Herrera Environmental Consultants, Inc.

Memorandum

To	Project File 04-02916-017
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From	Gina Catarra and Rob Zisette, Herrera Environmental Consultants
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Subject	Data Quality Assurance Review of Surface Water Data Collected for WSDOT's NPDES Permit

This memorandum presents a review of data quality for surface water samples collected during storm events at locations near Seattle (26 storm events) and Vancouver (28 storm events) from October 2006 to May 2007. The water samples were collected by Herrera Environmental Consultants (Herrera) for compliance with the National Discharge Elimination System (NPDES) permit issued to the Washington State Department of Transportation (WSDOT) by the Washington Department of Ecology. A summary of samples collected from each location is presented in Table 1. Aquatic Research of Seattle, Washington analyzed the samples collected from the Seattle locations and Test America of Beaverton, Oregon analyzed the samples collected from the Vancouver locations for:

- Total suspended solids using EPA Method 160.2
- Total phosphate using EPA Method 365.1
- Hardness using Standard Method 2340C
- Total and dissolved copper using EPA Methods 200.8 (ICP-MS by Test America) and 220.2 (BFAA by Aquatic Research)
- Total and dissolved zinc using EPA Methods 200.7 (ICP by Aquatic Research) and 200.8 (ICP-MS by Test America)
- Total petroleum hydrocarbons using NWTPH-Dx method
- Fecal coliform bacteria using Standard Methods 9222D and 9221E.

The laboratory's performance was reviewed in accordance with quality control (QC) criteria outlined in the *WSDOT Stormwater Characterization/Water Quality Management Effectiveness Monitoring Quality Assurance Project Plan* (QAPP) (WSDOT 2003).

Table 1. Sample location and frequency.

Site Name	Date Range	Number of Composite Samples [a]		Number of Grab Samples [a]	
		In	Out	In	Out
SR18 MP8.04 Pond	10/15/06 – 5/21/07	15	14	9	10
SR18 MP13.13 Swale	10/15/06 – 3/12/07	11	12	7	7
SR18 MP18.0 EB Offramp Ecology Embankment	11/21/06 – 5/21/07	11	11	5	5
SR18 MP18.0 WB Offramp Ecology Embankment	10/15/06 – 5/21/07	11	13	6	7
SR18 MP18.5 Ecology Embankment	11/06/06 – 4/18/07	12	13	6	7
SR18 MP20.46 Swale	10/15/06 – 5/22/07	14	13	8	9
I-5 MP15 Pond/Swale	11/05/06 – 5/04/07	19	19	8	8
I-205 MP34 Swale	12/11/06 – 5/04/07	13	13	9	8

[a] Sample count includes field duplicates

Quality control data summaries submitted by the laboratories were reviewed; raw data were not submitted by the laboratories. Data quality assurance (QA) worksheets summarizing QA review findings and actions were completed for each sampling event, and are included with the laboratory data. Data qualifiers (flags) were added to the sample results in the laboratory data reports. Data validation results are summarized below, followed by definitions of data qualifiers.

Custody, Preservation, Holding Times, and Completeness—Acceptable with Discussion

The samples were properly preserved and sample custody was maintained from sample collection to receipt at the laboratories. All samples were analyzed within the required holding times (Table 2). With the exception noted below, the laboratory reports were complete and contained results for all samples and tests requested on the chain-of-custody (COC) forms.

Table 2. Summary of sample collection requirements.

Parameter	Analytical Method	Bottle	Preservative	Holding Time
Hardness	SM 2340B	500 mL poly	Nitric acid to pH<2, cool to 4°C	6 months
Total suspended solids	EPA 160.2	1 L poly	Cool to 4°C	7 days
Total phosphate	EPA 365.1	250 mL poly	Sulfuric acid to pH<2, cool to 4°C	28 days
Total metals	EPA 220.7/200.7	500 mL poly	Nitric acid to pH<2, cool to 4°C	6 months
Dissolved metals	EPA 220.7/200.7	500 mL poly	Filter, nitric acid to pH <2 g, cool to 4°C	48 hours to filter; 6 months to analysis
Total petroleum hydrocarbons	NWTPH-Dx	500 mL amber glass	Hydrochloric acid to pH<2, cool to 4°C	14 days to extraction; 40 days to analysis
Fecal coliform bacteria	SM 9222D	4 oz poly autoclaved	Cool to 4°C	24 hours

