Pesticides in Salmonid-Bearing Streams: Intensive Sampling in an Agricultural Drain

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①Introduction

The Washington State Department of Ecology (Ecology) and Washington State Department of Agriculture (WSDA) have conducted surface water pesticide monitoring in salmon-bearing streams since 2003.

This project evaluated the current weekly sample regime against daily and passive sampling. Pesticide detections from weekly surface water samples were compared to daily water samples and passive samplers over 22 days.

Detections from passive samplers targeting hydrophobic and hydrophilic pesticides were compared to grab samples.

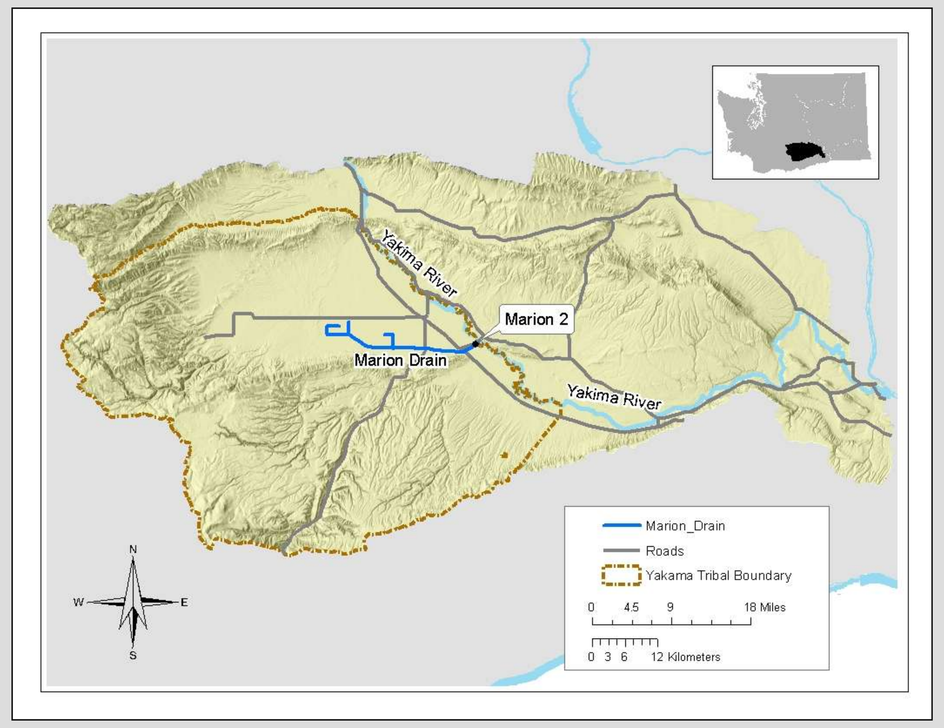

Figure 1. Marion Drain sample site in the Lower Yakima Watershed.

②Location

The study site was Marion Drain, a 19-mile agricultural drain that discharges into the Yakima River (Figure 1). Marion Drain is used by salmonids including: Chinook, Coho, and endangered Steelhead.

③Passive Samplers

Semi-Permeable Membrane Devices (SPMD)

An SPMD is a triolein-filled polyethylene tube compressed into a flat strip (Figure 2, right).

The SPMD concentrates hydrophobic (lipophilic) pesticides (e.g., organochlorine and pyrethroids).

Polar Organic Chemical Integrative Samplers (POCIS)

The POCIS consists of a resin/adsorbent mix between polyethersulfone membranes (Figure 2, left).

POCIS samplers perform optimally with hydrophilic pesticides. (e.g., herbicides and more water-soluble organophosphorus insecticides such as azinphos-methyl and malathion) .

Figure 2.
Left: **Three POCIS on a deployment carrier.**
Right: **SPMD on a spider carrier.**
Center: **Protective deployment canister. (Photo courtesy of EST, www.est-lab.com).**

Figure 3. Lower Marion Drain, site Marion 2.

