Design of Herbicide Concentration Monitoring Plans for Large-Scale Herbicide Treatments

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Objective: Monitoring herbicide concentrations following aquatic plant management actions can provide essential information necessary to interpret and assess management outcomes. The analysis of lake water samples following application of herbicides utilized for aquatic plant control can provide valuable information on herbicide dissipation and degradation patterns within lakes. When this information is paired with pre- and post-treatment aquatic plant data, it can also provide important insight into the observed target species control efficacy, native plant selectivity, and scale of impact.

This document provides guidance on the design of herbicide concentration monitoring plans for large-scale aquatic herbicide treatments. A large-scale herbicide treatment is defined in this document as an application of one or more aquatic herbicides that will result in a lake-wide herbicide concentration sufficient to impact target and/or non-target aquatic plant species, assuming complete dissipation throughout the waterbody. Guidance for the design of herbicide concentration monitoring associated with small-scale treatments can be found in this document.

Approach: An herbicide concentration monitoring plan template is available. The plan should include the following information:

- Lake name, county, and waterbody identification code (WBIC)
- Lake surface area, mean depth, and maximum depth
- Lake trophic status and lake type
- Herbicide active ingredient and application rate
- Treatment area and target species
- Calculated lake-wide (or epilimnetic) rate
- Map of lake with labeled sample sites and herbicide treatment areas
- Sample site lat/long coordinates
- Sampling intervals
- Instructions for in field sample collection, sample storage, and shipping
- A copy of the sample data sheet specific to the lake
- Contact information for person(s) coordinating the sampling

Sample sites:

- Three to four sampling sites should be sufficient to characterize herbicide concentrations in simple lake configurations (Figure 1). More than four sampling sites may be needed if the lake has a complex configuration, or there is an area of special concern (Figure 2).
- One sampling site should be located in the center of the lake in an area that is not directly treated. The other sites should be located in areas targeted for direct application of herbicide. If there are resources of concern downstream from the lake a site can be placed near or in the outflow of the lake.
- Sample locations should be located precisely on a map, and the numerical lat/long coordinates should be provided in decimal degrees for use in a GPS.

- Each sample location must have a SWIMS Station ID assigned to it. The WDNR's Surface Water Data Viewer can be used to find existing SWIMS Station IDs on a waterbody. Contact your regional DNR APM coordinator if you need a new SWIMS Station ID created for a sample location.
- If the lake is anticipated to be thermally stratified at the time of herbicide application, an additional sampling depth at approximately 5-10 feet below the thermocline[1] should be included at the deep hole site. The exact sampling depth should be determined using temperature profile data collected prior to the herbicide application. The sample must be taken from below the thermocline. Collecting data at this location will assess whether the herbicide mixed into the hypolimnion.

Sampling intervals:

Sampling intervals should be specified in the herbicide concentration monitoring plan. Sample time intervals are specified in hours after treatment (HAT) and days after treatment (DAT) and may vary slightly depending on lake type and trophic status. Sampling intervals may also vary depending on the specific herbicide being monitored; herbicides which require a very long contact exposure time (i.e., fluridone) may necessitate modified sampling intervals. If herbicide concentration monitoring has been conducted on a lake in the past, the sampling intervals may be shortened or lengthened appropriately. Contact your regional DNR APM coordinator for additional guidance on sampling intensity. Sample intervals should generally include:

- For all lakes:
    - 3 and 9 HAT, and 1, 2, 4, 7, 14, and 21 DAT to quantify the mean average concentration for the entire lake during the first three weeks after treatment.
- For seepage lakes:
    - Longer persistence of certain herbicides may be expected in seepage lakes due to lack of dissipation out of the waterbody. Samples should also be collected at 28 and 35 DAT, and then weekly thereafter until concentrations fall below detectable limits.
- For oligo-mesotrophic lakes:
    - Oligo- and mesotrophic lakes may encounter longer persistence of certain herbicides due to slower microbial degradation and breakdown. Samples may need to also be collected at 28 and 35 DAT, and then weekly thereafter until concentrations fall below detectable limits.
- For thermally stratified lakes:
    - In addition to integrated surface samples, a water sample (~5-10 feet below the thermocline) should be taken at the deep hole at 7 and 21 DAT.
- For florpyrauxifen-benzyl (e.g., ProcellaCOR™) treatment lakes:
    - The Wisconsin State Lab of Hygiene (WSLH) currently does not have the capability to analyze water samples for florpyrauxifen-benzyl, and samples are analyzed by EPL Bio Analytical Services (EPL). In addition to the post-treatment water samples, the lab requests that a single water sample be collected *prior* to the treatment as an untreated