Analytical method modifications from the QAPP included the following parameters:

- Test America analyzed total and dissolved copper and zinc by ICP-MS using EPA Method 200.8
- Test America analyzed fecal coliform by the multiple-tube fermentation technique using Standard Method 9221E.

No data were qualified based on analytical method changes.

Laboratory Reporting Limits—Acceptable with Qualification

The laboratory reporting limits and QAPP specified reporting limits are provided in Table 3. The laboratory reporting limits met the QAPP specified reporting limits for all analyses with the exception of total suspended solids analyzed by Test America. The Test America laboratory reporting limit for total suspended solids (4 mg/L) was four times greater than the QAPP specified reporting limit of 1 mg/L. A large percentage of results below reporting limits (not detected) may impair statistical analysis of data sets. No data were qualified based on laboratory reporting limits.

Table 3. Summary of QAPP and laboratory reporting limits.

Parameter	QAPP Reporting Limit	Aquatic Research Reporting Limit	Test America Reporting Limit
Hardness	2 mg/L	2 mg/L	0.1 mg/L
Total suspended solids	0.5 mg/L	0.50 mg/L	4 mg/L
Total phosphorus	0.002 mg/L	0.002 mg/L	0.02 mg/L
Total/dissolved copper	1 µg/L	1 µg/L	1 µg/L
Total/dissolved zinc	5 µg/L	5 µg/L	5 µg/L
TPH diesel	0.050 mg/L	0.050 mg/L; 0.10 mg/L	0.25 mg/L
TPH oil	0.10 mgl	0.10 mg/L	0.50 mg/L
Fecal coliform bacteria	Minimum: 2 MPN or CFU/100 mL Maximum: $2x10^6$ MPN or CFU/100 mL	2 CFU/100 mL $2x10^4$ CFU/100 mL	2 MPN/100 mL not reported

Two fecal coliform bacteria results collected on 12/11/06 and 1/02/07 from SR18 MP8 IN were reported by the laboratory as greater than the 20,000 MPN/100 mL maximum reporting limit. Data with a fecal coliform bacteria result reported as greater than 20,000 MPN/100mL were qualified as estimated at a value greater than the maximum detectable value (flagged with a G), as shown below in Table 4.

Table 4. Fecal coliform bacteria results qualified as greater than (G) due to greater than 200 colonies present at the highest dilution.

Sample ID	Date Collected	Sample Result	Qualifier
SR18 MP8 IN	12/11/06	>20,000	G
SR18 MP8 IN	1/02/07	>20,000	G

Method Blank Analysis—Acceptable with Qualification

Method blanks were analyzed at the required frequency. Method blanks did not contain levels of target analytes above the laboratory reporting limits.

Fecal coliform bacteria were detected in the negative control with samples collected on 12/24/06 indicating a potential high bias. Samples with fecal coliform bacteria results greater than the 2 MPN/100 mL reporting limit were qualified as estimated (J), as shown below in Table 5.

Table 5. Fecal coliform bacteria results qualified as estimates (J) due to a positive result in the negative control.

Sample ID	Date Collected	Reason for Qualification	Qualifier
I-205 IN	12/24/06	Positive result for negative control and positive sample result	J
I-205 OUT	12/24/06	Positive result for negative control and positive sample result	J
I-5 OUT	12/24/06	Positive result for negative control and positive sample result	J

Laboratory Control Sample Analysis—Acceptable with Discussion

Laboratory control samples were analyzed at the required frequency. The percent recovery values for all sampling events met the QAPP criteria (90 to 110 percent for metals analyses and 75 to 125 percent for all other analyses) with the exceptions noted below in Table 6.

