A Department of Ecology Report

Surface Water Monitoring Program for Pesticides in Salmon-Bearing Streams: DH-81 and Grab Sample Comparison Study

Abstract

Ecology's standard operating procedure (SOP) for sampling of pesticides in surface waters calls for the use of a U.S. Geological Survey DH-81 depth-integrating sampler in water between one and four feet deep. At depths less than or equal to one foot, the SOP allows the use of grab sampling with a handheld sample jar.

In 2011 a side-by-side comparison study of the two sampling methods was conducted to evaluate the need to collect depth-integrated samples for pesticides. Results showed no significant difference between the two methods for the three sites sampled. Recommendations for these sites include (1) using the grab sampling technique for sampling water depths of one to four feet deep and (2) discontinuing the use of the DH-81 sampler for these depths.

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Background

The Washington State Departments of Agriculture (WSDA) and Ecology (Ecology) are conducting a multi-year monitoring study to evaluate pesticide concentrations in surface waters. The study assesses pesticide presence in salmon-bearing streams during a typical pesticide-use season (e.g., March through October).

Ecology's standard operating procedure (SOP) EAP003 *Sampling of Pesticides in Surface Waters* (Anderson and Sargeant, 2010) calls for the use of a United States Geological Survey (USGS) DH-81 depth-integrating sampler in water between one and four feet deep (Figure 1). At depths less than or equal to one foot, the SOP allows the use of grab sampling with a handheld sample jar.

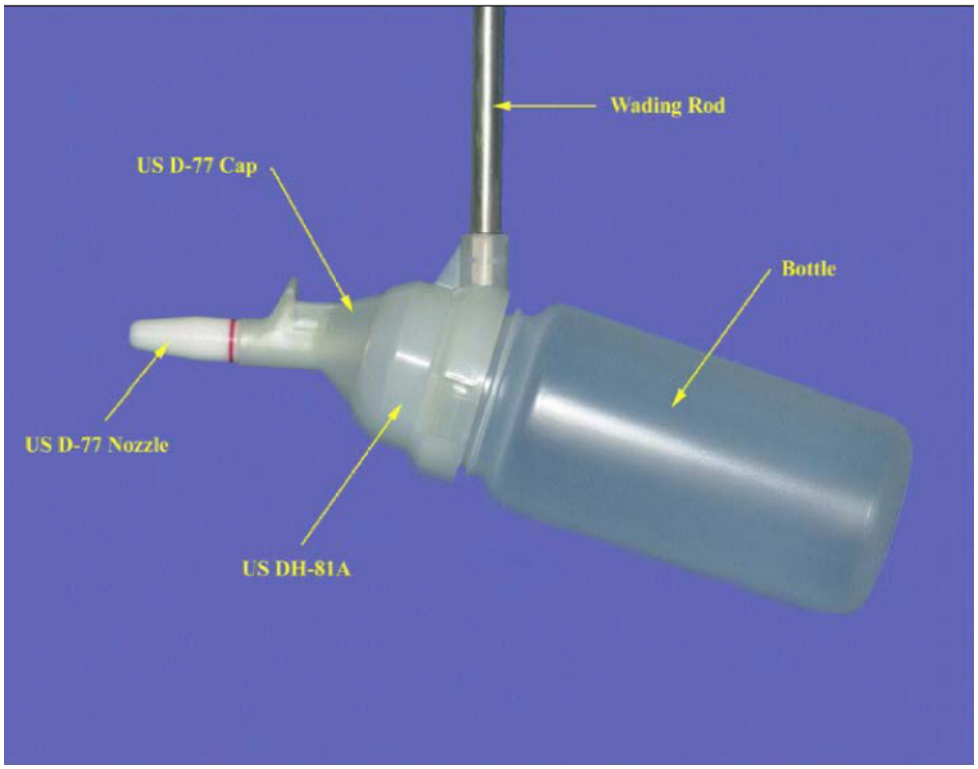

Figure 1. USGS DH-81 complete assembly.