④Methods

The study was carried out from April 24 to May 15, 2007.

Surface water samples were collected daily. A subset of 4 samples that would have been collected by weekly surveys were compared to the full set of 22 daily results.

Water and passive samples were analyzed for a suite of pesticides. Water samples were also analyzed for physical parameters (Table 1). Discharge, dissolved oxygen, pH, water temperature, and conductivity were collected on site.

Field replicates and field blanks were used to assure quality assurance and quality control (QA/QC) for all sample methods.

Table 1. Analyses conducted per sample method. [1]

Analysis	Grab Samples	POCIS	SPMD
Nitrogen containing pesticides	X	X	X
Organochlorine pesticides	X	X	X
Organophosphorus pesticides	X	X	X
Pyrethroid pesticides	X	X	X
Derivatizable acid herbicides	X	X	
Carbamate pesticides	X	X	
Total Organic Carbon (TOC)	X		
Dissolved Organic Carbon (DOC)	X		
Total Suspended Solids (TSS)	X		

[1] A full list of targeted analytes is available in the handout.

Passive samplers were deployed in an eddy on an instream cable (Figure 4). 5 SPMD or 6 POCIS were composited per canister. Sampler canisters were deployed in duplicate.

Passive samplers were extracted by Environmental Sampling Technologies (EST). All analyses were conducted by Ecology's Manchester Environmental Laboratory (MEL).

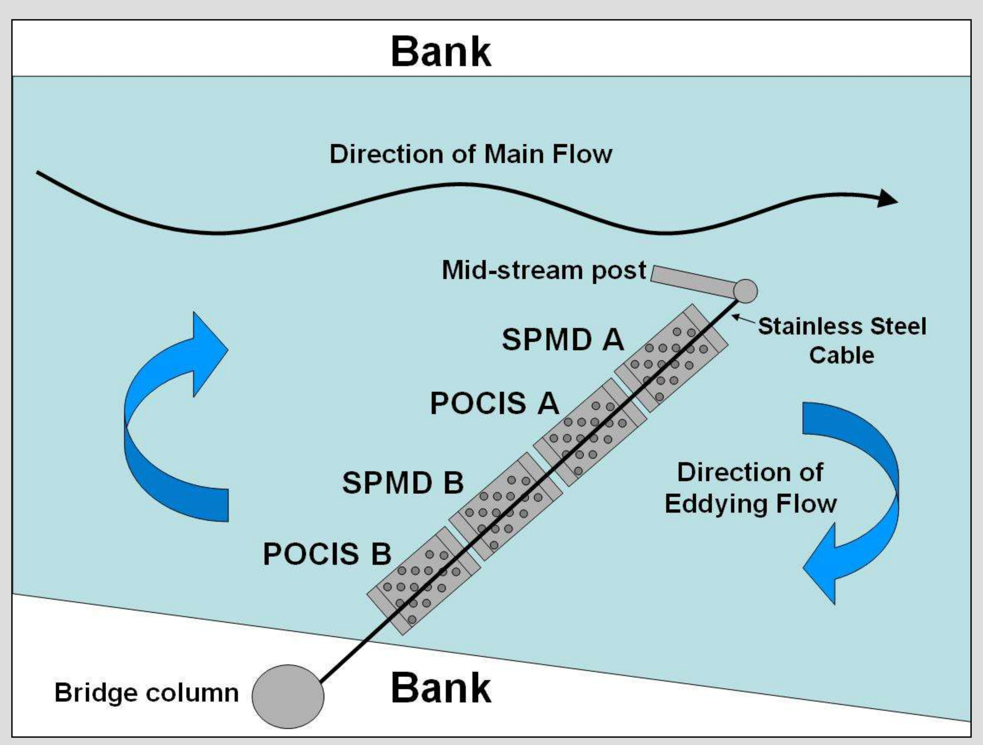

Figure 4. Passive sampler deployment in Marion Drain (not to scale).

