judgment and the validation guidelines. The compound tert-butyl alcohol did not meet the minimum relative response factor (RRF) requirement applied to all [volatile organic compound \(VOC\)](#) analytes in the National Functional Guidelines in the associated initial calibrations. Although EPA Method 8260 does not require a minimum RRF for tert-butyl alcohol, the non-detect results reported for this compound were rejected on the basis of professional judgment.

Non-detect results for 2,2-dichloropropane in 17 samples and naphthalene in 10 samples were qualified as estimated (UJ) because the percent difference (%D) in the associated continuing calibration verification standard (CCV) exceeded 25% maximum. Although EPA Method 8260 does not require the %D for these compounds to be less than 25% in the CCV, these data were qualified using professional judgment based on criterion established in the National Functional Guidelines.

The non-detect results for lead-210 in 5 soil samples from boring M120 and the water sample M-120 were qualified as estimated (UJ) because the method for Pb-210 by [gas-flow proportional counting \(GFPC\)](#) requires a minimum of five days for Bi-212 in-growth to occur before analysis and this minimum time requirement was not met. The non-detect result for radium-228 in water sample M-120 was qualified as estimated (UJ) because the GFPC instrument calibration had expired 4 days prior to analysis.

Results for the total tetrachlorodibenzo-p-dioxins and total tetrachlorodibenzofurans in sample M-120- 0.5 and M-120-10 listed in Table E-6 were qualified as estimated (J) by the validator because the reported result was less than the lowest calibration standard but greater than the estimated detection limit and these results had not been qualified by the laboratory.

The non-detect results for the pesticide naled in samples M120-0.5, M-120-10, M120-30, and the equipment blank EB-3 were qualified as estimated (UJ) due to the low recovery of this compound in the associated [continuing calibration verification \(CCV\) standard](#).

3.3 Interference Check Sample Results

Interference check sample (ICS) results were reviewed during full validation of the metals data for methods SW-846 6010B and SW-6020. **Table E-7** lists the sample results that were qualified based on ICS results. The results for cadmium, copper, and manganese in seven soil samples from the M120 boring analyzed by SW-846 Method 6020 were qualified as estimated with a possible high bias (J+) due the detection of these elements in the associated bracketing [ICSC](#) A solution data. No data from the SW-846 6010B analyses required qualification on the basis of ICS results.

3.4 Blank Contamination

In general, laboratory and field blanks were free of contamination. **Table E-8** lists the sample results that were qualified based on detected contamination in laboratory blanks such as method blanks, initial calibration blanks, and continuing calibration blanks, or equipment blanks. No data required qualification due to trip blank contamination. No data were qualified based on results of the field blank or pump blank because they were determined not to be relevant to the sample results after field collection activities were completed.

Laboratory Blanks

Results for thorium-230 in 13 soil samples were negated (B) based on the normalized absolute difference between the concentration and measurement uncertainty of this radionuclide in the associated method blanks and the samples. These negated results are not rejected but may be false positives totally attributable to blank contamination. The slightly higher result for Th-230 in sample M-117-5 was qualified as estimated (JB) due to the same method blank contamination.

Results for molybdenum in 8 soil samples were negated (U) at the reporting limit or reported concentration due to contamination in the associated laboratory preparation blank at a concentration below the reporting limit but above the method detection limit. [In the cases that the results were reported above the reporting limit in the samples, the reporting limits were raised to the concentration detected.](#)

Equipment Blanks

Results for acetone in 16 soil samples were negated (U) at the laboratory reported concentrations due to contamination of the associated equipment blank EB-2. Consistent with EPA guidelines for common contaminants, an action limit (AL) of 10 times the EB-2 acetone concentration was established and used to qualify all the associated soil samples with reported concentrations less than this AL value.

The result for zinc in soil sample M119-40 was qualified as estimated and possibly biased high (J+) due to contamination detected in the associated equipment blank EB-2.

The results for barium in water sample H-11 and for cobalt in water samples TR-9A and M-103A were qualified as estimated and possibly biased high (J+) due to contamination in the associated equipment blank EB-3.

