# Quality Assurance Project Plan

# Marion Drain
# Intensive Surface Water Sampling
# for Pesticides In Salmonid-Bearing Streams

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June 2007

303(d) Listings in this Study: None

Waterbody Number: Marion Drain WA-37-1025

Project Code: 07-510

**Approvals**

| | |
|---|---|
| Approved by: | May 2007 |
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# Abstract

Novel monitoring techniques are applied to evaluate short-term variability of surface water pesticide residues, complementing data obtained through the Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams. Currently, weekly grab sampling is conducted during the typical pesticide application period to evaluate pesticide occurrence in Washington State surface waters. Detected concentrations of pesticides are interpolated between weeks to generate an exposure assessment. This project proposes to evaluate short-term variability through daily grab sampling and the use of passive samplers over a 22-day period. Results from daily, weekly, and passive sampling methods will be analyzed to evaluate the existing monitoring method and regime. Passive sampling will be conducted through the use of Semipermeable Membrane Devices for hydrophobic pesticides and Polar Organic Chemical Integrative Samplers for hydrophilic pesticides. The study will be conducted at a current long-term monitoring site—the Lower Marion Drain, a tributary to the Lower Yakima River.

# Background and Problem Description

The Washington State Department of Agriculture (WSDA) and the Washington State Department of Ecology (Ecology) designed a multi-year monitoring study to characterize pesticide concentrations in salmonid-bearing streams during the typical pesticide use season. Data from the monitoring program are being used to develop accurate pesticide exposure assessments for Endangered Species Act (ESA) listed salmonid species. The data are provided to the U.S. Environmental Protection Agency (EPA) and the National Oceanic and Atmospheric Administration (NOAA) -Fisheries for ESA consultations on pesticides and salmon. WSDA uses monitoring data for pesticide registration decisions and to determine if pesticide mitigation efforts are successful.

Monitoring is conducted on a weekly basis and the sample regime extends for a minimum of three years. Subject watersheds were chosen due to the intensity of cropping, salmonid presence, and diversity of agriculture within the watershed (Figure 1). Monitoring locations evaluate specific land-use practices including:

- Urban, Western Washington - Thornton Creek in the Cedar-Sammamish watershed, Water Resource Inventory Area (WRIA) 8. 2003 – present.

- Eastern Washington Agriculture
    - Irrigated agriculture - Lower Yakima Watershed, WRIA 37 - Marion Drain, Sulphur Creek Wasteway, and the Spring Creek drainage. 2003 – present.

    - Tree fruit - Wenatchee-Entiat Watersheds, WRIAs 45 & 46 – Wenatchee, Peshastin, Brender, Mission, and Entiat drainages. 2007 – present.

- Western Washington Agriculture - Skagit-Samish Delta, WRIA 3 – Samish River, Indian Slough, Browns Slough, and Big Ditch/Maddox drainages. 2006 - present.

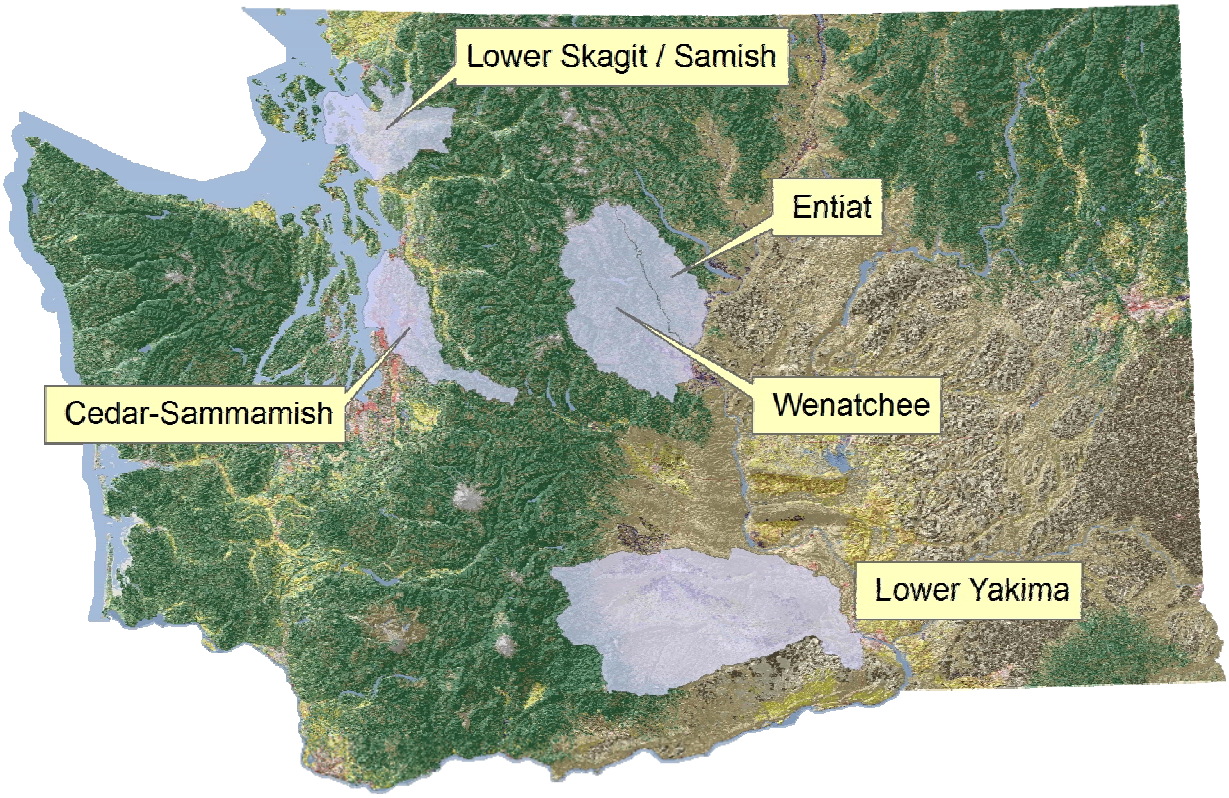



Figure 1. WRIAs included in current monitoring program.

## Marion Drain

Marion Drain discharges into the Yakima River 2.2 miles upstream of the mouth of Toppenish Creek at river mile 82.6 and is located within the Yakama Nation. Marion Drain is a 19-mile-long drainage ditch with a watershed area of approximately 85,786 acres. It primarily collects irrigation return flows from Harrah Drain, Toppenish Creek, Wanity Slough, and groundwater exfiltration from the northern plain. Approximately 59% of the watershed is in agricultural crops. The majority of this acreage is in apple (9%), hops (9%), and corn (9%) production (Burke et al., 2006).

The lower Marion Drain is located upstream of the intersection of Marion Drain and Indian Church Road (NAD 83, 46.3306W, 120.1989N) and is presented in Figures 2 and 3. The site integrates land-use practices of the entire watershed and has been monitored since 2003.



Figures 2 and 3. Lower Marion Drain sample site facing upstream (left) and downstream (right).

Thirty-one pesticide and degradate residues were detected in Lower Marion Drain surface waters from 2003-2006 (Table 1). Currently, the most frequently detected herbicides include terbacil, atrazine, 2,4-D, and trifluralin. Chlorpyrifos and malathion are the most frequently detected insecticides.

Table 1. Pesticide detections of the Lower Marion Drain. Results in µg/L.

