Evaluation of Field Analytical PCB Determinations Supporting Midsouth Leasing Property

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Executive Summary

A field laboratory, Environmental Chemistry Consulting Services, Inc. (ECCS), successfully analyzed soil samples for polychlorinated biphenyls (PCBs) in support of plant site remediation activities performed for the Midsouth Leasing Property in Crystal Springs, Mississippi. Approximately 10 percent of the soil samples collected during the program were split in the field and sent to a fixed laboratory, Paradigm Analytical Laboratories, Inc. (Paradigm), for confirmatory analysis. The field laboratory successfully implemented an extensive Quality Assurance/Quality Control (QA/QC) program, a program essentially as comprehensive and strict as those of fixed laboratories (see Appendix 2 for field laboratory reports). A careful examination of the field QA/QC results and the results of the split soil samples analyzed by both the field (ECCS) and the confirmatory (Paradigm) laboratories demonstrated the outstanding consistency and accuracy of the field laboratory. Comparison of results of the split samples analyzed by both laboratories showed excellent agreement across the full range of encountered Aroclor 1260 concentrations, including those near the PCB action level of 1.0 mg/kg, confirming the suitability of the field measurements for site characterization and decision-making.

- Both laboratories consistently met internal QA/QC criteria. Analytical systems were under control with regard to calibration, surrogate recoveries, matrix spikes, matrix spike duplicates, laboratory control samples, and blanks.
- Overall, 94.3% of split samples (*i.e.*, field *vs.* fixed laboratory) fell within the range of acceptable Relative Percent Differences (RPDs) for split soil samples.
- 92.6% of the duplicate sample pairs analyzed by the field laboratory fell within the acceptable range for RPDs for duplicate soil samples.
- 77.8% of the duplicate sample pairs analyzed by the fixed laboratory fell within the acceptable range for RPDs for duplicate soil samples.
- 97.9% of field laboratory results <1.0 mg/kg were confirmed by the fixed laboratory.
- The precision, accuracy, selectivity, and sensitivity of the field laboratory were excellent throughout the program.

1 Field Laboratory Method Procedures

The use of the field laboratory was approved by MDEQ and USEPA Region IV for assessment and confirmation of remediation on this project as discussed in Section 7.0 of this report. Both laboratories have consistently performed well during previous phases of assessment and remediation associated with the Kuhlman Electric project. In accordance with the approved QA/QC plan, ten percent of samples collected were split and sent to the fixed base laboratory, Paradigm, to confirm the field laboratory results and applicability of these results to the assessment and remediation programs.

The field method used for the determination of PCBs during this program was an abbreviated, modified version of approved methods (a mini-extraction modifying EPA Method 3500B for sample extraction, EPA Method 3665A for extract cleanup, and EPA Method 8082 for determination of PCBs). The method was very sophisticated for a field analysis protocol: surrogates were added to each sample to monitor extraction performance; analysis was carried out on a gas chromatograph using capillary columns and an electron capture detector (ECD); and quantitation was based on comparison to standards using daily 6-point calibration curves. Through the use of the gas chromatograph and ECD, the selectivity and sensitivity of the field method was equivalent to that of the fixed laboratory. The method was also similar to one previously demonstrated to be successful for PCBs by the EPA (USEPA, 1995).

1.1 Field Laboratory Sample Preparation and Extraction

For each sample, the field laboratory received a 9 oz. sample jar filled with soil that had been homogenized by the sample collectors. After processing the sample, as described below, field laboratory staff transferred soil from the original 9 oz. jar into a 4 oz. jar which was shipped to the fixed laboratory for confirmatory analysis. The field laboratory retained the balance of sample in the 9 oz. jar.

In the field laboratory, approximately 4 grams of each sample were weighed into a 20 mL scintillation vial. Approximately 10 grams of sodium sulfate were added to the vial and mixed with the soil until the mixture was free flowing. Surrogate solution containing decachlorobiphenyl [DCBP] and tetrachlorometaxylene [TCMX] was added, followed by addition of 8 mLs of solvent (80:20, isooctane:acetone). The container was then sealed and shaken for 3 thirty-second intervals. If the extract exhibited color following the shaking step, it was treated with sulfuric acid to remove interferants.