⑤Results

Daily versus Weekly results

Daily grab samples detected 15 pesticides. The weekly schedule detected all pesticides except Carbaryl.

No correlations were found between pesticides and the physical parameters.

Figures 5 to 7 show the detection patterns for selected pesticides. Non-detections are plotted as zero.

Positive detections below the Lower Practical Quantitation Limit (LPQL) were qualified as approximate concentrations.

Most weekly medians were within 10% of daily medians. Weekly samples also detected the maximum or near-maximum concentrations for Bentazon, Bromoxynil, Chlorpyrifos, and Malathion (Figure 5).

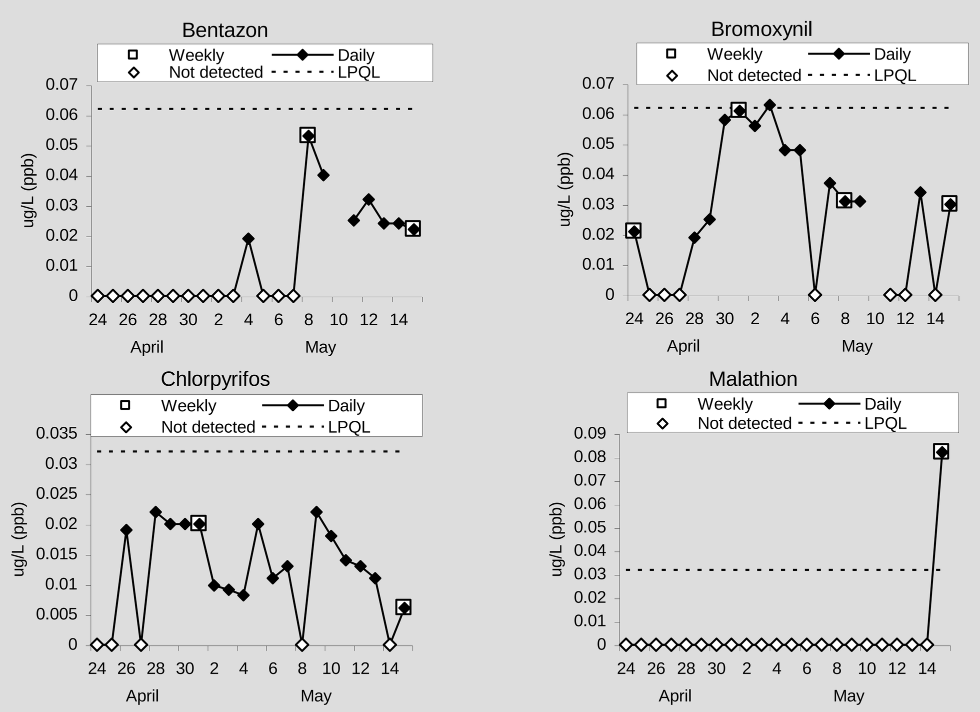

Figure 5. Pesticides with maximum or near-maximum detections by the weekly samples.

Weekly sampling did poorly for pesticides that showed isolated peaks, e.g., 2,4-D and Dicamba I (Figure 6). Maximum daily concentrations for these pesticides were often much higher than for weekly samples.

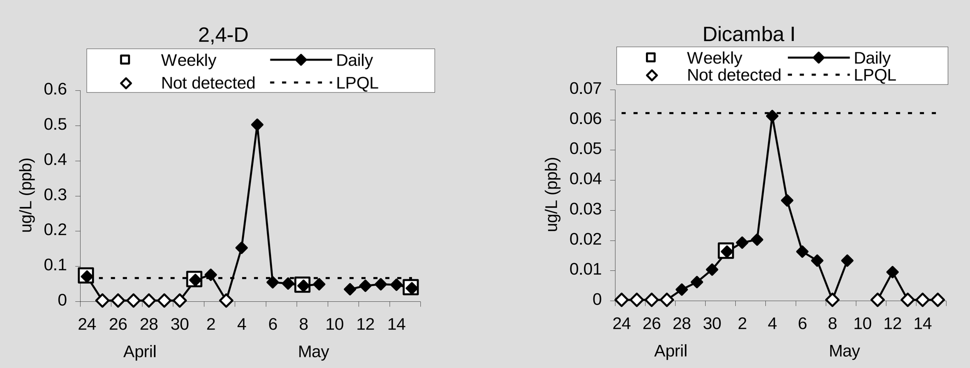

Figure 6. Examples of detection patterns for pesticides with isolated peaks.