[1] Zone of rapid temperature change with depth in a waterbody, where the water temperature changes at least 1 degree Celsius with every meter of depth.

control. This pre-treatment sample can be collected from any site at a time that is most convenient, but as close to the treatment date as possible

The actual sampling intervals may vary due to hazardous weather conditions, volunteer availability, and unique lake conditions. If a sample cannot be collected at the time noted in the plan, the sample should be collected as soon as reasonably possible, and the change should be recorded on the datasheet. Direct communication between the water sample collector and the herbicide applicator is necessary to ensure the collector is prepared to collect samples after treatment is completed.

A copy of your proposed monitoring plan should be sent to your regional DNR APM coordinator for review and approval well in advance of any proposed treatment. Once a monitoring plan is approved, your coordinator can provide assistance in obtaining the necessary sampling supplies (i.e., samples bottles, acid, etc.) from the respective lab.

Instructions for sample collection, sample storage, and shipping:

- Water samples should be collected using an integrated sampling device (Figure 3), which is used to collect a surface water sample from 0 to 6 feet deep.
- Upon arrival at the site, rinse the integrated sampler and composite water collection bottle three times with lake water before each sample collection.
- Take the water sample from the opposite side of the boat as you rinsed. Slowly lower the integrated sampler vertically to 6 feet deep (which is typically marked with a line). After reaching 6-foot depth, slowly pull sampler up vertically. If the sampling location is shallower than 6-feet, lower the sampler into the water column so that it remains at least 1 foot above the lake sediment bottom.
- Empty the contents of the integrated sampler into the composite water collection bottle by pushing the ball valve end against the bar installed across the bottle's mouth, which pops the ball valve up and releases water from the sampler (Figure 3).
- Gently mix the water in the composite bottle, and carefully pour the water into the sample bottles provided by the lab.
- If sampling at the deep hole below the thermocline, use a Van Dorn sampler on a measured rope. Follow the instructions found within this water chemistry protocol (page 5, steps 1-12) to collect a water sample at a discrete depth.
- Depending on the herbicide being analyzed, a small amount of acid may need to be added to each sample bottle.
    - The WSLH can analyze for 2,4-D, endothall, and copper; they will provide a sampling kit which will include bottles, labels, acid, datasheets, a shipping cooler, and sample handling instructions (Figure 4).
    - The sampling kit provided by EPL for florpyrauxifen-benzyl analysis contain amber bottles with a pre-measured amount of preservative already within them (Figure 5).
- Write the sampling site, sampling interval (e.g., 9 HAT), date (MM/DD/YY), and collection time (e.g., 18:35) on the bottle's label.
    - The WSLH will provide datasheets for use when collecting water samples (Figure 6). Similar datasheets can be printed off and included with samples sent to EPL. It is important to use a separate data sheet for each sampling interval that you monitor.

    - On each sampling sheet, include: lake name, county, WBIC, collector name, phone number, test requested (e.g., herbicide active ingredient), and sampling interval.
    - Within each row, write the site name, SWIMS station ID, sample depth, date, time, water temperature (see Figure 7 for Fahrenheit to Celsius conversion table), and wind direction and speed.
- Samples should be temporarily stored in a cooler for transport, and then in a refrigerator until shipped.
- Once all sample intervals are completed, the water samples and datasheets should be shipped overnight and with an ice pack to the appropriate lab. Samples should not be shipped on loose ice. Samples should not be shipped on a Friday, but rather refrigerated and shipped on the following Monday.
    - For analysis of 2,4-D, endothall or copper:
        - Wisconsin State Lab of Hygiene
          EHD Organic Chemistry Dept.
          2601 Agriculture Drive
          Madison, WI 53718

    - For analysis of florpyrauxifen-benzyl (e.g., ProcellaCOR™):
        - EPL Bio Analytical Services
          9095 W. Harristown Blvd.
          Niantic, IL 62551