Results for radium-226 in the water samples M-103A and H-11 were negated (B) based on radium contamination in the associated equipment blank EB-3. These negated results are not rejected but may be false positives totally attributable to blank contamination.

3.5 Surrogate Recoveries

No data were rejected or otherwise qualified on the basis of surrogate recovery evaluation.

3.6 Laboratory Control Samples

LCS and LCSD recoveries met QC acceptance criteria for the majority of analyses. **Table E-9** lists the results qualified based on LCS and LCSD recoveries that exceeded QC acceptance criteria.

The non-detect results for 3,3'-dichlorobenzidine in water sample M-120 and EB-3 were rejected (R) due to a recovery of less than 10% for this analyte in the LCS ~~and an RPD that exceeded the quality control acceptance criteria in the LCS/LCSD pair.~~

The organophosphorous pesticides in the LCS associated with both water sample M-120 and the equipment blank EB-3 exhibited high recoveries for nearly half or more the target analytes. No data were qualified based on the high recoveries because none of these organophosphorous pesticides were detected in any of the associated samples. As discussed in Section 3.9, this caused the relative percent differences (RPDs) for the LCS/LCSD pair to also be high.

3.7 Matrix Spikes

MS and MSD recoveries met the QC acceptance criteria for the majority of analyses. **Table E-10** lists the sample results qualified based on MS or MSD recoveries which were outside the laboratory acceptance criteria or required additional qualification per the National Functional Guideline rules.

Ten of the polychlorinated dibenzo-p-dioxin (PCDD) and dibenzofuran (PCDF) congener results and the associated homolog total results for soil sample M120-0.5 were qualified as estimated (J or UJ) based on MS recoveries less than the lower QC limit.

Positive results for antimony in 8 soil samples were qualified as estimated with a possible low bias (J-) and non-detects in 25 soils were qualified as estimated (UJ) due to associated MS/MSD recoveries less than the QC acceptance criteria. Non-detect results for antimony in 6 soils were rejected (R) as unusable due to MS and MSD recoveries less than 30%.

Positive results for aluminum in 19 soil samples were qualified as estimated with a possible high bias (J+) due to recoveries exceeding the QC acceptance criteria upper limit in the associated MS or MSD recoveries.

Results for barium in 19 soil samples were qualified as estimated (J) due to erratic recoveries (outside the QC acceptance criteria both high and low) in the associated MS/MSD results. Barium results for 10 other soil samples were qualified as estimated with a possible low bias (J-) due to recoveries less than the lower QC acceptance criteria in the associated MS/MSD pair.

Results for iron in 19 soil samples were qualified as estimated with a possible high bias (J+) due to an MSD recovery above the QC acceptance criteria in the associated MS/MSD pair.

Results for sodium in 16 water samples were qualified as estimated (J) due to an associated MS recovery less than the QC acceptance criteria in the MS/MSD pair.

Results for titanium in 8 soil samples were qualified as estimated with a possible high bias (J+) due to an associated post digestion spike recovery that exceeded the QC acceptance criteria.

Results for tungsten in 6 soil samples were qualified as estimated with a possible low bias (J-) and non-detect results were qualified as estimated (UJ) in 33 soil samples due to recoveries less than the QC acceptance criteria in the associated MS/MSD.

Results for alkalinity in the water samples M-117 and M-121 were qualified as estimated with a possible low bias (J-) due to associated MS/MSD recoveries less than the QC acceptance criteria and the alkalinity non-detect result for water sample H-11 was qualified as estimated (UJ) for the same reason.

3.8 Internal Standards

Internal standard (IS) performance was reviewed during full validation of the Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) and Gas Chromatography/Mass Spectrometry (GC/MS) data. Table E-10 lists all the results qualified during validation based on IS performance.

Detected and non-detect results for 25 of the PCDD and PCDF congeners and homolog groups in the M-120-10 soil sample were qualified as estimated (J and UJ, respectively) due to 9 IS recoveries below the QC acceptance criteria. Non-detect results for 21 of the PCDD and PCDF congeners and homolog groups in the M-120-30 soil sample were qualified as estimated (UJ) due to [7 to internal standard \(IS\)](#) recoveries below the QC acceptance criteria.