| Chemical | [1]Common Name | [2]Type | 2006, n=31 | | | 2005, n=29 | | | 2004, n=31 | | | 2003, n=18 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Freq | Median | Max | Freq | Median | Max | Freq | Median | Max | Freq | Median | Max |
| Terbacil | Sinbar | H | 84% | 0.096 | 0.68 | 86% | 0.12 | 0.46 | 67% | 0.088 | 0.37 | 76% | 0.0785 | 0.26 |
| Chlorpyrifos | Dursban | I-OP | 68% | 0.013 | 0.12 | 24% | 0.02 | 0.4 | 37% | 0.02 | 0.1 | 43% | 0.023 | 0.085 |
| Atrazine | Aatrex | H | 61% | 0.011 | 0.078 | 72% | 0.019 | 0.035 | 60% | 0.014 | 0.142 | 62% | 0.0059 | 0.017 |
| 2,4-D | several | H | 42% | 0.047 | 0.53 | 38% | 0.056 | 0.17 | 77% | 0.045 | 0.22 | 76% | 0.061 | 0.29 |
| Trifluralin | Treflan | H | 32% | 0.015 | 0.034 | 24% | 0.02 | 0.025 | 7% | 0.0153 | 0.023 | 19% | 0.0096 | 0.016 |
| Metolachlor | Stalwart | H | 26% | 0.011 | 0.033 | 28% | 0.011 | 0.012 | 7% | 0.0024 | 0.0038 | | | |
| Bentazon | Basagran | H | 23% | 0.1 | 0.27 | 14% | 0.0755 | 0.15 | 53% | 0.125 | 2.5 | 14% | 0.053 | 0.063 |
| Pendimethalin | Prowl | H | 16% | 0.035 | 0.061 | 28% | 0.028 | 0.065 | 13% | 0.046 | 0.126 | 43% | 0.044 | 0.1 |
| Malathion | several | I-OP | 13% | 0.018 | 0.024 | 30% | 0.0215 | 0.23 | 20% | 0.0275 | 3.05 | 10% | 0.0136 | 0.024 |
| Alachlor | Lasso | H | 13% | 0.014 | 0.11 | 14% | 0.021 | 0.058 | 10% | 0.005 | 0.04 | 10% | 0.0041 | 0.0061 |
| MCPA | several | H | 10% | 0.028 | 0.033 | 10% | 0.052 | 0.075 | 23% | 0.032 | 0.297 | 33% | 0.044 | 0.068 |
| Simazine | Simazine | H | 6% | 0.0175 | 0.018 | 45% | 0.021 | 0.033 | 17% | 0.022 | 0.031 | 5% | 0.002 | 0.002 |
| Diuron | Karmex | H | 6% | 0.06 | 0.11 | 21% | 0.0165 | 0.092 | 53% | 0.0255 | 0.16 | 24% | 0.015 | 0.041 |
| Ethoprop | Mocap | I-OP | 6% | 0.02 | 0.022 | 15% | 0.03 | 0.27 | 20% | 0.0485 | 0.18 | 5% | 0.046 | 0.046 |
| EPTC | Eptam | H | 6% | 0.0185 | 0.022 | 7% | 0.025 | 0.032 | 27% | 0.008 | 0.027 | 5% | 0.038 | 0.038 |
| Bromoxynil | Buctril | H | 6% | 0.055 | 0.066 | 3% | 0.04 | 0.04 | 23% | 0.034 | 0.081 | 38% | 0.0285 | 0.052 |
| Carbaryl | Sevin | I-C | 6% | 0.0795 | 0.09 | | | | | | | 5% | 0.14 | 0.14 |
| Metribuzin | Axiom | H | 3% | 0.049 | 0.049 | | | | | | | | | |
| Propargite | Omite | I-SE | | | | 3% | 0.092 | 0.092 | 3% | 2.144 | 2.144 | 5% | 0.015 | 0.015 |
| Bromacil | Hyvar | H | | | | | | | 23% | 0.0072 | 0.052 | 14% | 0.01 | 0.013 |
| Dimethoate | Dimethoate | I-OP | | | | | | | 13% | 0.0305 | 0.14 | 19% | 0.00625 | 0.13 |
| Hexazinone | Velpar | H | | | | | | | 10% | 0.009 | 0.036 | | | |
| Prometon | Pramitol 5PS | H | | | | | | | 7% | 0.0218 | 0.036 | | | |
| Disulfoton | Di-Syston | I-OP | | | | | | | 3% | 0.023 | 0.023 | | | |
| Azinphos methyl | Guthion | I-OP | | | | | | | | | | 10% | 0.0048 | 0.0064 |
| Diazinon | several | I-OP | | | | | | | | | | 5% | 0.007 | 0.007 |
| Dicamba I | Banvel | H | | | | | | | | | | 19% | 0.0105 | 0.012 |
| Diphenamid | | H | | | | | | | | | | 5% | 0.093 | 0.093 |
| Endosulfan II | Thionex | I-OC | | | | | | | | | | 5% | 0.004 | 0.004 |
| Endosulfan sulfate | | D | | | | | | | | | | 5% | 0.36 | 0.36 |
| Pentachlorophenol | Penta | WP | | | | | | | | | | 5% | 0.01 | 0.01 |

Results as reported by Manchester Environmental Laboratory

[1]Common Name: Most products have several trade names. Those with a distinct, most common product name are listed. Competing labels listed as 'several'.

[2]Use type descriptors: D = degradate compound, H = herbicide, I-C = carbamate insecticide, I-OC = chlorinated insecticide, I-OP = organophosphorus insecticide, I-SE = sulfite ester insecticide, WP = wood preservative

An average of five pesticides are present in any given Lower Marion Drain sample from March-October, 2003-2006. The number of pesticides in a mixture is greatest during the months of April through June (Figure 4).

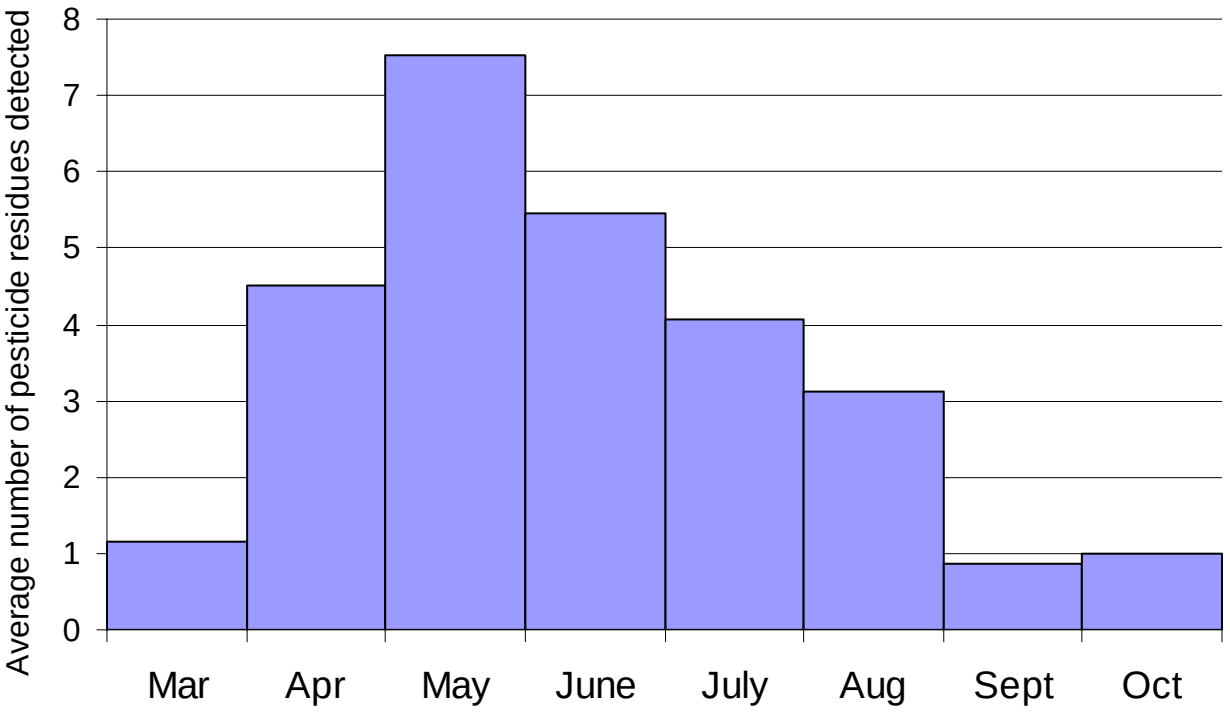
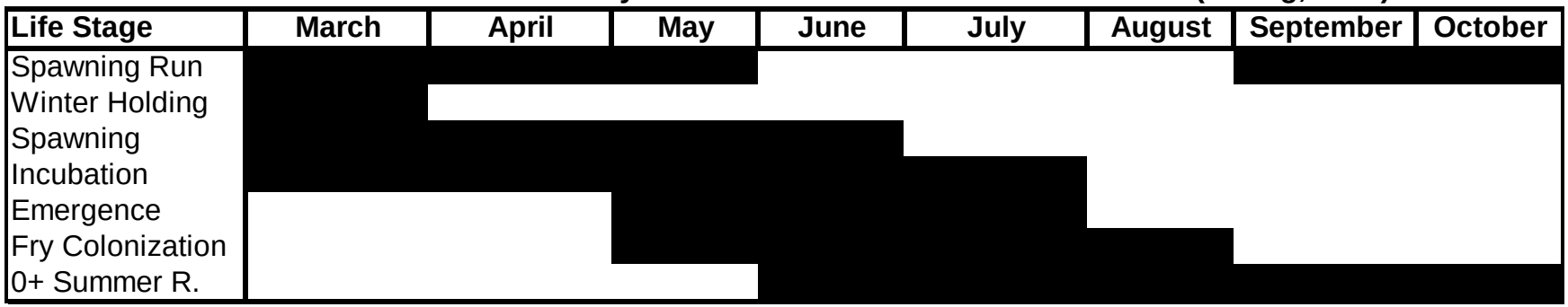



Figure 4. Average number of pesticide residues detected in a given sample of the Lower Marion Drain, 2003-2006.

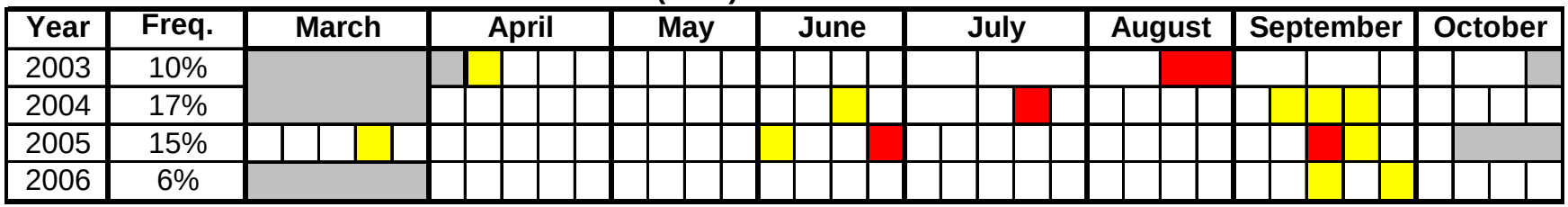
The majority of detections above toxicity endpoints are due to the organophosphorus insecticide chlorpyrifos (Figure 5). Chlorpyrifos was detected in eight-of-twelve sample events covering an exposure period of late April through mid-May. This period includes overlapping and sensitive life-stages of spawning, incubation, emergence, and fry colonization of summer steelhead in the Lower Yakima Basin (Haring 2001, Figure 5).