Figure 1. Example of Sample Locations in a Simple Seepage Lake

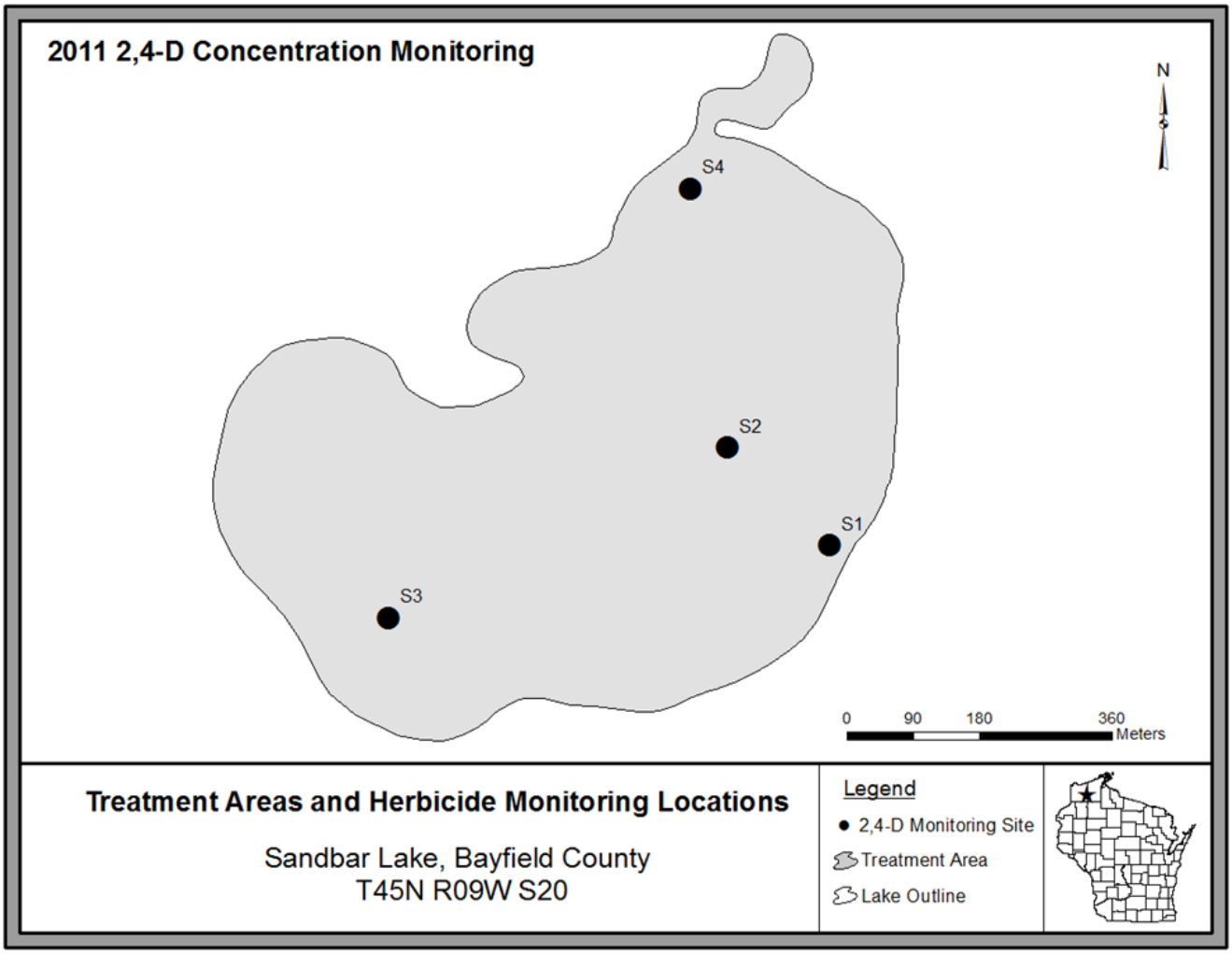

Figure 2. Example of Sample Locations in a More Complex Lake

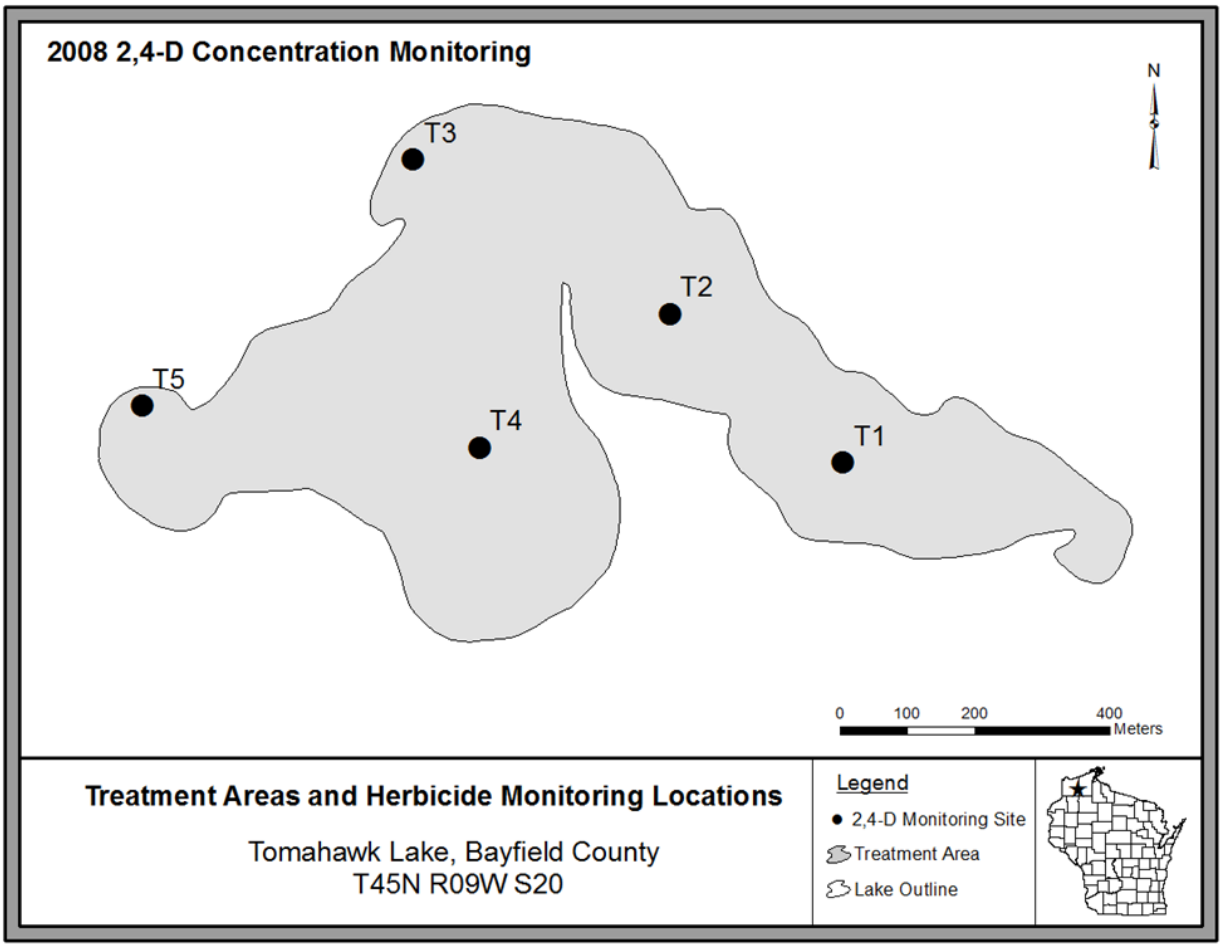

Figure 3. Photo of 6-foot integrated sampler (top) and composite water collection bottle (bottom).

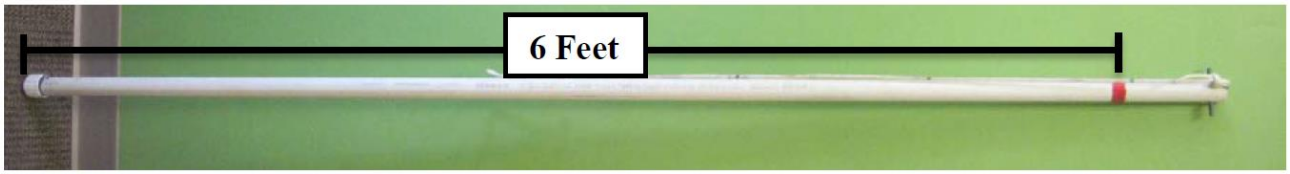

Figure 4. Photos of cooler, bottles, and sampling supplies provided by Wisconsin State Lab of Hygiene.

