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 NPDES Permit Surface Water Data

This memorandum presents a review of data quality for surface water samples collected during storm events at locations near Seattle (34 storm events), Olympia (6 storm events), and Vancouver (19 storm events) from November 2005 to May 2006. Aquatic Research Incorporated of Seattle, Washington analyzed the samples collected from Seattle and Olympia locations, and North Creek Analytical (NCA) of Portland, Oregon analyzed the samples collected from Vancouver locations for:

- Total suspended solids by EPA Method 160.2
- Total phosphate by EPA Method 365.1
- Hardness by Standard Method 2340C
- Total and dissolved copper by EPA Methods 200.8 (NCA) and 220.2 (Aquatic Research)
- Total and dissolved zinc by EPA Methods 200.7 (Aquatic Research) and 200.8 (NCA)
- Total petroleum hydrocarbons by NWTPH-Dx method
- Coliform bacteria by Standard Method 9222D

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).

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

Custody, Preservation, Holding Times, and Completeness—Unacceptable

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 1). 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 1. 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 365.2	250 mL poly	Sulfuric acid to pH<2, cool to 4°C	28 days
Total metals	EPA 200.7/200.8	500 mL poly	Nitric acid to pH<2, cool to 4°C	6 months
Dissolved metals	EPA 200.7/200.8	500 mL poly	Cool to 4°C	6 months
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 9222E	4 oz poly autoclaved	Cool to 4°C	8 hours

Analytical method modifications from the QAPP included the following parameters:

- Aquatic Research analyzed total and dissolved copper by graphite furnace using EPA method 220.2 to achieve a lower reporting limit than with ICP EPA method 200.7.

No data were qualified based on analytical method changes.

Sample BOSTAIN IN collected on 5/23/06 was not analyzed for total petroleum hydrocarbons due to laboratory equipment failure and loss of sample. All other samples submitted were analyzed as requested on the COC forms and no data were qualified due to loss of sample BOSTAIN-IN.

Bottles for samples SW3-Out and SW2-In may have been mislabeled for the refrigerated non-preserved and sulfuric acid preserved samples collected on 12/02/05. As shown in Table 2, results for samples SW3-Out and SW2-In were

rejected (R) for dissolved copper and zinc, total suspended solids, and total phosphate to indicate the uncertainty in correct sample identification.

Table 2. Summary of sample results qualified due to mislabeled sample bottles.

Sample ID	Sample Date	Parameter	Qualifier
SW3-Out	12/05/05	Dissolved copper	R
SW3-Out	12/05/05	Dissolved zinc	R
SW3-Out	12/05/05	Total suspended solids	R
SW3-Out	12/05/05	Total phosphate	R
SW2-In	12/05/05	Dissolved copper	R
SW2-In	12/05/05	Dissolved zinc	R
SW2-In	12/05/05	Total suspended solids	R
SW2-In	12/05/05	Total phosphate	R

Laboratory Reporting Limits—Acceptable with Qualification

The laboratory reporting limits and QAPP specified reporting limits are provided in Table 3. With the exception of dissolved metals (both laboratories) and total suspended solids (analyzed by NCA only), the laboratory reporting limits met the QAPP specified reporting limits for all analyses. The laboratory reporting limits for dissolved copper (1 µg/L) and dissolved zinc (5 µg/L) were five times greater than the QAPP specified reporting limits (0.2 µg/L for copper and 1 µg/L for zinc). The NCA 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	Laboratory Reporting Limit
Hardness	2 mg/L	2 mg/L
Total suspended solids	1 mg/L	0.50 mg/L; 4mg/L (NCA)
Total phosphorus	0.03 mg/L	0.02 mg/L
Total metals	1 µg/L (copper)/ 5µg/L (zinc)	1 µg/L (copper)/ 5µg/L (zinc)
Dissolved metals	0.2 µg/L (copper)/ 1µg/L (zinc)	1 µg/L (copper)/ 5µg/L (zinc)
Total petroleum hydrocarbons	5 mg/L	0.050 mg/L (diesel); 0.10 mg/L (motor oil)
Fecal coliform bacteria	2 MPN/100 mL(minimum); 2E6 MPN/100mL (maximum)	2 MPN/100 mL(minimum); 4000 MPN/100mL (maximum)

Several fecal coliform bacteria results collected on 5/22/06 and 5/23/06 were greater than the 4,000 MPN/100 mL reporting limit. Data with a fecal coliform bacteria result reported as greater than 4,000 MPN/100mL were qualified as estimated (J), as shown below in Table 4.

Table 4. Fecal Coliform Bacteria results qualified due to reporting limit exceedance.