In 2011 a side-by-side comparison study of the two sampling methods was conducted to evaluate the need to collect depth-integrated samples for pesticides. Benefits in changing sampling techniques from the DH-81 depth-integrating sampler to grab sampling include:

- Time savings: There will be greater efficiency sampling in the field, and less staff time will be spent washing DH-81 bottles.
- Reduces our waste stream: Acetone and hexane will no longer be used to clean DH-81 bottles.
- Cost savings: There will be no need to replace expensive DH-81 bottles, and there will be savings on chemical use.

The purpose of this data report is to provide results from the side-by-side monitoring and to provide recommendations on a sampling method.

Study Design and Methods

Sampling Sites and Frequency

Three sites where the DH-81 depth-integrated sampler is routinely used were included in this study. Two of these sites (Lower Big Ditch and Indian Slough) are located in the Skagit-Samish Water Resource Inventory Area (WRIA) 3 and one site (Marion Drain) is located in the Lower Yakima WRIA 37 (Table 1).

Upstream conditions at all three sites sampled for this study are similar. All are straight channels with no significant water inputs upstream of the sample sites. Water is fairly well mixed at all three sites.

Table 1. 2011 station locations and descriptions for the *DH-81 Grab Sample Comparison Study*.

Site	Latitude	Longitude	Location Description
Skagit-Samish Watershed			
Big Ditch downstream (BD-1)	48.3086	-122.3473	Upstream side of bridge at Milltown Road.
Indian Slough (IS-1)	48.4506	-122.4651	Inside upstream side of tidegate at Bayview-Edison Road.
Lower Yakima Watershed			
Marion Drain (MA-2)	46.3306	-120.1989	Approximately 15 meters upstream of bridge at Indian Church Road.

Sites were sampled during the eight-week period when the maximum number of pesticide detections was likely to occur (Sargeant et al, 2010). Sample dates and maximum water depths are presented in Table 2.

Table 2. Sample dates and water depths (feet) for *DH-81 Grab Sample Comparison Study*.

Lower Big Ditch and Indian Slough	Lower Big Ditch Maximum Water Depth	Indian Slough Maximum Water Depth	Marion Drain	Marion Drain Maximum Water Depth
April 25, 2011	3.5	2.7	April 25, 2011	1.95
May 3, 2011	3.4	2.45	May 3, 2011	1.75
May 9, 2011	4.05	2.7	May 11, 2011	2.3
May 17, 2011	> 4.05	3.25	May 25, 2011	> 4.0
May 23, 2011	3.4	2.6	June 1, 2011	3.7
June 6, 2011	3.6	2.8	June 7, 2011	3.8
June 14, 2011	3.5	1.9	June 15, 2011	3.55

Field Procedures and Laboratory Analyses

A full description of field procedures and laboratory analysis is included in Sargeant et al. (2010). All surface water samples were collected by USGS DH-81 depth-integrating sampling and by hand-compositing grab samples from quarter-point transects as close as possible in time. Techniques and equipment will be consistent with Ecology SOP EAP 003 *Sampling of Pesticides in Surface Waters* (Anderson and Sargeant, 2010).

Ecology's Manchester Environmental Laboratory (MEL) analyzed all pesticide samples. Laboratory methods are presented in Table 3. A full list of target analytes for this study is included in Sargeant et al. (2011).

Table 3. Summary of laboratory methods, 2011 (MEL, 2000, 2008).

Analyte	Analytical Methods[1]		
	Extraction	Analysis	Reference
Pesticides[2]	3510	GC/MS	8270
Herbicides	8151	GC/MS	8270 and 8251
Carbamates	3535M	LCMS/MS	8321A

[1] All analytical methods refer to EPA SW 846, unless otherwise noted.
[2] Pesticides refers to all forms tested unless indicated otherwise.
GC: gas chromatograph.
MS: mass spectrometry.
LC: liquid chromatography.