The current monitoring program uses weekly grab samples to characterize pesticide presence in surface water during the typical application season (Anderson et al. 2004, Burke et al. 2005, Burke et al. 2006, Anderson et al. 2007). During sequential detections, pesticide concentrations are interpolated between weeks for exposure assessment. It is unclear how representative weekly sampling is of pesticide occurrence and magnitude in surface waters.

**General Life Cycle of Yakima Basin Summer Steelhead (Haring, 2001)**




**Maximum (Risk) Residue Detections of the Marion Drain**




**Chlorpyrifos Residue Detections of the Marion Drain**

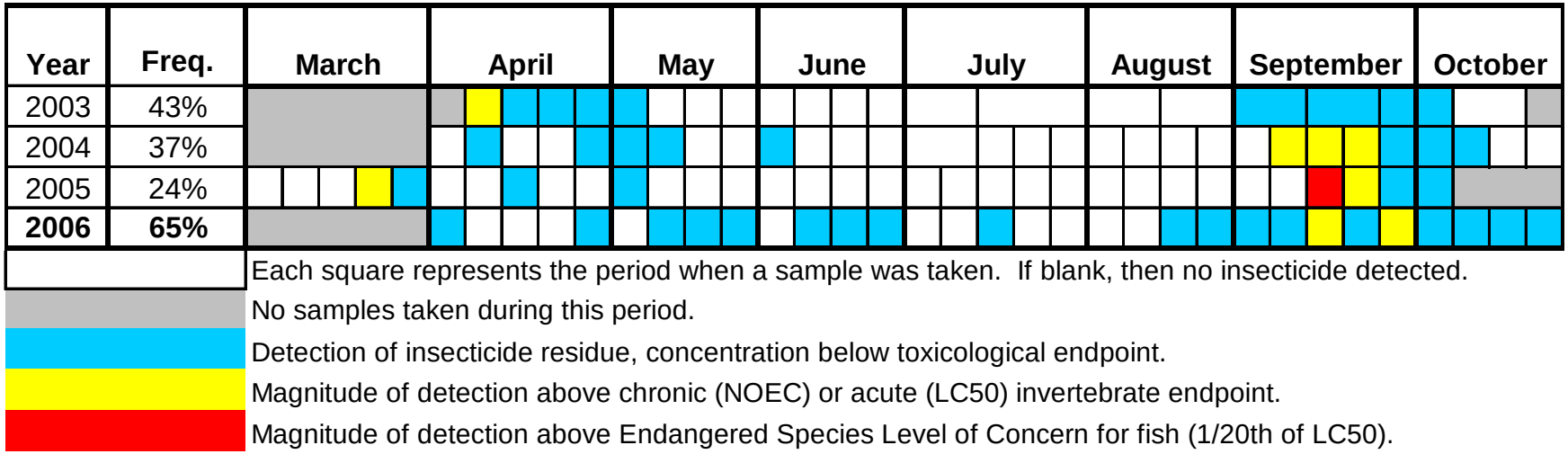



Figure 5. Detection profile of chlorpyrifos in the Marion Drain

## Project Description

The goal of this project is to evaluate the variability of pesticide occurrence and magnitude by modifying the temporal duration of sampling. Temporal duration is evaluated under passive (continuous), daily, and weekly monitoring. Understanding short-term variability of pesticides in surface waters will assist WSDA, EPA and NOAA-Fisheries to evaluate pesticide risk to salmonids.

As a complement to the existing monitoring program, pesticide presence in the Marion Drain will be investigated during a 22-day period from April 24 through May 15, 2007

Daily sampling will provide additional data on short-term pesticide flux during the application season. Sampling and analysis methods are the same as the existing monitoring project, allowing for direct comparison of daily- and weekly-derived exposure estimates.

Passive devices provide continuous sampling over the test period. Semipermeable membrane devices (SPMD) and Polar Organic Chemical Integrative Samplers (POCIS) will be deployed, in duplicate, to investigate variability of results and exposure:

- Within passive sampling methods (duplicates).
- Between passive samplers (results common to SPMD/POCIS analyses).
- Between passive and grab samples.

SPMD/POCIS samplers sequester dissolved fractions of residues, and surface water sampling analyzes whole water samples. Result comparisons will be made with this caveat understood. For the purposes of this project, passive sampling is considered experimental and is used to complement existing monitoring methods.

# Organization and Schedule

## Organization

| Name | Organization | Phone Number | Role |
|---|---|---|---|
| Chris Burke | EAP-WES-TSU | 360.407.6139 | QAPP development |
| Dan Dugger | EAP-WES-TSU | 509.454.4183 | Project manager |
| Jerry Jorden | EAP-WES-TSU | 509.454.7865 | Project assistance |
| Paul Anderson | EAP-WES-TSU | 360.407.7548 | Project assistance |
| Jim Cowles | Department of Agriculture | 360.902.2066 | Client |
| Dale Norton | EAP-WES-TSU | 360.407.6765 | Unit supervisor |
| Terri Spencer | Environmental Sampling Technologies | 816-232-8860 | SPMD/POCIS preparation and extraction |
| Bob Carrell | Manchester Laboratory | 360.871.8804 | Derivitizable pesticide, GCMS analysis |
| Dicky Huntamer | Manchester Laboratory | 360.871.8809 | LCMS analysis |
| Kamilee Ginder | Manchester Laboratory | 360.871.8826 | LCMS analysis |
| Jeff Westerlund | Manchester Laboratory | 360.871.8813 | GCMS pesticide analysis |
| John Weakland | Manchester Laboratory | 360.871.8820 | Organics supervisor |
| Dean Momohara | Manchester Laboratory | 360.871.8808 | Inorganics supervisor |
| Stuart Magoon | Manchester Laboratory | 360.871.8801 | Lab director |
| Bill Kammin | Ecology-EAP | 360.407.6964 | Quality assurance officer |

## Schedule

| **Environmental Information System (EIM) Data Set** | |
|---|---|
| EIM Data Engineers | Dan Dugger and Jerry Jorden |
| EIM User Study ID | CBUR0004 |
| EIM Study Name | SWMPPSS – Intensive Monitoring |
| EIM Completion Due | December 2007 |
| **Final Report** | |
| Report Author Lead | Dan Dugger |
| Data Summary to Client | August 2007 |
| Report Supervisor Draft Due | November 2007 |
| Report Client/Peer Draft Due | December 2007 |
| Report Final Due (Original) | February 2008 |

# Sample Design

## Site Selection

The lower Marion Drain was chosen for intensive sampling during a three-week period from April 24 through May 15. This reach integrates effects of the entire watershed and discharges to the Lower Yakima River. The lower Marion Drain was chosen during this time period due to:

- Intensity of cropping and diversity crops (Burke et al., 2006).
- Diversity of detected products (Table 1).
- Extent of pesticide mixture in samples (4-8 residues, Figure 4).
- Presence of the organophosphorus insecticide chlorpyrifos (Figure 5).
- Multiple life stages of Summer Steelhead (Figure 5).
- Fishery enhancement efforts of the Yakama Nation.

## Conventional Parameters

Conventional parameters will be collected to investigate pesticide source, fate, bioavailability, fisheries habitat, and general water quality.

| *Parameter* | *Influences (in part)* |
|---|---|
| • Total Suspended Solids | Sorption, water quality, habitat, and source indicator |
| • Total Organic Carbon | Organic sorption of pesticides |
| • Dissolved Organic Carbon | Organic sorption (dissolved) of pesticides |
| • Discharge | Load determination, habitat, and source indicator |
| • Conductivity | Dissolved ions, groundwater indicator |
| • Temperature | Activation energy, habitat, and water quality |
| • Dissolved oxygen and | Habitat, water quality, and breakdown pathway of pesticides |
| • pH | Habitat, water quality, ionization state, and breakdown pathway of pesticides |

## Pesticide Residue Testing

Three separate laboratory analyses are regularly conducted by the Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams and will be applied to surface water and POCIS samples (Appendix). The SPMD extract matrix restricts analysis to a single method (Appendix, see GCMS).

In addition to the regular analysis schedule, an attempt will be made to analyze for additional currently registered products commonly applied during this time period including:

- Insecticides
  - Pyrethroids - tralomethrin, deltamethrin, cis- and trans-permethrin
  - Organophosphate – dichlorovos, tetrachlorvinphos

- Herbicides (cycloate, oryzalin)

- Degradate and metabolites
  - Methyl paraoxon, disulfoton sulfone, diazinon oxon analog

These products successfully passed method development performance criteria of Manchester Environmental Laboratory (MEL)—responsible for pesticide sample analyses. The herbicides cycloate and oryzalin will not be testable in the SPMDs.

# Sampling Frequency

## Active Sampling

Weekly grab samples are used to characterize pesticide presence in surface water during the typical application season and are scheduled from February 15 through October 31, 2007. Daily samples will be compared against weekly sample results.

## Passive Sampling

Passive sampling is conducted using SPMD and POCIS. SPMDs continuously sample for hydrophobic compounds and the POCIS sampler continuously samples for hydrophilic, polar-organic compounds. The time-weighted average concentrations from the passive samplers will be compared to values generated from daily and weekly samples to evaluate the method.

SPMD and POCIS samplers are sold under USGA patent by Environmental Sampling Technologies (EST), www.est-lab.com.