Otherwise, the extract was decanted into injection vials and subsequently injected onto a gas chromatograph equipped with an electron capture detector.

1.2 Field Laboratory Analysis

Sample analysis was performed on an RTX-35, 30 m X 0.53mm ID X 0.5-micron film capillary column. Based on site history and prior analyses (and confirmed by this program), the PCBs were quantified as Aroclor 1260. Up to 9 Aroclor 1260 peaks were used to quantify the concentration of PCBs present, based on a 6-point calibration curve, which was generated each day. Continuing Calibration Verification (CCV) samples were also run regularly. Allowable surrogate recoveries were 60-140 % for both DCPB and TCMX. The nominal reporting limit was approximately 0.100 mg/kg, well below the target action level of 1.0 mg/kg.

1.3 Field Laboratory QA/QC

The QA/QC parameters of the field methodology are described in the field laboratory reports (Appendix 2). The field laboratory consistently met its QA/QC criteria, ensuring that the analytical system was under control with regard to calibrations, matrix spikes, matrix spike duplicates, laboratory control samples, and blanks. Sample surrogate recoveries were calculated on a real-time basis and re-extractions and re-analyses were performed on the infrequent occasions that allowable recoveries were not achieved.

2 Fixed Laboratory Method Procedures

The confirmatory laboratory, Paradigm, used approved EPA methods, including EPA Method 3545 for extraction, EPA Method 3665A for cleanup of the extract, and EPA Method 8082 for analysis of the extract for PCBs.

2.1 Fixed Laboratory Sample Preparation and Extraction

EPA Method 3545, Accelerated Solvent Extraction (or, Pressurized Solvent Extraction), was used to extract PCBs from the split samples sent to the fixed laboratory. Approximately 10 grams of soil were mixed and dried with approximately 20 grams of drying agent (sodium sulfate), then extracted in a pressurized, heated extraction device. Two extraction cycles were used.

2.2 Fixed Laboratory Analysis

The fixed laboratory used EPA Method 8082 for the analysis of samples (USEPA, 1997). The method was virtually the same as that of the field laboratory with regard to equipment and methodology.

2.3 Fixed Laboratory QA/QC

The fixed laboratory consistently met its QA/QC criteria, ensuring that the analytical system was under control with regard to calibrations, surrogate recoveries, matrix spikes, matrix spike duplicates, laboratory control samples, and blanks (See Appendix 3).

In July and August 2003, although Paradigm's internal surrogate recovery criteria were consistently met, it became apparent that surrogate recoveries for TCMX were somewhat low (numerous recoveries were reported between ~50-60%, and sometimes were as low as 40%). The low recoveries were often evident in nondetected samples, where matrix interferences would not be expected to affect surrogate quantitation. Gradient notified the fixed laboratory of this issue and requested that the chemists carefully review their preparation and analysis procedures. Paradigm was unable to find any obvious trends or reasons for the lower recoveries. Nonetheless, the extraction chemists were requested to take extra steps to ensure a quantitative transfer and within a few weeks their surrogate recoveries

returned to expected usual levels (80-100%). The laboratory carefully monitored the recoveries closely throughout the remediation.

At Gradient's request, several samples were reanalyzed by Paradigm in order to evaluate disparities demonstrated between concentrations reported by the fixed and field laboratory. The reanalyses results exhibited much better precision. The reanalyses results were reported in the project database and were used in our evaluation. The results are summarized in Table 5.

3 Comparison of Field Laboratory and Fixed Laboratory Results

3.1 Split Samples

The PCB (Aroclor 1260) data for all split samples are presented in Table 1. Other information regarding these samples, such as collection dates, depth of sample, *etc.*, are presented in Appendix 2.

Throughout this document we use the field laboratory results directly (expressed on an as received, or wet weight basis) to compare with the fixed laboratory results. This comparison is most appropriate for evaluating the performance of the field laboratory because it coincides exactly with how the field results were used on a real-time basis and in generating a conceptual site model. Also, for all calculations and plotting, all nondetects were set to values equal to the reporting limit.