Laboratory methods are discussed in the Quality Assurance (QA) Project Plan (Anderson and Sargeant, 2009); previous QA Project Plan (Johnson and Cowles, 2003) and the QA Project Plan addendum (Burke and Anderson, 2006); and the QA Project Plan Addendum 4 (Anderson, 2011).

Data Quality Objectives and Data Quality

Data quality objectives were met (Anderson, 2011). Twenty-one sample events were captured over an eight-week period, consisting of seven side-by-side sample events at the three sites. For the carbamate and pesticide MS analysis, 21 analysis runs were compared; for herbicides, 20 analysis runs were compared.

Performance of laboratory analyses is governed by QA and quality control (QC) protocols. The QA/QC protocol employs application of blanks, replicates, surrogates, and laboratory control samples, as well as matrix spike/matrix spike duplicates (MS/MSDs). Laboratory surrogate, blank, replicate, and control samples are analyzed as the laboratory component of QA/QC. Field blanks, replicates, and MS/MSDs integrate field and laboratory components. A full description of QA\QC will be provided in the 2009-2011 Triennial Report. A summary of laboratory and field data quality are presented below.

The eight-week (April 25 – June 14, 2011) comparison study period included the following QA\QC samples:

- Four field blanks: one each for herbicide and pesticide (GC\MS) analysis, two for carbamate analysis.
- Eight field replicates: three each for carbamate and pesticide (GC\MS) analysis, two for herbicide analysis.
- Three MS/MSDs: two for carbamate analysis, and one for herbicide analysis.

Field and Laboratory Blanks

During the eight-week period, there were no analyte detections in the field or laboratory blanks.

Field Replicate Results

Replicate sampling tests the reproducibility or precision of sampling results. Precision between replicate pairs was calculated using relative percent difference (RPD). For the three sites during the eight-week period, 16 analyte pairs were consistently identified and 2 analyte pairs were inconsistently identified in 480 replicate pairs. Inconsistently identified replicate pairs are those in which the compound was identified in one sample but not the other.

Field replicate results were very good. All field replicate pairs met the QA criteria of ≤ 50% RPD. The average RPD of consistent field replicate pairs was low, 8.2%. For the two inconsistent pairs, the detected result was an estimated result below the reporting limit.

Surrogates, Matrix Spikes, and Laboratory Control Samples

Surrogates are used to evaluate recovery for a group of compounds. The majority of surrogate recoveries fell within the control limits established by MEL. Sample results were qualified as estimates when surrogate recoveries did not meet MEL QC criteria.

MS/MSDs provide an indication of bias due to interferences from components of the sample matrix. The duplicate spike can be used to estimate analytical precision at the concentration of the spiked samples. The average recovery of the MS/MSD was 110.6%, and the average RPD between MS/MSD pairs was 21.8%. For most compounds, recovery and RPDs of MS/MSD pairs showed acceptable performance and were within defined limits for the project. Sample results were qualified as estimates if the MS/MSD recoveries did not meet MEL QC criteria

Laboratory control samples (LCS) are analyte compounds spiked into deionized water at known concentrations and subjected to analysis. They are used to evaluate accuracy of pesticide residue recovery for a specific analyte. The average percent recovery for the LCS and the LCS duplicates was 94.8%, and the average RPD between the LCS and duplicate pairs was 12.2%. For most compounds, recovery and RPDs of LCS and LCS duplicates showed acceptable performance and were within limits for the project. Sample results were qualified as estimates if the LCS recoveries did not meet MEL QC criteria.

Data Analysis and Reporting Methods

The 2011 data were compiled and organized using Excel® spreadsheet software and Access® database software (Microsoft Corporation, 2007). Water quality results from the laboratory work were also entered into Ecology's Environmental Information Management (EIM) database (www.ecy.wa.gov/eim).

