DEPARTMENT OF
ECOLOGY
State of Washington

Addendum to

Quality Assurance Project Plan

Sumas-Blaine Surficial Aquifer Long-Term Ambient Groundwater Monitoring

May 2012

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Publication Information

Addendum

This addendum is an addition to an original Quality Assurance Project Plan. The addendum is not a correction (errata) to the original plan.

This addendum is available on the Department of Ecology's website at www.ecy.wa.gov/biblio/0903111Addendum.html

Ecology's Activity Tracker Code for this study is 09-223.

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DEPARTMENT OF ECOLOGY
Environmental Assessment Program

May 22, 2012

TO: Doug Allen, Manager, Bellingham Field Office

THROUGH: Gary Arnold, Eastern Operations Section Supervisor, Environmental Assessment Program

FROM: Melanie Redding, Environmental Assessment Program

SUBJECT: Addendum to Quality Assurance Project Plan for Sumas-Blaine Surficial Aquifer Long-Term Ambient Groundwater Monitoring
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This is an addendum to *Quality Assurance Project Plan: Sumas-Blaine Surficial Aquifer Long-Term Ambient Groundwater Quality Monitoring*, which is available online at http://www.ecy.wa.gov/biblio/0903111.html. This addendum addresses the analytical modification necessary to achieve lower detection limits for bromide in groundwater.

Chloride/bromide ratios are a tool for identifying sources of groundwater contamination. The parameters chloride and bromide were originally included in the 2009 QAPP; however, the concentrations in groundwater are lower than originally anticipated. An analytical method with lower detection limits is needed. MEL proposed a modification to the approved EPA method 300.0 which is more sensitive, achieving a lower MDL.

The intent of this study is to characterize groundwater quality in the Sumas-Blaine Aquifer in Whatcom County, Washington. The Sumas-Blaine Surficial Aquifer is the primary drinking water source for the majority of residents in northern Whatcom County, and has been identified as one of the most severely contaminated aquifers in Washington State. Numerous groundwater studies have documented extensive nitrate contamination. Groundwater is contaminated with elevated concentrations of nitrate which exceed the drinking water standard and have been increasing over the last 20 years. The area has multiple nitrogen sources including dairy farms, raspberry farms, other irrigated agriculture, and on-site sewage systems.

If you have questions, please contact me at 360-407-6524 or mkim461@ecy.wa.gov.

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Bromide Method Detection Level Study

Chloride and bromide samples were collected with the intent to use the ion ratio as an indicator of groundwater contamination sources. Chloride/bromide ratios are a source-tracking tool used to distinguish between groundwater contamination (Table 1) from domestic sewage, stormwater run-off, agriculture, natural dissolution from aquifer materials, and precipitation (Davis et al., 1998; Vengosh and Pankratov, 1998).

Chloride and bromide are negatively charged ions, which are not readily degraded or attenuated in the subsurface by organic material or by sewage treatment processes (Vengosh and Pankratov, 1998). These attributes make chloride and bromide mobile ions which move readily with groundwater and make them conservative indicator parameters.

Bromide is naturally present in seawater, and it has been used in pesticides, industrial solvents, pharmaceuticals, water purification, and gasoline additives. Chloride is abundant in nature, and is present in seawater, on dining room tables, and it is pervasive in many products (e.g., road de-icers, disinfection products).

Table 1. Chloride/Bromide Ratios and the associated pollution sources.

Source	Range (mg/L)	Ref	Range (mg/L)	Ref
Precipitation	50 – 150	1		
Shallow groundwater	100 - 200	1		
Domestic sewage	300 – 600	1	275 – 521 (mean = 416)	2
Dissolution of Halite	1,000 – 10,000	1		
Stormwater runoff	10 - 100	1	9 – 165 (mean 34)	2
Road salt			> 600	2
Agricultural return flows			< 180	2

[1] Davis, 1998, [2] Vengosh and Pankratov, 1998,

Vengosh and Pankratov (1998) characterized drinking water bromide concentrations in the range of 1.57 to 0.40 mg/L. Davis et al. (1998) detected bromide concentrations in the range of 0.04 to 0.32 mg/L in groundwater. Information on ambient bromide concentrations in groundwater is scarce since there are no direct health concerns associated with bromide.

The ambient groundwater bromide concentration in the Sumas-Blaine Aquifer was unknown prior to sampling in 2009. Due to the proximity to the Pacific Ocean, and the presence of bromide-based pesticides detected in groundwater (Redding, 2007), the assumption was that bromide would occur at concentrations greater than the method detection limit of 0.2 mg/L. Unfortunately, virtually all of the 2009 bromide results were reported at concentrations less than detection limit.