**Semipermeable Membrane Devices (SPMD)**
SPMDs were developed by the USGS and are an established technology used to concentrate hydrophobic chemicals, pesticides in this case, from water (Huckins et al. 2006, wwwuax.cerc.cr.usgs.gov/spmd/index.htm, Figure 6). SPMDs measure dissolved, readily bioavailable forms of contaminants and mimic bioconcentration similar to the lipid-bearing tissues of organisms. The SPMD strongly sequesters compounds, minimizing desorption degradation and they are not confounded by biological loss processes of metabolism and depuration. Additionally, continuous sampling by SPMDs ensures episodic pesticide presence is captured, and a large volume of water (up to 70L per membrane over three weeks) is evaluated.

Passive sampling is based on membrane and lipid-water partitioning. The membrane is Low-Density Polyethylene (LPDE) containing transient cavities with a maximum diameter of 10

angstrom (Å). SPMDs may concentrate any non-ionic, organic compound with an octanol-water partitioning coefficient >1, but are more reliable with $K_{ow}$ values >200 (or log $K_{ow}$ > 3). Triolein is the sequestering medium and the fractional lipid content is 20%. Factors affecting uptake rate are complex but are maximized at log $K_{ow}$ between 5.0 and 6.5 with molecules containing cross sectional diameters < 10 Å.

The ambient concentration of contaminants may be estimated by rate of uptake and release by SPMDs. Performance reference compounds (PRCs) are spiked into the SPMDs prior to deployment and slowly transfer to the environment, providing this compound is not available in ambient water. The rate of release may be used to adjust uptake and sequestering rates (by incorporating loss processes) due to effects of water velocity, turbulence, temperature, and biofouling of SPMDs. In the absence of PRC evaluation, SPMD uptake/release may be estimated by the $K_{ow}$ of a compound and laboratory calibration studies.

Figure 6. Standard SPMD Membrane Mounted on a Spider Carrier.

**Polar Organic Chemical Integrative Samplers (POCIS)**

Whereas the SPMD is able to concentrate hydrophobic compounds, POCIS is able to concentrate hydrophilic, polar organic compounds (Figure 7) and was similarly developed by the USGS (Alvarez et al. 2004). The benefits of the POCIS sampler are similar to the SPMD, and 10L of water may be passed through the sequestering medium over a three-week period.

Similar to the SPMD, passive sampling is based on membrane diffusion and a sequestering medium. The POCIS sampler consists of resin/adsorbent mix between polyethersulfone membranes. The membranes have a 0.1 um pore diameter, two orders of magnitude larger than the SPMD diameter of 0.001 um. The sequestering mixture contains solutes, biobead resins, and carbon based sorbents which perform well with hydrophilic pesticides and pharmaceuticals.

POCIS samplers perform optimally with compounds containing a log $K_{ow}$ < 3 and the technology is able to provide a time-weighted average concentration for a number of hydrophilic pesticides. POCIS samplers increase the ability to target herbicides (e.g. trifluralin) and soluble organophosphorus (azinphos-methyl, malathion) insecticides. Calibration and uptake rates for compounds are less established than the SPMDs, but advances in uptake modeling complements laboratory-derived data. PRC spiking is not available for POCIS, so loss rates and interference factors are not estimable.

POCIS samplers have been successfully employed for detection and quantification of pesticides in a number of recent studies (Alvarez et al., 2004a, b; Charlestra, 2005; Sharpe, 2005; Vermeirssen et al., 2005; Chambers and Leiker, 2006).

Figure 7. Three standard POCIS on a deployment carrier.

# Quality Objectives

Field and analytical teams are expected to meet: (1) Quality Assurance and Quality Control (QA/QC) requirements for methods used in the *Surface Water Monitoring Program for Pesticides in Salmonid-Bearing Streams* and (2) this project (Johnson and Cowles, 2003; Burke et al., 2004, 2005, 2006; Burke and Anderson, 2006; Dugger et al., 2007; and Anderson et al.; 2007). The goal of quality assurance and control is to establish accurate, precise, and repeatable monitoring procedures.

Ecology personnel will calibrate and operate field monitoring equipment according to manufacturer's specifications, using Ecology Standard Operating Procedures where available (WDOE 2007, Johnson 2007) and established methods. POCIS deployment and blank samples are established in the same manner as the Ecology Standard Operating Procedure (SOP) for SPMDs (Johnson 2007). Field methods may be directly referenced to the USGS, American Public Health Association (Standard Methods), or American Society for Testing Materials (Alvarez et al., 2004; USGS, 2007; Rantz et al., 1983; APHA, 2005; ASTM, 2005-2007).

Laboratory analyses will be conducted by MEL and EST. The monitoring program will use field/laboratory blanks, replicates, matrix spike/matrix spike duplicates (MS/MSD), and laboratory control samples (LCS) and surrogates to ensure QA/QC. Twenty percent of the total laboratory budget is assigned to QA/QC, ensuring all QA/QC parameters are evaluated at a rate greater than 1 test per 20 samples or 1 test per batch (when < 20 samples) as defined in the EPA Superfund Methods for Organic Data Review (EPA 2005), Table 2. Deployments of SPMD and POCIS units are duplicated to investigate within method variability. Values exceeding performance measures will be appropriately qualified and recommended for corrective action (EPA 2004, 2005; USGS 2007).

Whole water and POCIS samples are tested against all laboratory methods, SPMDs are tested against a single, specific method (Appendix). Pesticide and herbicide controls presented under *Analysis* represent a combination of products from different analytical methods. See Appendix for specific compounds.

Table 2. Performance measures for quality assurance and control.

| Analysis | Field/Lab Replicates | MS/MSD | Surrogates and Lab. Control S. | Lowest Concentration of Interest | |
|---|---|---|---|---|---|
| | RPD | RPD | % Recovery | Surface W. | SPMD/POCIS |
| Herbicides | ±40 | ±40 | 40-130 | 30 ng/L | 10ng/POCIS or POCIS |
| Pesticide-Cl | ±40 | ±40 | 50-120 | 1 ng/L | 10ng/SPMD or POCIS |
| Pesticide-N | ±40 | ±40 | 30-105 | 20 ng/L | 10ng/SPMD or POCIS |
| Pesticide-OP | ±40 | ±40 | 30-150 | 5 ng/L | 10ng/SPMD or POCIS |
| Pesticide-Py | ±40 | ±40 | 30-130 | 5 ng/L | 10ng/SPMD or POCIS |
| Pesticide-Carb | ±40 | ±40 | 30-130 | 5 ng/L | 10ng/POCIS |
| TSS | ±20 | ±20 | 80-120 | 1 mg/L | |
| TOC | ±20 | ±20 | 80-120 | 1 mg/L | |
| DOC | ±20 | ±20 | 80-120 | 1 mg/L | |

RPD: Relative percent difference.
Pesticides: Cl-chlorinated, N-nitrogen containing, OP-organophosphorus, Py-pyrethroid, Carb-carbamate.

The lowest concentration of interest for SPMD/POCIS reflect the lower reporting limits achievable from MEL, EST, and contract laboratories. Lowest concentrations of interest for surface water samples are below reporting limits. Detections quantified below reporting limits will be appropriately qualified as estimates.

# Sampling Procedures

Deployment and retrieval procedures for SPMD/POCIS will follow the guidance in Huckins et al. (in press) and the Washington State Environmental Assessment (EA) Program SOP for SPMDs (Johnson, 2007). SPMDs (91 x 2.5 cm membrane containing 1 mL of >99% ultra high purity triolein), POCIS membranes/units (41cm$^2$, polyethersulfone membrane, pesticide adsorbent mix), stainless steel canisters (16.5 x 29 cm) and carrier devices used in deployment will be obtained from EST. Both products are preloaded onto the carriers by EST in a clean-room and shipped in solvent-rinsed metal cans under argon atmosphere.

Five SPMD membranes and six POCIS membranes will be used for each sample to ensure that sufficient residues are obtained for chemical analysis. Either five SPMDs or six POCIS membranes can fit in a single large canister (Figure 8). Four canisters will be deployed in the Marion Drain, two containing a sample and duplicate SPMD array and two containing a sample and duplicate POCIS array. The SPMDs and POCIS membranes will be kept frozen until deployed.

Figure 8. Large canister which may fit six POCIS membranes (two per carrier on left) or five SPMDs (right).

On arrival at the monitoring station, the cans will be pried open, spindles slid into the canisters, and anchored to the bottom upstream of the sampling area. Field personnel will wear nitrile gloves and not touch the membranes. The SPMD/POCIS will be located out of strong currents, situated in such a way as to minimize the potential for vandalism, and placed deep enough to allow for anticipated fluctuations in water level. Because SPMDs are efficient air samplers, this procedure should be done as quickly as possible. POCIS deployment will also be conducted rapidly, although risk of aerial uptake is not as substantive.

The SPMD/POCIS will be deployed for 22 days, within the 20-30 day period recommended by USGS and EST. The cans holding the SPMD/POCIS will be carefully sealed and maintained at or near freezing until they arrive at EST for extraction.

Surface water pesticide samples, Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), Total Suspended Solids, discharge, pH, conductivity, and dissolved oxygen will be taken daily during the 22-day deployment using established procedures (Johnson and Cowles, 2003; and updates). A data logger is on site continuously measuring temperature at 30-minute intervals (Bilheimer and LeMoine, 2004). Containers, preservation, and holding times are presented in Table 3.

Table 3. Containers, preservation, and holding times for surface water laboratory samples.

| Parameter | Sample size | Container | Preservation | Holding time |
|---|---|---|---|---|
| Herbicides and derivitizable pesticides | 1000 ml | Glass, Teflon lid | Cool to 4°C | 7 days |
| Carbamate pesticides, degradates and specialized products | 250 ml | Glass, Teflon lid | Acid preservative pH<3, 4°C | 28 days |
| Pesticides | 1000 ml | Glass, Teflon lid | Cool to 4°C | 7 days |
| TOC | 50 ml | 125 ml HDPE | Acid preservative pH<2, 4°C | 28 days |
| DOC | 50 ml | 125 ml HDPE | Filter (0.45 µm), Acid preservative pH<2, 4°C | 28 days |
| TSS | 1000 ml | 125 PE | Cool to 4°C | 7 days |

HDPE – High Density Polyethylene.
PE – Polyethylene.