Laboratory data were qualified as needed, and qualifiers are described in Table 4. Values qualified with a J, NJ, or E were used for statistical comparison purposes. In addition non-detect values (qualified with U, or UJ) were used in the statistical test to determine differences between the data sets (paired Prentice-Wilcoxon test).

Table 4. Definitions of data qualifiers.

Qualifier	Definition
No qualifier	The analyte was detected at the reported concentration. Data are not qualified.
E	Reported result is an estimate because it exceeds the calibration range.
J	The analyte was positively identified; the associated numeric value is the approximate concentration of the analyte in the sample.
NJ	The analysis indicates the presence of an analyte that has been "tentatively identified," and the associated numeric value represents its approximate concentration.
NAF	Not analyzed for.
NC	Not calculated.
REJ	The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet QC criteria. The presence or absence of the analyte cannot be verified.
U	The analyte was not detected at or above the reported sample quantitation limit.
UJ	The analyte was not detected at or above the reported sample quantitation limit. However, the reported quantitation limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately measure the analyte in the sample.

MEL, 2000, 2008; EPA, 1999, 2007.

For data analysis purposes, field replicates were arithmetically averaged.

To compare the two sampling methods (DH-81 and grab), a nonparametric paired Prentice-Wilcoxon (PPW) test was used. This test was calculated using WQHydro (Aroner, 2011). The PPW test is designed for use with multiple detection or reporting limits with matched paired data. The PPW test takes into account the magnitude of difference between the pairs. The null hypothesis for this study is: the difference between paired sampling results from the DH-81 and grab sampling is zero. The null hypothesis will be rejected when the two-tailed p-value from this test is ≤ 0.05.

The minimum detection limit (MDL) for the analyte was used as the non-detect censored value for analysis. NJ censored concentrations were used in the analysis.

Each sample was analyzed for approximately 170 pesticides and degradate compounds. In comparison to the number of pesticides analyzed, very few pesticides are detected at a site for a single sample event.

For the PPW test, as the number of tied data (e.g., a pair of non-detects) increases, the Z score will get smaller, providing less evidence against the null hypothesis (Helsel, 2005). Because the PPW test Z score could be influenced by the greater number of non-detects found in the WSDA data set, two sets of data were analyzed:

- The entire paired data set including all non-detect data, n=3496
- The paired data set where at least one result in the pair was a detection, n=178

The data set that excludes non-detect pairs is the most conservative data set to test.

In addition, data sets excluding non-detect pairs were compared by site and by type of laboratory analysis: herbicide, pesticide MS, and carbamate.

Results and Discussion

The percentage of detections (including inconsistent detections) for comparison was approximately 5.2% for lower Big Ditch and Marion Drain, and 4.8% for Indian Slough.

Of the 178 paired detections, there were 44 inconsistent detections (detection in only one of the pairs). Of the 44 inconsistent detections, 26 were for the grab sample pairs and 18 for the DH-81 pairs.

The following eight data sets from the DH-81 and grab sampling were compared using the PPW test:

- The entire paired data set compared including all non-detect data (n=3496).
- The paired data set where at least one result in the pair was a detection (n=178).
- The paired data set where at least one result in the pair was a detection for herbicide analysis (n=74).
- The paired data set where at least one result in the pair was a detection for pesticide MS analysis (n=76).
- The paired data set where at least one result in the pair was a detection for carbamate analysis (n=28).
- The paired data set where at least one result in the pair was a detection for Marion Drain (n=63).
- The paired data set where at least one result in the pair was a detection for Big Ditch (n=60).
- The paired data set where at least one result in the pair was a detection for Indian Slough (n=55).

Results are described in Table 5.

Table 5. Paired Prentice-Wilcoxon statistical test results for all data, data excluding non-detects in both pairs, and by type of analysis (excluding non-detects in both pairs).