Weekly samples also did poorly at detecting some rarely occurring pesticides like Carbaryl and Diuron (Figure 7).

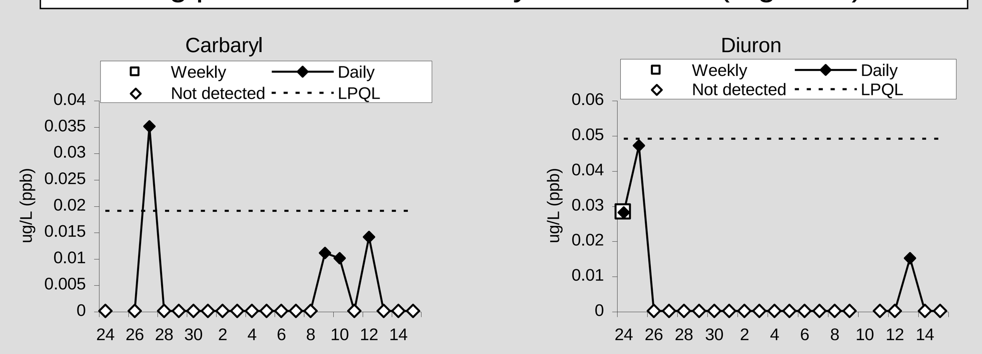

Figure 7. Examples of detection patterns for rarely occurring pesticides.

Passive Samplers versus Daily Grab Sampling

SPMD

SPMDs detected 5 more lipophilic compounds than the grab samples.

These included 4,4'-DDT, two DDT breakdown products, Endosulfan 1, and Trans-Nonachlor.

POCIS

2,4-D, Atrazine, Bentazon, MCPA, and Terbacil were found in both the POCIS and grab samples. However, the majority of pesticides found by grab sampling were not detected by the POCIS.

Pesticide detections in the POCIS blank and inconsistencies between the POCIS duplicates point to unknown quality control problems.

Comparison of Data to Toxicological Endpoints

Figure 8 compares grab sample pesticide detections to Washington state and federal toxicological endpoints. The weekly schedule is highlighted with bold border .

A single detection of Malathion was found above the chronic freshwater No Observable Effects Concentration (NOEC) for aquatic invertebrates.