Table 6. Summary of samples associated with laboratory control samples exceeding the QAPP control limits.

Location/Storm Event #	Sample Date	Analyte	QAPP Control Limits (%)	Method Control Limits (%)	Laboratory Control Standard Recovery (%)	Qualifier
Vancouver / 2	11/08/06	Total zinc	90-110	85-115	86	None
Vancouver / 2	11/08/06	Total copper	90-110	85-115	88	None
Vancouver / 6	12/14/06	Total zinc	90-110	85-115	88	None
Vancouver / 7	12/15/06	Dissolved zinc	90-110	85-115	88	None
Vancouver / 8	12/21/06	Total zinc	90-110	85-115	85	None
Vancouver / 9	12/24/06	Total zinc	90-110	85-115	86	None
Vancouver / 14	2/16/07	Total zinc	90-110	85-115	89	None
Vancouver / 15	2/20/07	Total copper	90-110	85-115	88	None
Vancouver / 16	2/22/07	Total zonc	90-110	85-115	89	None
Vancouver / 17	2/25/07	Total zinc	90-110	85-115	87	None
Vancouver / 22	4/7/07	Dissolved zinc	90-110	85-115	87	None
Vancouver / 23	4/9/07	Dissolved copper	90-110	85-115	87	None
Vancouver / 23	4/9/07	Total copper	90-110	85-115	88	None
Vancouver / 24	4/12/07	Dissolved copper	90-110	85-115	88	None
Vancouver / 26	4/18/07	Dissolved zinc	90-110	85-115	111	None
Vancouver / 26	4/18/07	Total copper	90-110	85-115	88	None
Vancouver / 26	4/18/07	Total zinc	90-110	85-115	87	None

Several laboratory control sample percent recovery values (ranging from 85 to 111 percent) analyzed with samples collected at the Vancouver sites exceeded the QAPP-specified control limit of 90 to 110 percent. Test America analyzed the samples collected at the Vancouver sites for zinc and copper using EPA Method 200.8 (ICM-MS). This method specifies control limits for laboratory control sample percent recovery values as a range from 85 to 115 percent. Because all laboratory control sample percent recovery values met the method specified control limits (see Table 6), no data were qualified for laboratory control sample recovery criteria exceedances.

Matrix Spike Analysis—Acceptable with Qualification

Matrix spike (MS) samples were analyzed for total phosphorus, hardness, and metals at the required frequency. The percent recovery values for the MS analyses met the control limits (90 to 110 percent for metals analyses and 75 to 125 percent for all other analyses) established by the QAPP with the exceptions noted below.

Percent recovery values for three project MS samples (two for dissolved copper and one for hardness) exceeded QAPP criteria (90 to 110 percent for metals analyses and 75 to 125 percent for all other analyses), as shown below in Table 7. Because all other batch quality control criteria were met, only the MS samples were qualified as estimated (J).

Table 7. Summary of matrix spike recovery criteria exceedances for project samples.

Sample ID	Sample Date	Analyte	QAPP Control Limits (%)	Matrix Spike Recovery (%)	Qualifier
SR18 Ditch In	11/2/06	Dissolved copper	90-110	119	J
SR18 EE Out	3/2/07	Dissolved copper	90-110	115	J
I-205 Out	2/28/07	Hardness	75-125	185	J

Laboratory Duplicate Analysis—Acceptable with Qualification

Laboratory duplicates or laboratory control sample duplicates were analyzed at the required frequency. The relative percent difference (RPD) was calculated for each compound if both duplicate values were greater than five times the reporting limit (RL). The difference between duplicate values was calculated if the detected compound concentration was less than five times the RL in either the sample or the field duplicate. A control limit of less than 25 percent RPD was established in the QAPP and a control limit of two times the RL was used to evaluate difference values. The relative percent difference (RPD) values met the control limits established by the QAPP, and the difference values were less than two times the RL, with the two exceptions noted below.