Data Set	Z score	p value 2-tailed	Significant at 95% confidence level
All data, n=3496	-0.58	0.56	No
Data where pair had a detected results, n=178	-0.00	1.00	No
Herbicide analysis, n=74	-1.44	0.15	No
Carbamate analysis, n=28	0.80	0.43	No
Pesticide MS analysis, n=76	1.11	0.27	No
Marion Drain analysis, n=63	1.05	0.30	No
Big Ditch (n=60)	-0.10	0.92	No
Indian Slough (n=55)	-0.33	0.74	No

For all data sets examined, the null hypothesis is accepted, since the test finds no statistically significant difference at the 95% confidence level between the DH-81 and grab sample results.

Table 6 provides summary statistics for data where at least one result of the pair was a detection (by analysis type and for all analysis), and the number of detections by pesticide type and for all analysis.

Table 6. Summary statistics for number of detections for DH-81 and Grab Sampling.

Statistic	Herbicides		Carbamates		Pesticide MS		Marion Drain		Big Ditch		Indian Slough		All Analysis (n=178)	
	Grab	DH-81	Grab	DH-81	Grab	DH-81	Grab	DH-81	Grab	DH-81	Grab	DH-81	Grab	DH-81
Mean[1] (ug/L)	0.076	0.077	0.102	0.144	0.170	0.157	0.047	0.050	0.213	0.195	0.101	0.121	0.120	0.121
Median [1] (ug/L)	0.036	0.033	0.025	0.029	0.051	0.048	0.036	0.038	0.050	0.047	0.034	0.035	0.037	0.038
Total Detections	68	62	23	23	67	69	58	57	52	51	48	46	158	154
Detection (NJs not included)	55	42	23	23	62	65	51	52	49	42	40	36	140	130

[1]: Mean and Median were estimated using the nonparametric Kaplan-Meir method.

For herbicide analysis, mean and median grab and DH-81 sample results were similar. For carbamate analysis, mean grab sample results were less than the DH-81 results, but median values were similar (0.004 ug/L difference). For pesticide MS analysis, mean grab results were greater than the DH-81, but median results were similar (0.003 ug/L difference). For all analysis groups combined, the mean and median results were similar (0.001 ug/L difference).

Median values for grab and DH-81 sampling were similar at each of the sites, within 0.003 ug/L. Confirmed detection frequency for the two sampling methods was similar at each of the sites, with less than 5% difference between the two sampling methods.

Detection frequency is compared in Table 6. Grab samples had 30% more confirmed herbicide detections than the DH-81. For pesticide MS, the DH-81 had 5% more confirmed detections. For carbamates, there was an equal number of confirmed detections. Overall, grab samples had 8% more total confirmed detections than the DH-81, or ten more total confirmed detections.

This study finds no significant difference between results using the grab sampling technique and the DH-81 technique. There is also little difference in the number of detections between the two sampling methods.

Conclusions and Recommendations

Sample results show there is no statistically significant difference (at the 95% confidence level) between the DH-81 and grab sample methods for pesticide sampling at the three sites. Summary statistics and total number of detections indicate very minor differences between the two methods for the three sites. Likely this is due to upstream conditions at the three sites, including no significant water inputs and good mixing of water in the channel.

Recommendations include:

- Approve the use of the grab sampling technique for pesticide sampling in water one to four feet deep, provided there is good mixing and no significant upstream water inputs.
- Update Ecology's *Sampling of Pesticides in Surface Water* SOP EAP003, and amend the QA Project Plan (Johnson and Cowles, 2003) to include the recommendation above.

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List of Acronyms

Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
LCS	Laboratory control samples
MEL	Manchester Environmental Laboratory
MS/MSD	Matrix spike/matrix spike duplicates
n	Number
PPW	Paired Prentice-Wilcoxon
QA	Quality assurance
QC	Quality control
RPD	Relative percent difference
WSDA	Washington State Department of Agriculture