# Measurement Procedures

Table 4 presents preparation and reference laboratory methods for analyses. All analysis conform to EPA SW 846 methodologies. Pesticide analysis methods do not strictly conform to a group of pesticides. For instance, the GC/MS *Pesticides* method analyzes for a number of herbicides, fungicides, insecticides, and degradate products. Reviewers of methods must refer to the Appendix to determine which products are associated with a specific analysis method. The number of samples, scheduled field QA/QC, range of results, and performance reporting limits of Manchester Environmental Laboratory are presented in Table 5.

Table 4. Target products, preparation, and analysis methods (EPA SW 846).

| **Target** | **Instrument** | **Preparation** | **Analysis** |
|---|---|---|---|
| Herbicides and derivitizable pesticides | Gas Chromatography/Mass Spectroscopy (GC/MS) | 3535M – Acid Herb. | 8270M |
| Carbamate pesticides, degradates and specialized products | High Performance Liquid Chromatography/Mass Spectrometry (LC/MS) | 3535M – Carbamate | 8321AM |
| Pesticides | GC/MS | 3535M | 8270M |
| TOC | Combustion and NDIR | NA | 415.1 |
| DOC | Combustion and NDIR | NA | 415.1 |
| TSS | Oven, 105$^{o}$C | NA | 150.2 |

Table 5. Samples anticipated QA/QC, range of results, and performance reporting limits.

| Analysis | Samples (inc. QA/QC) | QA/QC | Range of Results | Reporting Limit |
|---|---|---|---|---|
| Surface Water | | | | |
| Herbicides and derivitizable pesticides | 27 | MS/MSD, R, B | 1-1000 ng/L | 79 ng/L |
| Carbamate pesticides, degradates, and specialized products | 27 | MS/MSD, R, B | 1-1000 ng/L | 50 ng/L |
| Pesticides | 27 | MS/MSD, R, B | 1-1000 ng/L | 32 ng/L |
| TOC | 26 | R, B | 1-10 mg/L | 1 mg/L |
| DOC | 26 | R, B | 1-10 mg/L | 1 mg/L |
| TSS | 26 | R, B | 1-1000 mg/L | 1 mg/L |
| SPMD/POCIS | | | | |
| Herbicides and derivitizable pesticides | 3 POCIS | [1]R, B | 1-1000 ng/L | 10 ng/POCIS |
| Carbamate pesticides, degradates and specialized products | 3 POCIS | [1]R, B | 1-1000 ng/L | 10 ng/POCIS |
| Pesticides – GCMS | 3 SPMD<br>3 POCIS | [1]R, B | 1-1000 ng/L | 10 ng/SPMD or POCIS |

MS/MSD – Matrix Spike, Matrix Spike Duplicate.
R – Field replicate.
B – Field blank.
[1]The SPMD and POCIS tests will each consist of a field blank, deployment array, and replicated deployment array.

The success of comparable monitoring depends on consistent application of field and laboratory procedures. EST, MEL, and field personnel will adhere closely to the methods and procedures described in this Quality Assurance (QA) Project Plan, and established within the program (Johnson and Cowles 2003, and updates).

EST will extract the SPMDs (referred to as dialysis) and perform gel permeation chromatography (GPC) cleanup on the extracts. Hydrophilic compounds are eluted from the POCIS sequestering medium with HPLC grade methanol. EST Standard Operating Procedures for dialysis, cleanup, and extraction include E15, 15, 19, 21, 44, 44, 48, and 54. The dialysis method used by EST is a patented procedure, described in Huckins et al. (in press). EST's dialysis and GPC methods are documented in SOPs which are on file at Ecology. All extracts are sent to Manchester Environmental Laboratory for analysis (Table 4).

The total cost of analysis for this project is estimated at $39,354 (Table 6). This cost estimate is based on the MEL 50% discounted price; true cost is 2X for analyses conducted at MEL. Environmental Sampling Technologies provides SPMD-UHP, Dialysis+GPC, Spikes, POCIS membranes and extraction at a 5% discount. EST provides extraction blanks at no charge. All other analyses are performed by MEL. Targeting of pyrethroid compounds in SPMDs, use of deuterated C-13 surrogates, and testing of POCIS extracts led to inclusion of $2,000 for MEL method development.

Table 6. Estimate of laboratory and equipment costs of intensive monitoring by daily pesticide sampling and passive sampling using SPMDs and POCIS.

| **Surface Water Sampling** | | | | |
|---|---|---|---|---|
| **Test** | **Samples** | **Quality Control** | **Cost/sample** | **Total*** |
| Herbicides and derivitizable pesticides | 22 | 5 | 185 | 4995 |
| LCMS and carbamate pesticides | 22 | 5 | 185 | 4995 |
| Pesticides – GCMS | 22 | 5 | 450 | 12150 |
| TOC | 22 | 4 | 30 | 780 |
| DOC | 22 | 4 | 32 | 832 |
| TSS | 22 | 4 | 10 | 260 |
| **Surface Water Total** | **132** | **27** | | **24,012** |

| **SPMD/POCIS** | | | |
|---|---|---|---|
| **Description** | **Price ($)** | **Quantity** | **Total*** |
| SPMD-UHP | 52.25 | 15 – 5 sample, 5 duplicate and 5 for field blank. | 783.75 |
| Dialysis + GPC | 251.75 | 15 | 3776.25 |
| Spikes | 0.95 | 15 | 15.25 |
| POCIS membrane | 47.50 | 18 – 6 sample, 6 duplicate and 6 for field blank. | 855 |
| POCIS extraction | 71.50 | 18 | 1287 |
| Large canisters | 350 | 4 | 1500 |
| POCIS holders | 40 | 4 | 160 |
| PRC – Analysis (PCB) | 95 | 3 – SPMD | 285 |
| Herbicides and derv. | 250 | 3 – POCIS | 750 |
| LCMS and carbam. | 250 | 3 – POCIS | 750 |
| Pesticides – GCMS | 530 | 6 – 3 SPMD, 3 POCIS | 2180 |
| Method development | 2000 | To Manchester Environmental Laboratory | 2000 |
| **SPMD/POCIS total** | | | **15,342** |
| **Project Total** | | | **39,354** |

*Price reflects existing discount.
UHP – Ultra high purity triolein.

# Quality Control Procedures

## Field

EST will spike each SPMD membrane with PRCs prior to field deployment, including the field trip blank and day-zero blank (see Laboratory QA). PRCs are generally selected by the octanol-water partitioning coefficient ($K_{ow}$) of a compound. Sampling rates of compounds with $K_{ow}$ values $\geq 4.4$ are sensitive to site hydrodynamics (Huckins et al., 2002). Booij et al., 2006, found PRC release rates for products with $K_{ow}$ values from 4.2-5.6 were fairly consistent. An attempt was made to define the upper bound of PRC release through evaluation of PCB 155 ($K_{ow}$ 6.41) and 205 ($K_{ow}$ 7.3), yet the majority of PRC was sequestered (>90%) negating PRC evaluation.

PRCs selected for this test contain an organophosphorus insecticide, pyrethriod, and are augmented with two PCB congeners (Table 7). The chlorpyrifos and permethrin PRCs are selected to be representative of targeted organophosphorus (primarily chlorpyrifos) and pyrethroid (primarily permethrin) insecticides, respectively. PCB congeners 4 and 29 have been successfully employed as PRCs for organochlorine pesticide compounds (Table 7, Johnson, 2007; Johnson and Norton, 2005).

PRCs are spiked at a total equivalent concentration (all membranes summed) of the upper calibration curve for contaminants, 1 µg array or 0.2 µg per membrane. MEL will provide the PRC spiking solution to EST. PRCs are not used for POCIS analyses, constituent concentrations are estimated from laboratory derived calibrations.

Table 7. Performance reference compounds used with SPMDs.

| PRC | $K_{ow}$ | Comment | Ref. |
|---|---|---|---|
| PCB-4 | 4.65 | Chlorinated products, lower range of PRCs. | 1,2 |
| c-13 chlorpyrifos | 4.7 | Target compound, representative of OP pesticides, confirmation of PRC performance in lower range. | 1,3 |
| PCB-29 | 5.6 | Middle range of PRCs performance. | 1,2 |
| c-13 trans permethrin | 6.1 | Targeted products, upper range of PRC performance, representative of pyrethroid pesticides. | 4 |

[1]Values obtained from USGS Water Calculator v5 17 Jan 07.xls. If multiple log Kow values were found in the literature, a mean value was selected using the t test at 95% confidence for rejection of outliers.
[2]Source reference: Hawker, D.W. and Connell, D.W. 1988. Octanol-water partition coefficients of Polychlorinated Biphenyl Congeners. Environmental Science and Technology, 22:382-387.
[3]Confirmation of (1) by, EPA 2000. Reregistration Eligibility Science Chapter for Chlorpyrifos: Fate and Environmental Risk Assessment Chapter. www.epa.gov/oppsrrd1/op/chlorpyrifos/efedrra1.pdf
[4]EPA 2006. The Agency Revised Risk Assessment for the Reregistration Eligibility Decision on Permethrin After Public Comments, Phase III. Obtainable from Regulations.gov, docket search EPA-HQ-OPP-2004-0385-0069.pdf

Because SPMDs sample vapors while being exposed to air, a field trip blank is needed to record potential chemical accumulation during deployment, retrieval, and transport. The field blank SPMD is opened to the air for the same amount of time it takes to open and place the SPMD array in the water, then the blank is resealed and refrigerated. The blank is stored frozen and taken back into the field and opened and closed again to mimic the retrieval process. The blank is processed and analyzed the same as deployed SPMDs. Although POCIS is not as rigorous an

air sampler as SPMDs, a POCIS trip blank will be employed to ensure consistent application and comparability between methods. Trip blanks are also included for grab samples.