A comparison of all field and the fixed laboratory results for June 2002 – May 2004 is illustrated in Figure 1. The regression line, its equation, and the coefficient of determination (R^2, [Zar, 1984]) are also presented in the figure (and is presented in all similar figures in this report). The field results correlated strongly with the fixed laboratory results. The field results tended to be greater than the fixed laboratory results.

Figures 2 through 4 compare the field and fixed laboratory results for shorter time periods during June 2002 through January 2004, illustrating that the comparability was consistently superb throughout the program.

To evaluate precision and accuracy further, the Relative Percent Difference (RPD; RPD =([field-fixed]/{[field + fixed]/2} X 100%)) was calculated for each pair of split samples (see Table 1). For this data analysis, we evaluated the split sample data against an RPD criterion of 100%. This criterion was used by EPA Region IV at the Anniston, Alabama site (CHMM, 2000; USEPA Region IV, 2000). Unfortunately, USEPA Region IV's data validation guidance does not specify a criterion for split sample precision, other than to note whether precision was acceptable, provisional, or unacceptable; based on our analysis the precision is acceptable (USEPA Region IV, 1999). For the purposes of our evaluation, nondetects were set to detected values equal to the reporting limit.

Figure 5 plots the RPD *versus* the fixed lab concentration (Paradigm). Figure 6 presents the median RPD along with percentile information, for split samples organized into concentration ranges: ≤ 10 mg/kg; between 10 and ≤ 100 mg/kg; and > 100 mg/kg. Both figures demonstrate that generally, lower concentration ranges exhibit acceptable RPDs. There were too few samples with concentrations > 100 mg/kg to be able to evaluate a trend.

Overall, the precision and accuracy of the field data as reflected in the RPD determinations were excellent (see Table 1). In only a few instances (9 out of 143, or 6.3%) did RPDs of split samples exceed 100% and these were primarily for samples with fairly low concentrations. Poor precision can be caused by a number of things, including poor instrument performance or inconsistent analysis methods, but, especially in the case of soils, a difficult, heterogeneous sample matrix is often the reason. Soil contamination is prone to heterogeneity for semivolatile organics like PCBs because PCBs adhere to soil particles and do not generally get mixed well in the environment. This trait of soil contamination is recognized by regulatory agencies and is reflected in the larger RPD tolerances for soil samples relative to aqueous samples (USEPA Region I, 1996).

3.2 Duplicate Samples

Table 2 presents the data for the duplicate samples pairs that were analyzed by both the field laboratory and the fixed laboratory. Field and fixed duplicate pair results were evaluated for precision using criteria presented for non-aqueous matrices in USEPA's Region I data validation guidelines (USEPA Region I, 1996). Region I's precision criterion is RPD $\leq$ 50% for non-aqueous duplicate results that are greater than 2 times the quantitation limit. For results less than 2 times the quantitation limit, if the difference between the results was less than the quantitation limit, the results were deemed to have demonstrated acceptable precision. This allows for evaluation of the results, taking into consideration the increased variability of data near the sample quantitation limit (USEPA Region I, 1996). For the field laboratory 101 of the 114 duplicate pair analyses (88.6%) met RPD criteria. For the fixed laboratory, 96 of the 114 pairs (84.2%) met RPD criteria.

A comparison of the concentrations of the samples and their duplicates (June 2002- May 2004) is presented in Figure 7 (field laboratory) and Figure 8 (fixed laboratory). Based on a statistical evaluation of the reported concentrations, both laboratories demonstrated very good precision (*i.e.*, high R^2 very close to 1.0).

Figure 9 presents the RPD of the field duplicate analyses *versus* the average concentration for the pair (June 2002-May 2004). As expected, the magnitude of the RPD tends to increase at low concentrations. Figure 10 presents the equivalent information for the fixed laboratory.