[Two hundred eighty p](#)Positive and non-detect results for aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, and manganese, molybdenum, nickel, selenium, silver, thallium, tungsten, vanadium, and zinc were qualified as estimated (J and UJ, respectively) in the water samples listed in **Table E-11** due to associated IS recovery nonconformances. No data were rejected on the basis of IS recoveries.

3.9 Laboratory Duplicates

The evaluation of laboratory duplicate precision included an assessment of the agreement between LCS and LSCDs, MS and MSDs, and matrix duplicates, as measured through [relative percent difference \(RPD\)](#). **Table E-12** lists the results qualified during validation based on laboratory duplicate precision.

LCS/LCSD

The RPD for the LCS and LCSD results for dimethoate exceeded the acceptance limit. The non-detected results reported for this analyte in soil samples M120-0.5, M120-10, and M120-30 were qualified as estimated (UJ) on the basis of the RPD.

The non-detect results for all of the organophosphorous pesticides in water sample M-120 were qualified as estimated (UJ) because more than half of all the analytes in the LCS and LCSD exhibited RPDs exceeding the QC acceptance criteria.

The non-detect results for 5 of the organophosphorous pesticides in equipment blank EB-3 were qualified as estimated (UJ) because those analytes in the LCS and LCSD exhibited RPDs exceeding the QC acceptance criteria.

The organophosphorous pesticides LCS/LCSD pairs associated with both water sample M-120 and the equipment blank EB-3 exhibited high RPDs for nearly half or more the target analytes due to high recoveries in the LCS. [The recoveries are discussed in Section 3.6.](#) No data were qualified based on the high [RPDs/recoveries](#) because none of these organophosphorous pesticides were detected in any of the associated samples.

MS/MSD

Positive and non-detect results for 13 PCDD and PCDF congeners and the homolog groups in sample M-120-0.5 were qualified as estimated (J and UJ, respectively) due to RPDs that exceeded the [quality assurance \(QA\)](#) acceptance criteria for the associated MS/MSD.

The non-detect result for hexachlorobutadiene in soil sample M-118-50 was qualified as estimated (UJ) because the RPD in the associated MS/MSD exceeded QA acceptance criteria for this compound.

[Fifty-one](#) ~~The~~ positive results for barium, magnesium, and sodium in the soil samples identified in Table E-12 were qualified as estimated (J) due to RPD results in the associated MS/MSD that exceeded the QA acceptance criteria.

Matrix Duplicates

Positive and non-detect results for perchlorate in 14 soil samples were qualified as estimated (J and UJ, respectively) due to an RPD that exceeded the QC acceptance criteria in the associated laboratory matrix duplicate.

3.10 Field Duplicates

The results of the six soil field duplicate pairs and one groundwater field duplicate pair collected during the Upgradient investigation were evaluated during validation. RPDs were compared to the objectives established in the QAPP of 30% RPD for aqueous samples and 50% RPD for solid samples. **Table E-13** lists the results qualified during validation based on field duplicate precision nonconformances.

The RPDs for aluminum, barium, iron, manganese, titanium, and zinc exceeded the acceptance limits in the groundwater sample field duplicate pair TR-8/TR-8D. The results for these analytes in the field duplicate pair TR-8/TR-8D and the associated groundwater samples [M-103A](#), [TR-7A](#), and [TR-8A](#) were qualified as estimated (J) on the basis of RPDs.

Results for calcium in the soil sample field duplicate pair M120-40/M120-40D and the associated M120 boring samples [M120-0.5](#), [M120-10](#), [M120-20](#), [M120-30](#), [M120-5](#), [M120-50](#), [M120-60](#), and [M120-80](#) were qualified as estimated (J) due to the RPD exceeding the QC acceptance criterion.

The copper and lead results for the soil sample field duplicate pair M117-20/M-117-20D and the associated soil samples [M116-10](#), [M116-20](#), [M116-30](#), [M116-40](#), [M116-5](#), [M116-50](#), [M117-0.5](#), [M117-10](#), [M117-30](#), [M117-40](#), [M117-5](#), [M117-50](#), [M117-60](#), [M117-80](#), and [M117-80D](#) were qualified as estimated (J) due to the RPDs for these analytes exceeding the QC acceptance limits.