The laboratory duplicate RPD values for two fecal coliform bacteria samples collected at station SR18 Ditch Out on 11/6/06 and 3/11/07 exceeded the QAPP criterion of less than 25 percent, as shown below in Table 8. Because all other batch quality control criteria were met, only samples

SR18 Ditch Out collected on 11/6/06 and 3/11/07 were qualified as estimated (J), as shown in Table 8.

Table 8. Summary of laboratory duplicate criteria exceedances.

Sample Date	Parameter	Sample ID	RPD (%)	Qualifier
11/06/06	Fecal coliform bacteria	SR18 Ditch Out	67	J
3/11/07	Fecal coliform bacteria	SR18 Ditch Out	50	J

Field Duplicates—Acceptable with Qualification

Field duplicates were analyzed for total suspended solids, total phosphorus, hardness, metals, fecal coliform bacteria, and petroleum hydrocarbons. The QAPP specified that field duplicates shall be collected at a frequency of one per sample event, assuming all eight sites (16 stations) are sampled for each event. Thus, the QAPP specified a field duplicate collection frequency of one per 16 samples (6 percent). As shown in Table 9, field duplicates were collected at the required frequency. No data were qualified because of field duplicate sampling frequency.

Table 9. Frequency of field duplicate sample collection.

Sample Type	Number of Samples Collected	Number of Field Duplicates Collected	Percentage
Composite	208	15	7.2%
Grab	120	12	10%

With the exceptions noted below, field duplicate precision met the QAPP-specified criterion of less than 35 percent RPD (40 percent RPD for fecal coliform bacteria). In addition, a criterion of less than two times the reporting limit was used if the sample concentration was less than five times the reporting limit. Table 10 summarizes the eight samples that were qualified as estimated (J) for field duplicate RPD exceedance. No other data associated with the sample batch were qualified due to field duplicate criteria exceedance because other quality control criteria were met.

Table 10. Summary of field duplicate criteria exceedances.

Sample Date	Parameter	Sample ID	RPD (%)	Qualifier
12/11/06	Fecal coliform bacteria	SR18 Ditch Out	50	J
1/3/07	Total suspended solids	SR18 MP8 Out	50	J
3/11/07	Fecal coliform bacteria	Vault Out	50	J
3/12/07	Total suspended solids	SR18 Swale Out	37	J
12/21/06	Total suspended solids	I-5 In	Diff = 5 x RL	J
1/2/07	Total copper	I-205 In	38	J
1/2/07	Total zinc	I-205 In	49	J
2/15/07	Fecal coliform bacteria	I-205 Out	50	J

Data Quality Assessment Summary

In general, the data quality for all parameters was found to be acceptable based on holding time, reporting limit, method blank, control standard, matrix spike, laboratory duplicate, and field duplicate criteria. However, the Test America reporting limit for total suspended solids was eight times greater than specified by the QAPP. Elevated reporting limits may impair data interpretation. Fecal coliform bacteria results for two samples exceeded the maximum plate count and were qualified as estimated (G). In addition, some data were qualified as estimated (J) due to exceedance of criteria for matrix spikes (three values), laboratory duplicates (two values), and field duplicates (eight values) exceedance of criteria.

Usability of the data is based on the guidance documents previously noted. Upon consideration of the information presented here, the data are acceptable as qualified.

Definition of Data Qualifiers

The following data qualifier definitions (with the exception of "G") are taken from *USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review* (USEPA 2002).

U The material was analyzed for, but was not detected above the level of the associated value. The associated value is either the sample quantitation limit or the sample detection limit.

J The associated value is an estimated quantity.

UJ The material was analyzed for, but was not detected. The associated value is an estimate and may be inaccurate or imprecise.

R The data are unusable. (Note: analyte may or may not be present.)

G The associated value is less than or equal to the actual value.

References

USEPA. 2002. Contract laboratory program national functional guidelines for inorganic data review. EPA-540/R-01/008. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington, D.C.

WSDOT. 2003. WSDOT Stormwater Characterization/Water Quality Management Effectiveness Monitoring, Quality Assurance Project Plan. Prepared for Washington State Department of Transportation, Environmental Affairs Office, Water Quality Program. October 2003.