Sample ID	Date Collected	Sample Result	Qualifier
SR18 8.0 IN	5/22/06	4,000	J
SR525 SWALE IN	5/23/06	4,000	J
SR525 RETAIN IN	5/23/06	4,000	J
BOSTAIN IN	5/23/06	4,000	J

Method Blank Analysis—Acceptable

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

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 5.

Several laboratory control sample percent recovery values (ranging from 85 to 115 percent) analyzed with samples collected at the Vancouver sites (SW2-in, SW2-out, SW4-in, and SW4-out) exceeded the QAPP specified control limit of 90 to 110 percent. NCA analyzed the samples collected at the Vancouver sites for zinc and copper using EPA method 200.8, which has method specified control limits for laboratory control sample percent recovery values of 85 to 115 percent. Because all laboratory control sample percent recovery values met the method specified control limits (see Table 5), no data were qualified for laboratory control sample recovery criteria exceedances.

Table 5. Summary of laboratory control sample recovery criteria exceedances.

Location/Storm Event #	Sample Date	Analyte	QAPP Control Limits (%)	Method Control Limits (%)	Laboratory Control Standard Recovery (%)	Qualifier
Vancouver / 5	1/10/06	Total zinc	90-110	85-115	89	None
Vancouver / 6	1/13/06	Total copper	90-110	85-115	88	None
Vancouver / 8	1/18/06	Total copper	90-110	85-115	88	None
Vancouver / 8	1/18/06	Dissolved zinc	90-110	85-115	87	None
Vancouver / 9	1/20/06	Total zinc	90-110	85-115	87	None
Vancouver / 9	1/20/06	Dissolved zinc	90-110	85-115	87	None
Vancouver / 10	1/27/06	Total zinc	90-110	85-115	87	None
Vancouver / 10	1/27/06	Dissolved zinc	90-110	85-115	86	None
Vancouver / 13	2/1/06	Total copper	90-110	85-115	115	None
Vancouver / 15	2/28/09	Dissolved zinc	90-110	85-115	89	None
Vancouver / 16	3/5/06	Total zinc	90-110	85-115	89	None
Vancouver / 16	3/5/06	Dissolved zinc	90-110	85-115	89	None
Vancouver / 19	3/16/06	Total zinc	90-110	85-115	85	None

Matrix Spike Analysis—Acceptable with Discussion

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 (75 to 125 percent) established by the QAPP with the exception noted below.

A batch sample was analyzed as the MS sample for total phosphorus with samples SW4-in and SW4-out collected on 1/20/06. The percent recovery value (13 percent) did not meet the 75 to 125 percent criteria. No data were qualified because the concentration of phosphorus in the native sample was greater than 15 times the spike amount added to the sample.

Laboratory Duplicate Analysis—Acceptable

Laboratory duplicates or laboratory control sample/laboratory control sample duplicates were analyzed at the required frequency. The relative percent difference (RPD) was calculated for each compound where 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 (30 percent for fecal coliform bacteria) 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.

Field Duplicates—Acceptable with Qualification

Field duplicates were analyzed for total suspended solids, total phosphorus, hardness, and metals. Field duplicates were not analyzed for fecal coliform bacteria or petroleum hydrocarbons. The QAPP specified that a field duplicate sample be collected at a frequency of one per sample event. As shown in Table 6, field duplicates were not collected at the required frequency. No data were qualified because of field duplicate sampling frequency.

Table 6. Frequency of Field Duplicate Sample Collection

Site	Number of Events	Number of Field Duplicates Collected	Percentage of Events Sampled
Seattle	34	9	26
Olympia	6	0	0
Vancouver	19	3	16

With the exceptions noted below, field duplicate precision met the QAPP specified criterion of less than 35 percent RPD. In addition, a criterion of less than 2 times the reporting limit was used if the sample concentration was less than 5 times the reporting limit. Table 7 summarizes the three 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 7. Summary of field duplicate criteria exceedances.

Sample Date	Parameter	Sample ID	Duplicate ID	RPD (%)	Qualifier
11/30/05	TSS	BOS OUT	Duplicate	40	J
1/13/06	Total copper	Swale Out #1	Swale Out #2	51	J
2/24/06	Total copper	SR525 Swale-in #1	SR525 Swale-in #2	37	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 laboratory reporting limits for dissolved copper and dissolved zinc were five times greater than those specified by the QAPP, and the NCA reporting limit for total suspended solids was four times greater than specified by the QAPP. Elevated reporting limits may impair data interpretation. Fecal coliform bacteria results for four samples exceeded the maximum plate count and were qualified as estimated. In addition, some data were rejected (R) based on incorrect sample identification and exceedance of criteria for field duplicates.

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 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.)

References

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

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.