The RPDs for arsenic, calcium, and copper exceeded the acceptance limits in the soil field duplicate pair M119-0.5/M-119-0.5D. The results for arsenic, calcium, and copper in the field duplicate pair and the associated soil samples [M119-10](#), [M119-20](#), [M119-32](#), [M119-40](#), [M119-5](#), and [M119-50](#) were qualified as estimated (J) on this basis.

The results for copper and zinc in the soil field duplicate pair M117-80/M-117-80D and the associated soil samples [M116-10](#), [M116-20](#), [M116-30](#), [M116-40](#), [M116-5](#), [M116-50](#), [M117-0.5](#), [M117-10](#), [M117-30](#), [M117-40](#), [M117-5](#), [M117-50](#), [M117-60](#) were qualified as estimated (J) due to RPDs for copper and zinc exceeding the QC acceptance criterion.

3.11 ICP Serial Dilution

Serial dilution results were reviewed during the validation of the ICP and ICP/MS data. No data were estimated or otherwise qualified on the basis of serial dilution results.

3.12 Quantitation

Table E-14 lists the results that were qualified during validation based on quantitation issues. These results were limited to PCDD and PCDF congeners and homologs where reporting limits were elevated during validation for some non-detect results. These results met the compound identification criteria stipulated in the method, but, according to the laboratory's [standard operating procedure \(SOP\)](#), were not

reported as positive results because the concentrations were less than ½ of the lowest calibration standard. The laboratory reported these results as non-detects at the actual sample results levels; however, during validation the detection limits for the sample results listed in the table below were raised to ½ of the lowest calibration standard since the laboratory considers these results to be non-detect at this level.

[Eight radiochemical results were originally rejected by the laboratory due to low abundance. During data validation it was determined that the analytes were not detected above the PQLs and the results were qualified "U" as non-detect.](#)

3.13 Other Issues

Table E-15 lists results for methanol in 28 soil samples that are probably attributable to cross-contamination during shipping. Soil samples for VOC analyses that were field preserved in methanol were shipped to the laboratory in zipper-lock bags containing other soil samples in brass sleeves and caps that were being submitted for the fuel alcohol analyses, including methanol. EMAX alerted ENSR of the suspicious number of methanol detections in the sleeved soil samples before the field operation was complete and the surface soils were recollected and shipped without associated methanol vials. Methanol was not detected in any of these resampled surface soils, indicating that the methanol detected in the original samples was likely attributable to cross-contamination during shipping. The methanol results for the original surface soil results were rejected (R) and all of the subsurface soil samples with methanol detections were qualified as probable contamination during shipping (Z). Some results were also qualified as estimated (J) on the basis of precision in the duplicate analyses. This poor precision is probably attributable to inconsistent levels of cross-contamination between samples in different sleeves and caps and was therefore not discussed in the field duplicate precision section of this report.

3.14 Rejected Results

Table E-16 lists all the sample data points that were rejected as unusable during validation. Rejected results values were removed from the database; hence, the result column appears empty. The reasons these results were rejected were discussed in the previous Sections 3.2, 3.6, 3.7, and 3.13. This information is summarized and discussed in the paragraphs below by analyte.

The data for 3,3'-dichlorobenzidine in water samples M120 and EB-3 were rejected due to very poor recovery for this analyte in the associated LCS. The rejected values were nondetects at the reporting limit.

Benzidine related compounds are subject to oxidative loss during extraction and concentration using EPA Method 8270 and frequently exhibit poor chromatographic behavior. 3,3'-dichlorobenzidine has not been identified as a [Site Related Chemical \(SRC\)](#) at the Tronox Henderson facility.

The rejected data for antimony in 6 soil samples from boring M118 were due to a very low matrix spike recovery in the associated M118-50 sample. Matrix spike recovery problems for antimony in soil are common and probably attributable to strong matrix absorption. Antimony is identified as an SRC at the Tronox Henderson facility.