Field replicates will provide estimates of the total variability in the surface water grab and SPMD/POCIS deployments (field + laboratory). Results reflect the process of sample duplication, extraction efficiency, and recovery of targeted compounds. Duplication of SPMD/POCIS deployments represents a significant effort of the project to investigate within method variability.

MS/MSD results reflect the process of sample duplication (field), analyte degradation, matrix interaction (sample/standard), extraction efficiency and analyte recovery. MS/MSDs are scheduled for surface water grab samples. An MS/MSD is not included for SPMD and POCIS. While an MS/MSD would be helpful, a comprehensive evaluation would involve deployment of two additional SPMD and POCIS arrays. MS/MSDs may be performed on the sample extracts but the quantity of extract may not be sufficient for MS/MSDs and the three different POCIS analysis methods. Additionally, SPMD and POCIS extracts may be run multiple times to ensure consistency of the method.

## Laboratory

Laboratory QC samples for this project are at the discretion of Manchester Environmental Laboratory and Environmental Sampling and Technology. Laboratory performance for pesticide samples has been established by MEL and reviewed in Johnson and Cowles, 2003; Anderson et al., 2004; Burke et al., 2005, 2006; Burke and Anderson, 2006; Dugger et al., 2007; and Anderson et al., 2007. In addition to regular MEL SOPs, the laboratory QA/QC consists of blanks, replicates, surrogates, laboratory control samples and continuous calibration standards. These are recommended by EPA Solid Waste 846 procedures and the Superfund Methods for Organic (and Inorganic) Data Review (EPA 2004; EPA 2005). The rate of QA/QC is one test per 20 samples, batch or greater. Given the daily sampling regime and seven day holding period, samples will likely be analyzed in seven separate batches.

EST will prepare the following method blanks for each SPMD deployment:

- Spiking blank-SPMD exposed while spiking the SPMDs, to represent laboratory background. This blank is held frozen at EST and later dialyzed with project samples.
- Day-zero SPMD blank to serve as a reference point for PRC loss.
- Dialysis blank-SPMDs from the same lot as the project batch, to represent background during dialysis and cleanup.
- Day-zero blank SPMD, prepared just prior to dialysis, to serve as a control.

- Reagent blank to assess contamination independent of the SPMDs. As a less potent air sampler, POCIS blanks will consist of reagent, extraction, and the trip blank previously mentioned.

The EST blanks will be saved frozen at MEL and analyzed in the event there is evidence of significant contamination in the samples or other problems needing further investigation. (The field blank will serve as the reference point for PRC loss for this project.) MEL will also analyze their own method blanks with each batch of samples.

EST will add surrogate compounds to each SPMD sample prior to dialysis. Surrogates are presented in Table 8 and are used to calculate dialysis and analysis recovery for a class of compounds. The full suite of pesticide surrogates are applied to SPMDs prior to dialysis and POCIS membranes following elution.

Table 8. Pesticide surrogates.

| Surrogate Compound | Surrogate |
|---|---|
| 1,3 Dimethyl-2-nitrobenzene | Nitrogen pesticides |
| 2,4,6-Tribromophenol | Herbicide |
| 2,4-Dichlorophenylacetic acid | Herbicide |
| Decachlorobiphenyl | Chlorinated pesticides |
| Gamma-BHC-d6 | Chlorinated pesticides |
| Triphenyl phosphate | Organophosphorus pesticides |
| C-13 Carbaryl | Carbamate pesticides |

# Data Management Procedures

Field data and observations will be recorded in a bound notebook of waterproof paper.

The data package from MEL will include a case narrative discussing any problems encountered in the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers. The data package should also include all associated QC results. This information is needed to evaluate the accuracy of the data and to determine whether quality objectives were met. This should include results for all method blanks, check standards/LCS blanks, surrogate compounds, and matrix spikes/duplicates included in the sample batch.

All project data will be entered into Excel spreadsheets. All entries will be independently verified for accuracy by another individual on the project team.

All project data will be entered into Ecology's Environmental Information Management System (EIM). Data entered into EIM follow a formal Data Validation Review Procedure where data are reviewed by the project manager of the study, the person entering the data, and an independent reviewer.

# Audits and Reports

## Audits

MEL participates in performance and system audits of their routine procedures. Results of these audits are available on request.

## Reports

A data summary will be prepared for the client during August 2007. A draft report will be prepared for review by the client and other interested parties during December 2007. The report will be finalized within one-to-two months, depending on when review comments are received.

The analysis report will include:

- Maps of the study area showing monitoring station.
- Coordinates and detailed descriptions of station.
- Descriptions of field and laboratory methods.
- Discussion of data quality and the significance of any problems encountered in the analyses.
- Summary tables of the chemical and ancillary data.
- Description of methods used to calculate water column concentrations.
- Comparison of weekly, daily, and passive sampling results.
- Recommendations for future monitoring.

# Data Verification

MEL will conduct a review of all laboratory data and case narratives. MEL will verify that methods and protocols specified in the QA Project Plan were followed; that all calibrations, checks on quality control, and intermediate calculations were performed for all samples; and that the data are consistent, correct, and complete, with no errors or omissions. Evaluation criteria will include the acceptability of holding times, instrument calibration, procedural blanks, spike sample analyses, precision data, laboratory control sample analyses, and appropriateness of data qualifiers assigned. MEL will prepare written data verification reports based on the results of their data review. A case summary will meet the requirements for a data verification report.

To determine if project quality objectives have been met, the project lead will compare results on field and laboratory QC samples to quality objectives. To evaluate whether the targets for reporting limits have been met, the results will be examined for non-detects to determine if any values exceed the lowest concentration of interest.

The project lead will review the laboratory data packages and MEL's data verification report and validate the data. Based on these assessments, the data will be either accepted, accepted with appropriate qualifications, or rejected and re-analysis considered.

# Data Quality (Usability) Assessment

Once the data have been verified, the project lead will determine if the data can be used to make the calculations, determinations, and decisions for which the project was conducted. If the results are satisfactory, data analysis will proceed and include, but not necessarily be limited to, the following.

Water column concentrations of dissolved pesticides will be calculated using the most recent version of the SPMD Water Calculator spreadsheet developed by USGS. Currently this is v5_10Jan07.xls, David Alvarez, Columbia Environmental Research Center. The approach involves calculating SPMD sampling rates from PRC-derived sampling rates, using an empirical uptake model described in Huckins et al. (2006). The spreadsheet is locked to prevent errors in calculation. Total concentrations of constituents will be estimated using the relationships and modeling with TOC similar to that developed by Meadows et al., 1998.

The most recent POCIS calibration data (Alvarez et al., 2004b and unpublished, 2007) and models will also be used to estimate surface water concentrations. Total concentrations for these compounds will be estimated using an analogous relationship with TOC as that developed by Meadows et al., 1998. All POCIS water column concentrations are considered estimates.

Time-weighted surface water average concentrations will be compared to weekly results, which normally would have occurred on April 24, May 1, 8, and 15, 2007.

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# Appendix. Performance Limits of Pesticide Testing

Table A-1. Mean Performance Lower Practical Quantitation Limits (µg/L).