Figure 5. Photos of amber sampling bottles and labels provided by EPL Bio Analytical Services.

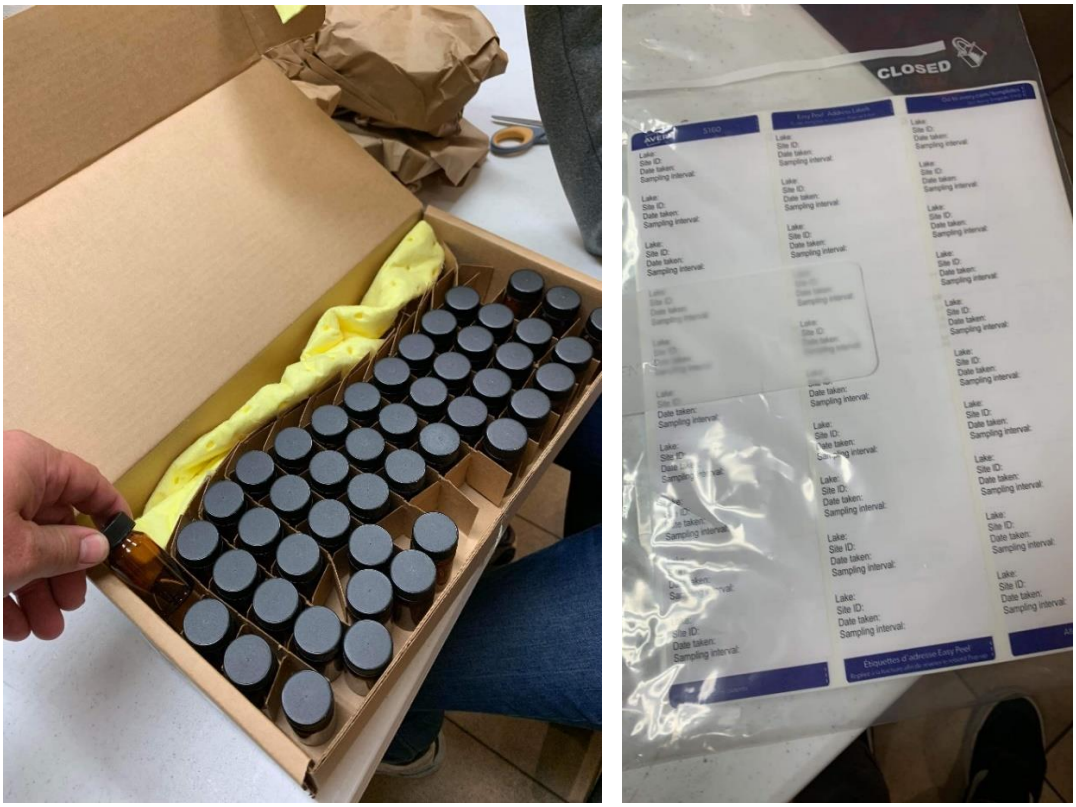

Figure 6. Example of a Sample Data Sheet

_____ Lake, _____ County				Herbicide Sampling Data Sheet		
Account number:				**Sample Matrix:**	Surface Water (SU)	
DNR User ID:				**Project:**	HerbicideMonitoring	
WBIC:				**Collector Name:**		
				Phone Number:		
Test Requested:						
Sample Interval:						
Site	**Station ID**	**Sample Depth**	**Date**	**Time (24:00)**	**Water Temp in C**	**Wind Direction and Speed**

Figure 7. Fahrenheit to Celsius conversion table.

Convert Fahrenheit to Celsius

T(°C) = (T(°F) - 32) × 5/9

Degree F	Degree C	Degree F	Degree C	Degree F	Degree C	Degree F	Degree C
50	10.0	60	15.6	70	21.1	80	26.7
51	10.6	61	16.1	71	21.7	81	27.2
52	11.1	62	16.7	72	22.2	82	27.8
53	11.7	63	17.2	73	22.8	83	28.3
54	12.2	64	17.8	74	23.3	84	28.9
55	12.8	65	18.3	75	23.9	85	29.4
56	13.3	66	18.9	76	24.4		
57	13.9	67	19.4	77	25.0		
58	14.4	68	20.0	78	25.6		
59	15.0	69	20.6	79	26.1		