[TheFive](#) data points for methanol in surface soils were rejected because these results appeared to be attributable to cross-contamination during shipping and could not be duplicated when the affected samples were recollected. The original methanol results have been replaced by the data from the resampled soil which was not cross-contaminated.

[TheSixty-six](#) results for tert-butyl alcohol in soil and water analyses were rejected due to a low RRF in the initial calibration for this compound. All these rejected values were nondetects for tert-butyl alcohol at the reporting limit. This compound is identified in EPA Method 8260 as having poor purging efficiency which frequently causes a low RRF; however, it is not a System Performance Check Compound and therefore the RRF did not result in rejection of the initial calibration by the laboratory. This compound is not identified as a SRC at the Tronox Henderson facility.

4.0 EVALUATION OF DATA QUALITY INDICATORS

Data validation information was used to evaluate the data quality indicators (DQI) of precision, accuracy, representativeness, comparability, completeness, and sensitivity for results in the Henderson Upgradient investigation dataset. Each of these DQI parameters is discussed in sections below.

4.1 Precision

Precision is the measure of agreement among repeated measurements of the same property under identical or substantially similar conditions. Field precision was assessed through the collection and measurement of field duplicates and expressed as the RPD of the sample and field duplicate pair results. The field duplicate RPD results which caused the application of validation qualifiers are discussed in Section 3.10 of this report and listed in Table E-13. In general the field duplicate precision was acceptable

for all analytes except a limited set of metals. This limited metals data set was qualified as estimated but usable and represents only 1.3% of the total data points.

Laboratory precision was assessed through the RPD results for matrix duplicates, LSC/LCSD pairs, and MS/MSD pairs. Laboratory precision nonconformances which resulted in the application of validation qualifiers are discussed in Section 3.9 of this report and listed in Table E-12. In general, the laboratory duplicate precision was acceptable. Exceptions included several PCDD/PCDF congeners and hexachlorobutadiene in two MS/MSD pairs; the metals barium, magnesium, and sodium in two MS/MSD pairs; numerous organophosphorous pesticides in two LCS/LCSD pairs, and perchlorate in one matrix duplicate. Results associated with these duplicates were qualified as estimated but usable and represent only 0.89% of the total data points. No data was rejected based on precision.

4.2 Accuracy

Accuracy is the degree of agreement between an observed value and an accepted reference or true value. Laboratory accuracy was assessed during the validation using the recoveries of positive control samples, i.e., MS and MSD, LCS and LCSD, and surrogate spikes. The spike recoveries which resulted in the application of validation qualifiers are discussed in Sections 3.6 and 3.7 of this report and listed in Tables E-9 and E-10. In general the laboratory accuracy was acceptable. Exceptions included twelve PCDD/PCDF congeners associated with one MS/MSD pair; alkalinity associated with one MS/MSD pair; and the metals antimony, aluminum, barium, iron, sodium, titanium, and tungsten in several MS/MSD pairs. Results associated with these recovery nonconformances were qualified as estimated but usable, except for six results for antimony which were rejected. The number of rejected data points based on spike recovery accuracy is 0.09 % of the total number of data points, and the number of qualified points represents 2.5% of the total data points collected.

Accuracy is also indirectly addressed via the negative control samples for field activities, i.e. trip, equipment, and field blanks, as well as laboratory negative control samples such as method blanks and calibration blanks. Blank results validation resulted in qualifying 44 results as described in Section 3.4 which represents only 0.5% of the total data points collected. No data were rejected based on blank results.

Bias as a component of accuracy is also evaluated with the validation of holding time, calibration, interference check sample, [LCS](#), internal standard performance, and quantitation results discussed in Sections 3.1, 3.2, 3.3, [3.6](#), 3.8, and 3.12 of this report. Collectively these evaluations resulted in the qualification of 5.6% and the rejection of 0.74% of the total data points.

Evaluation of the remaining QC elements that contribute to accuracy, such as mass spectrometer tuning, serial dilution results, compound or element identification, peak integration and mass spectral matches,

chemical yield, and calculation/transcription verifications, did not result in the qualification or rejection of any data points during validation.