In the majority of the figures described above, RPDs were allowed to be either positive or negative in order to evaluate data trends (*e.g.*, if either the bonafide sample or its duplicate were consistently higher or lower). They were positive when the field sample result was greater than the duplicate result and negative when the field sample result was less than the duplicate result. For Figure 10, however, we present the mean of the absolute value of the RPDs (*e.g.*, an RPD of –18% becomes 18%) for the duplicate analyses for both the field laboratory and the fixed laboratory. Figure 11 again demonstrates that the precision of the field laboratory compares favorably with that of the fixed laboratory.

For the field laboratory, only a few pairs of duplicate samples exceeded the allowable RPD goal of 50%, and these exceedances were likely to be caused by sample heterogeneity. Likewise, for the fixed laboratory, only a few duplicate pairs exhibited RPDs greater than 50%.

3.3 Action Level Decisions

An important aspect of field chemistry programs relates to the reliability of real-time decisions based on field results. The performance of the field chemistry program with respect to the action level of 1.0 mg/kg was excellent in this regard. Tables 3 and 4 summarize our findings. The fixed laboratory confirmed the field finding of < 1.0 mg/kg 46 times out of 47 (97.9%).

3.4 Summary

Overall, the agreement between the results of the field laboratory and the fixed laboratory was excellent. This conclusion is based on the high correlations achieved in the regressions of field results *versus* fixed laboratory results; the near 100% accuracy in determining PCBs near the action level of 1.0 mg/kg; the high precision attained by the field laboratory; and the virtual absence of significant QA/QC issues in the field laboratory throughout the program.

4 References

CHMM. 2000. "Split Sampling Guideline for the Anniston PCB Site. Anniston, Calhoun County, Alabama." Prepared for USEPA Region IV. April 21.

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U.S. Environmental Protection Agency Region I (USEPA Region I). 1996. "Region I, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses." July, Revised December.

U.S. Environmental Protection Agency Region IV (USEPA Region IV). 1999. "Data Validation Standard Operating Procedures for Contract Laboratory Program Routine Analytical Services. Revision 2.1." July.

U.S. Environmental Protection Agency Region IV (USEPA Region IV). 2000. "Quality Assurance Project Plan for the Anniston PCB Site, Calhoun County, Aniston, Alabama. Region IV." January.

Zar, JH. 1984. *Biostatistical Analysis*. Prentice-Hall, Inc., Englewood Cliffs, NJ. 718pp.