| Chemical | [1]Use | Parent | [2]Analysis Method | [3]WSDA 2003 LPQL | [3]WSDA 2004 LPQL | [3]WSDA 2005 LPQL | [3]WSDA 2006 LPQL |
|---|---|---|---|---|---|---|---|
| 1-Napthtol | Degradate/C | carbaryl | LCMS | 0.19 | 0.13 | | 0.065 |
| 3-Hydroxycarbofuran | Insecticide/C | carbofuran | LCMS | 0.19 | 0.13 | 0.11 | 0.063 |
| Aldicarb | Insecticide/C | | LCMS | 0.19 | 0.13 | 0.1 | 0.063 |
| Aldicarb sulfone | Degradate/C | aldicarb | LCMS | | | 0.10 | 0.095 |
| Aldicarb sulfoxide | Degradate/C | aldicarb | LCMS | | | 0.11 | 0.069 |
| Aldicarb sulfoxide+s | Degradate/C | aldicarb | LCMS | 0.19 | 0.13 | 0.16 | |
| Bendiocarb | Insecticide/C | | LCMS | 0.19 | 0.13 | 0.131 | |
| Carbaryl | Insecticide/C | | LCMS | 0.19 | 0.13 | 0.11 | 0.054 |
| Carbofuran | Insecticide/C | | LCMS | 0.19 | 0.13 | 0.104 | 0.063 |
| Dioxacarb | Insecticide/C | | LCMS | 0.19 | 0.13 | | |
| Diuron | Herbicide | | LCMS | | | | 0.055 |
| Linuron | Herbicide | | LCMS | | | | 0.064 |
| Methiocarb | Insecticide/C | | LCMS | 0.19 | 0.13 | 0.11 | 0.100 |
| Methomyl | Insecticide/C | | LCMS | 0.19 | 0.13 | 0.12 | 0.055 |
| Methomyl oxime | Degradate/C | methomyl | LCMS | | | | 0.070 |
| Oxamyl | Insecticide/C | | LCMS | 0.19 | 0.13 | 0.11 | 0.071 |
| Oxamyl oxime | Degradate/C | oxamyl | LCMS | | | | 0.092 |
| Promecarb | Insecticide/C | | LCMS | 0.19 | 0.13 | 0.093 | 0.101 |
| Propoxur | Insecticide/C | | LCMS | 0.19 | 0.13 | 0.11 | 0.054 |
| 2,3,4,5-Tetrachlorophenol | Degradate/WP | PCP | GCMS-H | 0.087 | 0.079 | 0.081 | 0.079 |
| 2,3,4,6-Tetrachlorophenol | Degradate/WP | PCP | GCMS-H | 0.087 | 0.079 | 0.081 | 0.079 |
| 2,4,5-T | Herbicide | | GCMS-H | 0.125 | 0.079 | 0.081 | 0.079 |
| 2,4,5-TP (Silvex) | Herbicide | | GCMS-H | 0.125 | 0.079 | 0.081 | 0.079 |
| 2,4,5-Trichlorophenol | Fungicide | | GCMS-H | 0.5 | 0.079 | 0.081 | 0.079 |
| 2,4,6-Trichlorophenol | Fungicide | | GCMS-H | 0.495 | 0.079 | 0.081 | 0.079 |
| 2,4-D | Herbicide | | GCMS-H | 0.16 | 0.079 | 0.081 | 0.078 |
| 2,4-DB | Herbicide | | GCMS-H | 0.19 | 0.079 | 0.081 | 0.079 |
| 3,5-Dichlorobenzoic Acid | Herbicide | | GCMS-H | 0.16 | 0.079 | 0.084 | 0.079 |
| 4-Nitrophenol | Degradate/H-OP | multiple | GCMS-H | 0.29 | 0.079 | 0.238 | 0.079 |
| Acifluorfen (Blazer) | Herbicide | | GCMS-H | 0.64 | 0.079 | 0.085 | 0.079 |
| Bentazon | Herbicide | | GCMS-H | 0.235 | 0.079 | 0.082 | 0.078 |
| Bromoxynil | Herbicide | | GCMS-H | 0.16 | 0.079 | 0.093 | 0.079 |
| Dacthal (DCPA) | Herbicide | | GCMS-H | 0.125 | 0.079 | 0.081 | 0.079 |
| Dicamba I | Herbicide | | GCMS-H | 0.16 | 0.079 | 0.081 | 0.078 |
| Dichlorprop | Herbicide | | GCMS-H | 0.17 | 0.079 | 0.081 | 0.079 |
| Diclofop-Methyl | Herbicide | | GCMS-H | 0.24 | 0.079 | 0.081 | 0.079 |
| Dinoseb | Herbicide | | GCMS-H | 0.24 | 0.079 | 0.083 | 0.079 |
| Ioxynil | Herbicide | | GCMS-H | 0.16 | 0.079 | 0.103 | 0.079 |
| MCPA | Herbicide | | GCMS-H | 0.315 | 0.079 | 0.081 | 0.079 |
| MCPP (Mecoprop) | Herbicide | | GCMS-H | 0.315 | 0.079 | 0.077 | 0.079 |
| Pentachlorophenol | Wood Preservative | | GCMS-H | 0.08 | 0.079 | 0.080 | 0.079 |
| Picloram | Herbicide | | GCMS-H | 0.16 | 0.079 | 0.081 | 0.079 |

Continued…

Table A-1 continued. Mean Performance Lower Practical Quantitation Limits (µg/L).

| Chemical | [1]Use | Parent | [2]Analysis Method | [3]WSDA 2003 LPQL | [3]WSDA 2004 LPQL | [3]WSDA 2005 LPQL | [3]WSDA 2006 LPQL |
|---|---|---|---|---|---|---|---|
| Triclopyr | Herbicide | | GCMS | 0.13 | 0.079 | 0.079 | 0.079 |
| 2,4'-DDD | Degradate/OC | DDT | GCMS | 0.018 | 0.079 | 0.083 | 0.032 |
| 2,4'-DDE | Degradate/OC | DDT | GCMS | 0.018 | 0.079 | 0.083 | 0.032 |
| 2,4'-DDT | Degradate/OC | DDT | GCMS | 0.018 | 0.079 | 0.082 | 0.032 |
| 4,4'-DDD | Degradate/OC | DDT | GCMS | 0.018 | 0.079 | 0.083 | 0.032 |
| 4,4'-DDE | Degradate/OC | DDT | GCMS | 0.018 | 0.079 | 0.082 | 0.032 |
| 4,4'-DDT | Degradate/OC | DDT | GCMS | 0.018 | 0.079 | 0.082 | 0.032 |
| Acephate | Insecticide/OP | | GCMS | | 1.594 | 1.500 | 0.032 |
| Alachlor | Herbicide | | GCMS | 0.335 | 0.112 | 0.12 | 0.032 |
| Aldrin | Insecticide/OC | | GCMS | 0.018 | 0.079 | 0.083 | 0.032 |
| Alpha-BHC | Insecticide/OC | | GCMS | 0.018 | 0.079 | 0.077 | 0.032 |
| Ametryn | Herbicide | | GCMS | 0.033 | 0.031 | 0.035 | |
| Atraton | Herbicide | | GCMS | 0.052 | 0.047 | 0.048 | |
| Atrazine | Herbicide | | GCMS | 0.039 | 0.032 | 0.037 | 0.032 |
| Azinphos Ethyl | Insecticide/OP | | GCMS | 0.053 | 0.05 | 0.06 | 0.032 |
| Azinphos methyl | Insecticide/OP | | GCMS | 0.053 | 0.05 | 0.052 | 0.032 |
| Benefin | Herbicide | | GCMS | 0.05 | 0.047 | 0.208 | 0.032 |
| Bensulide | Herbicide/OP | | GCMS | | 15.187 | 1.500 | 0.032 |
| Benzamide, 2,6-dichloro- | Degradate/H-OP | dichlobenil | GCMS | 0.22 | | | |
| Beta-BHC | Insecticide/OC | | GCMS | 0.018 | 0.079 | 0.076 | 0.032 |
| Bolstar (Sulprofos) | Insecticide/OP | | GCMS | 0.023 | 0.022 | 0.034 | |
| Bromacil | Herbicide | | GCMS | 0.135 | 0.126 | 0.126 | 0.032 |
| Butachlor | Herbicide | | GCMS | 0.199 | 0.189 | 0.185 | |
| Butylate | Herbicide | | GCMS | 0.066 | 0.063 | 0.080 | 0.032 |
| Captafol | Fungicide | | GCMS | 0.063 | 0.394 | 0.41 | |
| Captan | Fungicide | | GCMS | 0.089 | 0.213 | 0.21 | 0.032 |
| Carbophenothion | Insecticide/OP | | GCMS | 0.033 | 0.031 | 0.049 | |
| Carboxin | Fungicide | | GCMS | 0.199 | 0.189 | 0.186 | 0.032 |
| Chlorothalonil (Daconil) | Herbicide | | GCMS | 0.079 | 0.075 | 0.084 | 0.032 |
| Chlorpropham | Herbicide | | GCMS | 0.132 | 0.127 | 0.121 | 0.032 |
| Chlorpyrifos | Insecticide/OP | | GCMS | 0.026 | 0.025 | 0.029 | 0.032 |
| Cis-Chlordane (Alpha-Chlordane) | Insecticide/OC | | GCMS | 0.017 | 0.079 | 0.083 | 0.032 |
| Cis-Nonachlor | Insecticide/OC | | GCMS | 0.018 | 0.079 | 0.258 | 0.032 |
| Coumaphos | Insecticide/OP | | GCMS | | 1.504 | 1.497 | 0.032 |
| Cyanazine | Herbicide | | GCMS | 0.05 | 0.047 | 0.051 | 0.032 |
| Cycloate | Herbicide | | GCMS | 0.066 | 0.063 | 0.067 | 0.032 |
| Delta-BHC | Insecticide/OC | | GCMS | 0.018 | 0.079 | 0.078 | 0.032 |
| Demeton (O+S) | Insecticide/OP | | GCMS | | | 0.023 | |
| Demeton-O | Insecticide/OP | | GCMS | 0.033 | 0.022 | 0.022 | |
| Demeton-S | Insecticide/OP | | GCMS | 0.033 | 0.022 | 0.093 | |
| Di-allate (Avadex) | Herbicide | | GCMS | 0.345 | 0.221 | 0.211 | 0.032 |
| Diazinon | Insecticide/OP | | GCMS | 0.027 | 0.026 | 0.032 | 0.032 |

Continued…

Table A-1 continued. Mean Performance Lower Practical Quantitation Limits (µg/L).