4.3 Representativeness

Representativeness is the measure of the degree to which data suitably represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Aspects of representativeness addressed during validation include the review of sample collection information in the ~~chain-of-custody (COC)~~ documentation, conformity of laboratory analyses to workplan intentions, adherence of the documented laboratory procedures to method requirements, and completeness of the laboratory data packages. Most of the issues identified during this evaluation did not result in the qualification of laboratory but did involve resubmittals of data from the laboratories to correct problems that were discovered during the validation process. All of these issues were resolved. Other aspects of data representativeness such as adherence to recommended holding times, instrument calibration requirements, and field and laboratory precision assessments are discussed in Sections 3.1, 3.2, 3.9, and 3.10 of this report.

One additional issue of representativeness was the probable false positives due to methanol cross-contamination that occurred during shipping of certain soil samples. This issue, including its resolution, is discussed in Section 3.13 above.

4.4 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system, expressed as a percentage of the number of valid measurements that were or should have been collected. Valid data is defined as all the data points judged to be valid, i.e. not rejected, as a result of the validation process.

Field completeness is defined as the percentage of samples actually collected versus those intended to be collected per the Workplan. The goal stated in the QAPP for this project was greater than 90% field completeness. A comparison of the Workplan sample tables with the database sample IDs indicates that actual field completeness was 99.1%, exceeding the goal established for the project. This field completeness calculation is based on the total analytical suites planned in Table 2 and Table 4 of the Workplan compared to the COC requests sent to the laboratories. Planned samples from depths that were excluded due to the water table depth were not included in the calculation. All COC requests were faithfully executed by the laboratories.

Laboratory completeness is defined as percentage of valid data points versus the total expected from the laboratory analyses. The objective stated in the QAPP for this project was greater than 95% laboratory completeness. Actual laboratory completeness was 100% on the basis of sample analysis, i.e., all

requested analyses were performed and reported by the laboratories, and 99% completeness based on valid data (only 1% of the data was rejected during data validation).

4.5 Comparability

Comparability is a qualitative expression of the measure of confidence that two or more data sets may contribute to a common analysis. Because this project was an initial site investigation for most of the parameters, involving new wells and new soil borings, there was no historical data set for comparisons. Comparability of data within the investigation was maximized by using standard methods for sampling and analysis, reporting data, and data validation. In general, standard [Resource Conservation and Recovery Act \(RCRA\)](#) program methods from SW-846 were employed for all analyses with the exception of methods for which no SW-846 method exists (e.g. some wet chemistry parameters) or if no laboratory was certified by NDEP for the appropriate SW-846 method. In this event, alternate, EPA or other accepted methods were utilized. To ensure that multiple laboratories did not contribute results for the same analytes on different samples, analyses were distributed amongst the laboratories on both a method and matrix basis. In the few cases where the methods were different then the matrix was also different. The other laboratories each had unique analyte sets as explained in the introduction, so no instances of multiple methods for the same analyte/matrix pair occurred in this dataset.

4.6 Sensitivity

Sensitivity is the capability of a method or instrument to discriminate between measurement responses representing different levels of the variable of interest and particularly the capability of measuring a constituent at low levels. For the EPA methods employed in this project sensitivity is measured by the method detection limit (MDL) and reporting limit (RL). Both nominal MDLs and RLs were provided by the laboratories in Table 7 of the Workplan and were verified during validation. Reporting limits in general were adjusted sample quantitation limits based on the low point of calibration and corrected for sample-specific factors such as exact aliquot size, dry weight for soils, dilutions, etc. Some EMAX RLs and MDLs were elevated slightly above the adjusted low point of calibration and statistical MDL values but were in conformity with SOP and Workplan specified values. In general the MWH reporting limits were based on MDLs so no estimated values between the MDL and RL (laboratory J flagged) were provided.