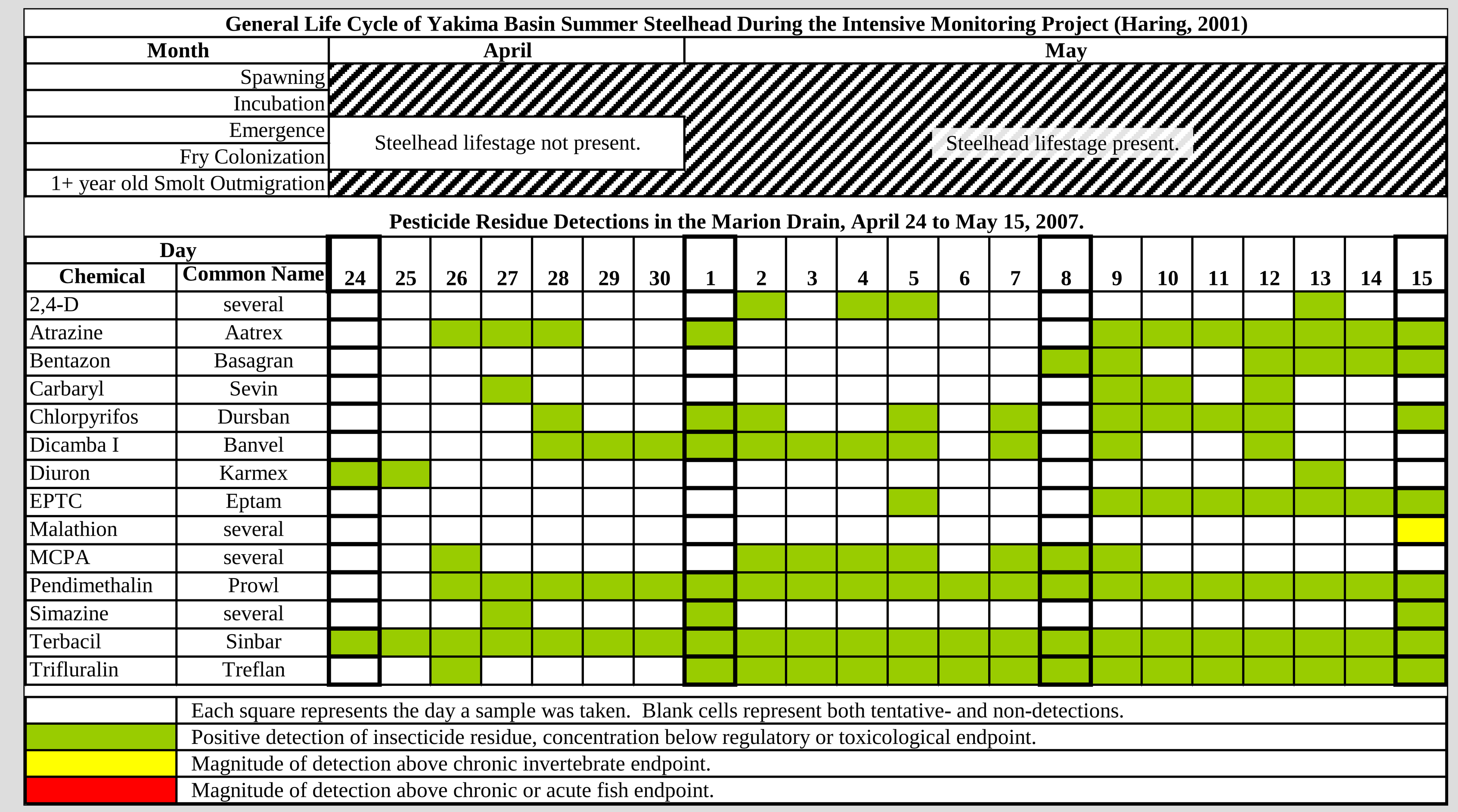

Figure 8. Pesticide residue detections and Summer Steelhead life history (general) for Marion Drain.

⑥Discussion

Weekly samples were effective at detecting pesticide presence and median values but less effective at detecting maximum concentrations and pesticides that are transient. Targeted samples tied to specific pesticide applications would enhance the ability for long-term weekly monitoring to detect maximum pesticide risk.

Additional detections by the SPMDs reflect lowered reporting limits through the absorbed concentration of legacy organochlorine pesticides. Alternate analyses (e.g.; Large Volume Injection or Gas Chromatography by Electron Capture Detector [GC/ECD]) could increase grab sample detection rates for legacy compounds.

The sources of quality control problems in the POCIS are unknown and may be unique to this study. Other studies have shown POCIS are useful in detecting polar compounds (Charlestra, 2005; Vermeirssen et al., 2005). Further research into polar samplers may provide passive alternatives to surface water grab sampling.

Summary of Findings

1. Weekly sampling provides a good measure for median pesticide concentrations.
2. Targeting specific pesticide applications should improve the detection of maximum concentrations.
3. Developments in polar organic passive samplers should be assessed as a complement to the current sampling program.

References

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