SplitSamples By Date

SampleID	SampDate	FieldDupO	MobileNo	FieldResult	FieldUnits	FieldQual	ParaResult	ParaUnits	ParaQual	RPD	PercSolids
MSL-GP03-002	6/6/2002		3772	7.4	mg/Kg WW		11	mg/Kg DW		-39.13043	93.1
MSL-GP05-002	6/7/2002		3778	20	mg/Kg WW		12	mg/Kg DW		50	90.6
MSL-GP06-002	6/7/2002		3781	0.1	mg/Kg WW	U	0.11	mg/Kg DW	U	-9.52381	90.9
MSL-GP08-002	6/7/2002		3786	0.77	mg/Kg WW		0.38	mg/Kg DW		67.82609	85
MSL-GP04-002	6/7/2002		3775	0.1	mg/Kg WW	U	0.1	mg/Kg DW	U	0	95
MSL-GP15-001	6/8/2002		3807	2.5	mg/Kg WW		3.4	mg/Kg DW		-30.50847	87.2
MSL-GP19-001	6/8/2002		3820	68	mg/Kg WW		74	mg/Kg DW		-8.450704	91.1
MSL-GP21-002	6/8/2002		3827	3.4	mg/Kg WW		1.9	mg/Kg DW		56.60377	87.8
MSL-GP30-002	6/9/2002		3854	49	mg/Kg WW		21	mg/Kg DW		80	83
MSL-GP24-001	6/9/2002		3835	3.8	mg/Kg WW		1.5	mg/Kg DW		86.79245	89.2
MSL-GP29-001	6/9/2002		3850	53	mg/Kg WW		37	mg/Kg DW		35.55556	86.3
MSL-GP31-001	6/11/2002		3859	0.36	mg/Kg WW		0.1	mg/Kg DW	U	113.0435	90
MSL-GP12-006	6/13/2002		3871	200	mg/Kg WW		110	mg/Kg DW		58.06452	89.2
MSL-GP11-005	6/13/2002		3863	170	mg/Kg WW		98	mg/Kg DW		53.73134	88.2
MSL-GP10-005	6/13/2002		3866	160	mg/Kg WW		190	mg/Kg DW		-17.14286	85.5
MSL-GP16-006	6/22/2002		3885	0.2	mg/Kg WW		0.24	mg/Kg DW		-18.18182	83.4
MSL-GP19-006	6/22/2002		3892	26	mg/Kg WW		21	mg/Kg DW		21.2766	90.8
MSL-GP19-008	6/28/2002		3973	0.1	mg/Kg WW	U	0.1	mg/Kg DW	U	0	94.2
MSL-HSA-001-001	3/31/2004		R001	0.88	mg/Kg WW		1.15	mg/Kg DW		-26.60099	
MSL-HSA-004-001	4/1/2004		R011	0.1	mg/Kg WW	U	0.1	mg/Kg DW	U	0	
MSL-HSA-008-001	4/1/2004		R022	0.1	mg/Kg WW	U	0.105	mg/Kg DW	U	-4.878049	
MSL-HSA-001-004	4/2/2004		R028	0.1	mg/Kg WW	U	0.107	mg/Kg DW	U	-6.763285	
MSL-DP-015-001	4/13/2004		R040	0.1	mg/Kg WW	U	0.117	mg/Kg DW	U	-15.6682	
MSL-DP-013-001	4/13/2004		R034	0.1	mg/Kg WW	U	0.111	mg/Kg DW	U	-10.42654	
MSL-DP-024-001	4/14/2004		R069	0.1	mg/Kg WW	U	0.106	mg/Kg DW	U	-5.825243	
MSL-DP-030-001	4/14/2004		R087	0.1	mg/Kg WW	U	0.128	mg/Kg DW	U	-24.5614	
MSL-DP-022-001	4/14/2004		R063	0.1	mg/Kg WW	U	0.0908	mg/Kg DW	U	9.643606	
MSL-DP-017-001	4/14/2004		R047	35	mg/Kg WW		4.68	mg/Kg DW		152.8226	
MSL-DP-027-002	4/14/2004		R079	0.1	mg/Kg WW	U	0.105	mg/Kg DW	U	-4.878049	
MSL-DP-040-001	4/15/2004		R117	0.1	mg/Kg WW	U	0.12	mg/Kg DW	U	-18.18182	
MSL-DP-042-002	4/15/2004		R125	0.1	mg/Kg WW	U	0.121	mg/Kg DW	U	-19.00452	
MSL-DP-032-001	4/15/2004		R093	0.1	mg/Kg WW	U	0.121	mg/Kg DW	U	-19.00452	
MSL-DP-052-001	4/16/2004		R155	0.1	mg/Kg WW	U	0.109	mg/Kg DW	U	-8.61244	
MSL-DP-045-001	4/16/2004		R133	2.1	mg/Kg WW		4.14	mg/Kg DW		-65.38462	
MSL-DP-046-001	4/16/2004		R136	0.13	mg/Kg WW		0.126	mg/Kg DW	U	3.125	
MSL-DP-055-001	4/16/2004		R164	0.1	mg/Kg WW	U	0.117	mg/Kg DW	U	-15.6682	