To determine if the adjusted reporting limits for all project analytes were low enough to meet the project sensitivity requirements a comparison of the project Data Quality Levels (DQLs), based on EPA Region 9 Preliminary Remediation Goals (PRGs) for industrial soils, was made with all the laboratory RLs associated with non-detect results. This comparison yielded only three results, for N-nitroso-di-N-propylamine in the M-120 soils, where the reported RL for a non-detect was above the industrial PRG value. Only industrial PRGs were used for comparison because future land use at the site is limited to industrial/commercial, not residential. N-nitroso-di-N-propylamine is not a SRC for this project. Water DQLs for this project were based on the lower of the EPA Region 9 tap water PRGs or the Federal

Maximum Contaminant Levels (MCLs) for drinking water. Laboratory RLs for a total of 77 analytes were above the corresponding water DQL for all the water samples analyzed. These analytes met the RL goals stated in the Workplan.⁵⁷ The DQLs for these analytes are not routinely achievable using the conventional EPA methods selected for this project.

5.0 CONCLUSIONS

One hundred percent of the laboratory data for the Upgradient Investigation was validated using standardized guidelines and procedures recommended by EPA and NDEP. 90% of the results for this project were accepted as reported by the laboratory without additional qualification based on validation actions and should be considered valid for all decision-making purposes.

A subset of the laboratory results was qualified during validation and those results are summarized in Tables E-5 to E-16. The qualified data are grouped in these tables based on the reason for qualification (see Table E-2) and the qualifier symbols, or flags applied (see Table E-1). 8.9% of the results of the total analytical dataset for this project were qualified as estimated due to minor QC problems with precision, accuracy, and representativeness. Based on guidance in the U.S. EPA data usability document (EPA, 1992), estimated data are considered usable with the appropriate interpretation (e.g., consideration of the potential bias).

The results that were rejected due to more serious QC problems with spike recoveries and calibrations constituted only 1.1% of the total analytical dataset for this project. These rejected results are considered unusable and should not be used for decision making purposes. Details of the rejected results are discussed in Section 3.14 of this report. The overall impact of these rejected results on the usefulness of the project data is minimal. Most of the rejected results pertain to nondetects for two analytes, 3, 3-dichlorobenzidine and tert-butyl alcohol, which were not SRCs for this project. Results for methanol which were rejected on the basis of cross-contamination were replaced by data from acceptable reanalyses after resampling at the same locations. Antimony results for 6 soil samples from one boring (M-118) were rejected and antimony is a SRC for this project. The impact of these rejected antimony results is minimal however, given that the usable antimony results from this same boring were all several orders of magnitude below the industrial soil PRG value.

All the qualified results were evaluated with respect to the data quality indicators and compared to the QAPP and Workplan goals. Details of this evaluation are discussed in Section 4 of this report. Based on the results of data validation the overall goals for data quality were achieved for this project.

6.0 REFERENCES

- EPA. 1992. Guidance for Data Useability in Risk Assessment. Part A.
- EPA, 1999 USEPA “Contract Laboratory Program National Functional Guidelines for Organic Data Review”
- EPA, 2001 USEPA “Draft Region 9 Superfund Data Evaluation/Validation Guidance”
- EPA, 2004 USEPA “Contract Laboratory Program National Functional Guidelines for Inorganic Data Review”
- EPA, 2005 USEPA Analytical Services Branch (ASB) “National Functional Guidelines for Chlorinated Dibenzo-p-Dioxins (CDDs) and Chlorinated Dibenzofurans (CDFs) Data Review”
- ENSR, February 2006 Upgradient Investigation Workplan Addendum, Tronox Facility, Henderson, Nevada
- ENSR, August 2006 DRAFT Quality Assurance Project Plan, Tronox LLC Facility Henderson, Nevada
- DOE, 1997 Department of Energy “Evaluation of Radiochemical Data Usability”
- NDEP, 2006 NDEP “Guidance on Data Validation, BMI Pant Sites and Common Areas Projects, Henderson, Nevada”
- NUREG, 2004 USEPA, Department of Energy, Department of Defense, Department of Homeland Security, Nuclear Regulatory Commission, National Institute of Standards and Technology, US Geological Survey, Food and Drug Administration “ Multi-Agency Radiological Laboratory Analytical Protocols Manual (MARLAP)”