In order to use chloride/bromide ratios as an indicator of groundwater contamination an effective analytical method with a lower detection limit is needed. MEL proposed a modification to the approved EPA method 300.0 which is more sensitive, achieving a lower MDL. This addendum presents the results of the MDL study that verify that MEL can achieve a lower MDL using EPA method 300.0 with a larger loop size.

Analytical Method Modification

The EPA-approved method for bromide analysis is method 300.0. The reporting limit in the original QAPP (Redding, 2009) for bromide was 0.2 mg/L. After the 2009 results indicated that the majority of results were below the detection limit, it was decided to investigate whether lower detection limits could be achieved.

MEL proposed to use a 250 uL sample (aliquot) loop instead of a 50 uL loop. The 50 uL loop is typically used; however, the EPA method does not specify which size sample loop to use. The sample loop size is adjusted to achieve the required level of sensitivity.

Analytical MDL Statistical Analysis

Table 2 characterizes three independent MDL studies, each consisting of eight replicates. The analytical results of these studies and the statistical analysis are presented in the table below. The grand mean percent recovery was 0.04984%, and the mean MDL for these three studies was 0.016 ppm (parts per million). (Feddersen, 2012)

Table 2. MDL Study Results

Work Order	1201045	1108095	1203044
Date Analyzed	1/17/2012	8/24/2011	3/7/2012
Analyte	Br	Br	Br
Spike Concentration	0.05	0.05	0.05
Units	ppm	ppm	ppm
Replicate 1	0.051	0.0508896	0.05
Replicate 2	0.042	0.0535377	0.045
Replicate 3	0.05	0.0581712	0.049
Replicate 4	0.041	0.0549271	0.057
Replicate 5	0.058	0.0541634	0.049
Replicate 6	0.036	0.0530798	0.041
Replicate 7	0.039	0.0601236	0.044
Replicate 8	0.055	0.0582729	0.046
Student's t value8	2.998	2.998	2.998
Mean	0.0465	0.0553957	0.047625
Standard Deviation	0.0080534	0.003144	0.0048385
MDL (t-value*StdDev)	0.0241441	0.0094257	0.0145057
LOQ (10*StdDev)	0.0805339	0.03144	0.0483846
High Spike Check	OK	OK	OK
Low Spike Check	OK	OK	OK
S/N (Mean/StdDev)	5.7739637	17.619459	9.8430039
Mean % recovery	93%	111%	95%
Mean MDL for all three analytical study dates:	**0.016025**		

StdDev = Standard deviation

MEL Proposed Analytical Solution

MEL has demonstrated that they can lower the bromide reporting limit from 0.2 mg/L down to 0.05 mg/L by using a larger sample size, using the same EPA method 300.0 (approved). Table 3 describes the analytical method and the reporting limits.

Table 3. Summary of laboratory measurements, methods, and reporting limits.

Parameter	Method	Normal Reporting Limit	New Reporting Limit
Nitrate+Nitrite-N	4500 NO3I	0.01 mg/L	0.01 mg/L
Chloride	EPA 300.0	0.1 mg/L	0.1 mg/L
Bromide	EPA 300.0	0.2 mg/L	0.05 mg/L

Proof of Concept Proposal

EPA and USGS currently use this technique to assist in identifying groundwater contamination sources. Additionally it has been increasingly reported in the literature as a valuable groundwater tool. Any indicators of groundwater contamination sources would be extremely valuable for Ecology staff to use to help mitigate and prevent contamination.
Add chloride and bromide samples onto existing groundwater studies to determine the effectiveness of Cl/Br Ratios as an indicator of contamination sources. The following groundwater studies are proposed for this trial sampling:

- Sumas-Blaine Long-term Groundwater Quality Monitoring Network
- Crab Creek
- Hangman Hills

Cost

These samples will need to be analyzed two times; once for chloride and once for bromide. The sampling loop will need to be changed between ion analyses. The transition of time to change and re-calibrate the loop will result in a cost of $60 per batch of samples. The cost to run chloride samples is $13.50 and the cost of bromide is $13.50. The total costs are described in Table 4.

Table 4. Laboratory budget

Study	Cost per Sample = $13.50	Change Cost per Batch = $60
Sumas Blaine	35 samples = $472.50	$60
Crab Creek	15 samples = $202.50	$60
Hangman Hills	10 samples = $135.00	$60
Total = $990	$ 810.00	$180

References

Davis, S. N., Whittemore, D.O., and Fabryka-Martin, J., 1998. "Uses of Chloride/Bromide Ratios in Studies of Potable Water," Ground Water, Volume 36, Number 2, pp. 338-350.

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Vengosh, A, and Pankratov, I., 1998. "Chloride/Bromide and Chloride/Fluoride Ratios of Domestic Sewage Effluents and Associated Contaminated Ground Water," Ground Water, Volume 36, Number 5, pp. 815- 824.