MSL-DP-059-001	4/17/2004	R177	0.67	mg/Kg WW		0.32	mg/Kg DW	70.70707
MSL-DP-064-001	4/17/2004	R193	0.1	mg/Kg WW	U	0.119	mg/Kg DW U	-17.3516
MSL-DP-057-001	4/17/2004	R171	0.1	mg/Kg WW	U	0.121	mg/Kg DW U	-19.00452
MSL-DP-067-001	4/17/2004	R202	0.8	mg/Kg WW		0.616	mg/Kg DW	25.9887
MSL-DP-078-001	4/19/2004	R235	0.17	mg/Kg WW		0.104	mg/Kg DW U	48.17518
MSL-DP-068-001	4/19/2004	R205	0.1	mg/Kg WW	U	0.12	mg/Kg DW U	-18.18182
MSL-DP-076-001	4/19/2004	R230	3.9	mg/Kg WW		3.07	mg/Kg DW	23.81636
MSL-DP-071-001	4/19/2004	R214	0.36	mg/Kg WW		0.216	mg/Kg DW	50
MSL-DP-087-003	4/20/2004	R264	0.1	mg/Kg WW	U	0.116	mg/Kg DW U	-14.81481
MSL-DP-089-001	4/20/2004	R268	1.3	mg/Kg WW		1.23	mg/Kg DW	5.533597
MSL-DP-093-003	4/20/2004	R282	0.1	mg/Kg WW	U	0.11	mg/Kg DW U	-9.52381
MSL-DP-079-001	4/20/2004	R238	3.8	mg/Kg WW		2.68	mg/Kg DW	34.5679
MSL-DP-094-001	4/21/2004	R283	0.25	mg/Kg WW		0.141	mg/Kg DW	55.75448
MSL-DP-096-001	4/28/2004	R290	0.88	mg/Kg WW		0.258	mg/Kg DW	109.3146
RLP-DP-016-001	4/28/2004	AA025	0.36	mg/Kg WW		0.245	mg/Kg DW	38.01653
RLP-DP-005-001	4/28/2004	AA009	1.6	mg/Kg WW		0.655	mg/Kg DW	83.81375
RLP-DP-012-001	4/28/2004	AA019	1.4	mg/Kg WW		0.712	mg/Kg DW	65.15152
RLP-DP-034-001	4/29/2004	AA056	0.65	mg/Kg WW		0.373	mg/Kg DW	54.15445
RLP-DP-028-001	4/29/2004	AA047	0.55	mg/Kg WW		0.32	mg/Kg DW	52.87356
RLP-DP-026-001	4/29/2004	AA044	0.41	mg/Kg WW		0.169	mg/Kg DW U	83.24698
RLP-DP-017-001	4/29/2004	AA026	0.1	mg/Kg WW	U	0.11	mg/Kg DW U	-9.52381
RLP-DP-041-001	4/29/2004	AA069	0.1	mg/Kg WW	U	0.123	mg/Kg DW U	-20.6278
MSL-DP-102-001	4/30/2004	R303	0.1	mg/Kg WW	U	0.107	mg/Kg DW U	-6.763285
RLP-DP-043-001	4/30/2004	AA073	0.14	mg/Kg WW		0.144	mg/Kg DW U	-2.816901
RLP-DP-048-001	4/30/2004	AA084	0.31	mg/Kg WW		0.202	mg/Kg DW	42.1875
MSL-DP-102-002	4/30/2004	R304	0.1	mg/Kg WW	U	0.107	mg/Kg DW U	-6.763285
RAL-DP-003-001	5/3/2004	BB003	0.12	mg/Kg WW		0.101	mg/Kg DW U	17.19457
RLP-DP-052-002	5/3/2004	AA101	0.41	mg/Kg WW		0.131	mg/Kg DW U	103.1423
RLP-DP-053-003	5/4/2004	AA114	0.1	mg/Kg WW	U	0.0976	mg/Kg DW U	2.42915
MSL-TR-001-001	5/10/2004	R343	3.6	mg/Kg WW		2.36	mg/Kg DW	41.61074
MSL-TR-002-006	5/10/2004	R353	31	mg/Kg WW		29.6	mg/Kg DW	4.620462
MSL-TR-004-005	5/11/2004	R367	0.49	mg/Kg WW		0.4	mg/Kg DW	20.22472
MSL-TR-003-001	5/11/2004	R355	4.4	mg/Kg WW		2.03	mg/Kg DW	73.71695
MSL-TR-005-001	5/13/2004	R368	2.3	mg/Kg WW		1.77	mg/Kg DW	26.04423