| Chemical | [1]Use | Parent | [2]Analysis Method | [3]WSDA 2003 LPQL | [3]WSDA 2004 LPQL | [3]WSDA 2005 LPQL | [3]WSDA 2006 LPQL |
|---|---|---|---|---|---|---|---|
| Dichlobenil | Herbicide | | GCMS | 0.065 | 0.063 | 0.068 | 0.032 |
| Dicofol (Kelthane) | Insecticide/OC | | GCMS | 0.051 | 0.315 | 0.274 | 0.319 |
| Dieldrin | Inseciticide/OC | | GCMS | 0.018 | 0.079 | 0.076 | 0.080 |
| Dimethoate | Insecticide/OP | | GCMS | 0.027 | 0.025 | 0.032 | 0.032 |
| Diphenamid | Herbicide | | GCMS | 0.099 | 0.094 | 0.091 | 0.032 |
| Disulfoton (Di-Syston) | Insecticide/OP | | GCMS | 0.02 | 0.019 | 0.035 | 0.032 |
| Diuron | Herbicide | | GCMS | 0.195 | 0.189 | 0.19 | 0.033 |
| Endosulfan I | Insecticide/OC | | GCMS | 0.018 | 0.079 | 0.083 | 0.080 |
| Endosulfan II | Insecticide/OC | | GCMS | 0.018 | 0.079 | 0.083 | 0.080 |
| Endosulfan Sulfate | Insecticide/OC | | GCMS | 0.018 | 0.079 | 0.083 | 0.032 |
| Endrin | Insecticide/OC | | GCMS | 0.018 | 0.079 | 0.083 | 0.080 |
| Endrin Aldehyde | Degradate/OC | endrin | GCMS | 0.018 | 0.079 | 0.083 | 0.080 |
| Endrin Ketone | Degradate/OC | endrin | GCMS | 0.018 | 0.079 | 0.077 | 0.032 |
| EPN | Insecticide/OP | | GCMS | 0.033 | 0.031 | 0.036 | 0.032 |
| Eptam | Herbicide | | GCMS | 0.066 | 0.063 | 0.064 | 0.032 |
| Ethalfluralin (Sonalan) | Herbicide | | GCMS | 0.05 | 0.047 | 0.047 | 0.032 |
| Ethion | Insecticide/OP | | GCMS | 0.023 | 0.022 | 0.023 | 0.032 |
| Ethoprop | Insecticide/OP | | GCMS | 0.027 | 0.025 | 0.029 | 0.032 |
| Fenamiphos | Insecticide/OP | | GCMS | 0.05 | 0.047 | 0.054 | 0.032 |
| Fenarimol | Fungicide | | GCMS | 0.099 | 0.094 | 0.091 | 0.032 |
| Fenitrothion | Insecticide/OP | | GCMS | 0.023 | 0.022 | 0.024 | |
| Fensulfothion | Insecticide/OP | | GCMS | 0.033 | 0.031 | 0.032 | |
| Fenthion | Insecticide/OP | | GCMS | 0.023 | 0.022 | 0.026 | |
| Fenvalerate (2 isomers) | Insecticide/Py | | GCMS | | | 0.083 | 0.032 |
| Fluridone | Herbicide | | GCMS | 0.199 | 0.189 | 0.180 | 0.064 |
| Fonofos | Insecticide/OP | | GCMS | 0.02 | 0.019 | 0.023 | 0.032 |
| Gamma-BHC (Lindane) | Insecticide/OC | | GCMS | 0.018 | 0.079 | 0.082 | 0.032 |
| Heptachlor | Insecticide/OC | | GCMS | 0.018 | 0.079 | 0.083 | 0.032 |
| Heptachlor Epoxide | Degradate/OC | heptachlor | GCMS | 0.018 | 0.079 | 0.083 | 0.032 |
| Hexachlorobenzene | Fungicide | | GCMS | 0.018 | 0.079 | 0.079 | 0.032 |
| Hexazinone | Herbicide | | GCMS | 0.05 | 0.047 | 0.048 | 0.080 |
| Imidan | Insecticide/OP | | GCMS | 0.036 | 0.035 | 0.041 | 0.032 |
| Malathion | Insecticide/OP | | GCMS | 0.027 | 0.025 | 0.032 | 0.032 |
| Merphos (1 & 2) | Herbicide/OP | | GCMS | 0.04 | 0.038 | 0.055 | |
| Metalaxyl | Fungicide | | GCMS | 0.199 | 0.189 | 0.34 | 0.032 |
| Methamidophos | Insecticide/OP | | GCMS | | 1.594 | 1.7 | 0.032 |
| Methidathion | Insecticide/OP | | GCMS | | 1.594 | 1.47 | 0.319 |
| Methoxychlor | Insecticide/OC | | GCMS | 0.088 | 0.079 | 0.076 | 0.032 |
| Methyl Chlorpyrifos | Insecticide/OP | | GCMS | 0.027 | 0.025 | 0.026 | 0.032 |
| Methyl Parathion | Insecticide/OP | | GCMS | 0.023 | 0.022 | 0.034 | 0.032 |
| Metolachlor | Herbicide | | GCMS | 0.133 | 0.127 | 0.121 | 0.032 |
| Metribuzin | Herbicide | | GCMS | 0.033 | 0.031 | 0.056 | 0.032 |

Continued….

Table A-1 continued. Mean Performance Lower Practical Quantitation Limits (µg/L).

| Chemical | [1]Use | Parent | [2]Analysis Method | [3]WSDA 2003 LPQL | 2004 LPQL | 2005 LPQL | 2006 LPQL |
|---|---|---|---|---|---|---|---|
| MGK264 | Synergist/I | | GCMS | 0.263 | 0.252 | 0.26 | 0.032 |
| Mirex | Insecticide/OC | | GCMS | 0.018 | 0.079 | 0.081 | 0.032 |
| Molinate | Herbicide | | GCMS | 0.066 | 0.063 | 0.223 | |
| Naled | Insecticide/OP | | GCMS | | 1.594 | 1.502 | 0.032 |
| Napropamide | Herbicide | | GCMS | 0.099 | 0.094 | 0.096 | 0.080 |
| Norflurazon | Herbicide | | GCMS | 0.066 | 0.063 | 0.071 | 0.032 |
| Oxychlordane | Degradate/OC | chlordane | GCMS | 0.018 | 0.079 | 0.088 | 0.032 |
| Oxyfluorfen | Herbicide | | GCMS | 0.134 | 0.127 | 0.121 | 0.032 |
| Parathion | Insecticide/OP | | GCMS | 0.027 | 0.025 | 0.030 | 0.032 |
| Pebulate | Herbicide | | GCMS | 0.066 | 0.063 | 0.064 | 0.032 |
| Pendimethalin | Herbicide | | GCMS | 0.05 | 0.046 | 0.051 | 0.032 |
| Pentachloroanisole | Degradate/WP | PCP | GCMS | 0.018 | 0.079 | 0.080 | |
| Pentachlorophenol | Wood Preservative | | GCMS | 0.08 | 0.079 | 0.080 | 0.080 |
| Phenothrin | Insecticide/Py | | GCMS | | | 0.061 | 0.032 |
| Phorate | Insecticide/OP | | GCMS | 0.023 | 0.022 | 0.029 | 0.319 |
| Profluralin | Herbicide | | GCMS | 0.079 | 0.075 | 0.081 | |
| Prometon (Pramitol 5p) | Herbicide | | GCMS | 0.032 | 0.031 | 0.033 | 0.032 |
| Prometryn | Herbicide | | GCMS | 0.033 | 0.031 | 0.043 | 0.032 |
| Pronamide (Kerb) | Herbicide | | GCMS | 0.169 | 0.127 | 0.127 | 0.032 |
| Propachlor (Ramrod) | Herbicide | | GCMS | 0.079 | 0.075 | 0.078 | 0.032 |
| Propargite | Insecticide/SE | | GCMS | 0.066 | 0.063 | 0.063 | 0.032 |
| Propazine | Herbicide | | GCMS | 0.033 | 0.031 | 0.035 | 0.032 |
| Resmethrin | Insecticide/Py | | GCMS | | | 0.061 | 0.064 |
| Ronnel | Insecticide/OP | | GCMS | 0.023 | 0.022 | 0.024 | |
| Simazine | Herbicide | | GCMS | 0.033 | 0.031 | 0.031 | 0.032 |
| Sulfotepp | Insecticide/OP | | GCMS | 0.02 | 0.019 | 0.023 | 0.032 |
| Tebuthiuron | Herbicide | | GCMS | 0.05 | 0.047 | 0.054 | 0.037 |
| Terbacil | Herbicide | | GCMS | 0.099 | 0.093 | 0.090 | 0.032 |
| Terbutryn (Igran) | Herbicide | | GCMS | 0.033 | 0.031 | 0.035 | |
| Trans-Chlordane (Gamma) | Insecticide/OC | | GCMS | 0.018 | 0.079 | 0.083 | 0.032 |
| Trans-Nonachlor | Insecticide/OC | | GCMS | 0.018 | 0.079 | 0.080 | 0.032 |
| Triadimefon | Fungicide | | GCMS | 0.086 | 0.082 | 0.087 | 0.032 |
| Triallate | Herbicide | | GCMS | 0.099 | 0.094 | 0.098 | 0.032 |
| Trifluralin (Treflan) | Herbicide | | GCMS | 0.05 | 0.047 | 0.054 | 0.032 |
| Vernolate | Herbicide | | GCMS | 0.066 | 0.063 | 0.066 | |

[1]I = insecticide, OC = organochlorine, OP = organophosphorus, Py = pyrethroid, SE = sulfite ester, WP = wood preservative.

[2]LCMS = High performance liquid chromatography/mass spectroscopy. Carbamate analyses run by HPLC in 2003. 2003 results run by PSC/Maxxum analytical laboratory in Vancouver, BC.

GCMS = Gas chromatography/mass spectroscopy. 2003 results run by GCMS and Atomic Emission Detection (AED).

GCMS-H = Herbicide GCMS method SW 846 8270M has been used throughout entirety of project.

[3]Average of lower performance (reporting) values, per analyte for all batches over each study year (15-31 batches per year).

LPQL: Lower performance practical quantitation limit.