**SEA GRANT PROJECT SUMMARY FORM (90-2)**

**TITLE:** Glyphosate runoff dynamics in tributaries draining into Lake Erie  
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**KEYWORDS:** Glyphosate, surface water monitoring, chemograph, loading

**OBJECTIVES:**
Overall, this project aims to better understand the potential for glyphosate runoff and transport through river systems in the Lake Erie watershed. Glyphosate is the most heavily used herbicide in row-crop agriculture, which is the dominant land use in the Sandusky River Basin. We need a better understanding of its runoff pattern due to concerns that glyphosate could impact human health. Furthermore, recent research has found glyphosate in the Sandusky River, and others suggest that glyphosate could play a role in the increase in DRP loadings from farm fields from the mid-1990s.

More specifically, our objectives are:
1. To validate a newly developed novel chromatographic method (LC-MS/MS) for measuring glyphosate in surface water samples
2. To analyze glyphosate in two tributaries draining into the Sandusky River using an intensive stratified sampling technique over two years in order to measure their temporal concentration trends and compare the effects of the geologic and hydrologic properties of the two watersheds on these trends
3. To assess if runoff of glyphosate is transport or source limited and compare glyphosate runoff to other nutrients (i.e., suspended sediments, total and dissolved phosphorus, nitrate) and pesticides (atrazine) to better understand factors controlling runoff.

**METHODOLOGY:**
*Field Sampling:* We will collect samples for glyphosate analysis from monitoring stations located in the Honey Creek and Rock Creek subwatersheds that drain into the Sandusky River and ultimately Lake Erie (Fig 1). Both watersheds have high agricultural land use (81% and 72%, respectively) dominated by corn and soybean row-crops with a smaller percent of winter wheat and both have high glyphosate application rates (USDA-NASS data, 2015). Honey Creek has an area of 389 km$^2$ and Rock Creek has an area of 89 km$^2$. Due to their small sizes, these creeks are hydrologically flashy with high peak concentrations of chemicals over short periods of time (Baker and Richards 2004). Water samples will be collected year round, with more intensive sampling during the growing season each year from April to August. Water samples from Honey Creek will be collected from monitoring station at Melmore, OH, located adjacent to USGS gaging station# 4197100. Water samples from Rock Creek will be collected from monitoring station at Tiffin, Ohio, adjacent to the USGS gaging station# 4197170. Water will be continuously pumped by a submersible pump from the creek into a sampling well in the sampling station. The monitoring stations are

![Fig 1: Map of the Rock and Honey Creek sampling locations within the Sandusky River watershed.](image)
equipped with ISCO autosamplers that will collect water as frequently as every 8 hours per day (3 samples/day) on high flow days, and 3 times a week, during low flow days. This will result in collection of up to 21 samples per week during high flow conditions and around ~ 200 samples per growing season from each station. During the non-growing seasons from September to March, water samples will be collected, 1 to 3 times a week depending on several factors, such as precipitation, detection frequencies, and other weather related events. This will add another 30 to 50 samples to a total of ~ 250 samples per station each year. Samples will be collected for two calendar years including two full growing seasons.

**Chromatographic method development:** We are developing a novel chromatographic method to measure glyphosate concentrations in various environmental matrices using liquid chromatograph triple quadrupole mass spectrometer or LC-MS/MS. This is the optimal method for analyzing glyphosate because the low detection limit (0.05 μg/L) allows for precise trace level measurements in surface water samples. This is a rapid and direct method suitable for analyzing a large number of samples and minimizing elaborate sample preparation that often leads to loss of analyte and uses additional time and resources. For pesticide extraction from the water samples, we will use a solid phase extraction (SPE) technique consisting of centrifugation, extraction using anion exchange cartridges, and then analysis on the LC-MS/MS system. For samples with high sediment content, the sediment phase will be extracted by centrifuging with methanol. This method reduces sample volume relative to our current pesticide analysis (1L to 0.05L) and could lead to better sample clean up preparation for all samples in the laboratory.

**Data analyses:** Overall, these data will be used to identify the timing of glyphosate runoff along with peak, time-weighted mean, and flow-weighted mean concentrations. In addition, we will be able to calculate glyphosate loads from these watersheds using the stratified Beale Ratio Estimation technique (Richards et al. 1996). From these analyses, we will be able to produce clear guidance on whether glyphosate ever approaches drinking water limits in raw water and if so, when that occurs, along with longer-term concentrations indicating chronic exposure. We will be able to compare our observed data to on-going ecotoxicology studies to examine the potential for trace level exposure. To better understand why we may be observing differing trends in glyphosate runoff, we will analyze existing tillage and cover crop transects currently collected by the Seneca Conservation District for other on-going projects, and examine any trends in crop coverage for each subwatershed. To identify whether glyphosate runoff is limited by hydrology or source pools, we will use a combination of Lorenz curves, that quantifies temporal inequalities for stratified sampling, and spectral density plots, which provides insights into time-series data. This approach was recently used for DRP and total P data in Williams et al. (2016), which suggest P was largely controlled by hydrology rather than by source. This also suggests a legacy component to P runoff. To ensure appropriate comparisons among the data, we will revisit this analysis for the same analytes in Williams et al. (2016) along with atrazine, nitrate, and suspended sediments for the same years we will be analyzing glyphosate runoff.

**RATIONALE:**
Glyphosate is a broad spectrum, non-selective herbicide, introduced in 1974, and is widely used in agriculture for crops such as corn and soybean. A very popular commercial brand containing glyphosate as an active ingredient is Round Up. After the introduction of genetically modified crops in 1994, the use of glyphosate has significantly increased. According to National Agriculture Statistics Service, glyphosate use in agriculture for corn in the state of Ohio has increased 20 times from less than 150 metric tons in 1990 to 3100 metric tons in 2015 (Fig 2), with similar trend in soybean. Alarming, glyphosate use could continue to increase as an unintended consequence of cover crop best management practices, which are promoted to reduce nutrient runoff from farm fields. Glyphosate, being a non-selective herbicide is popularly used for terminating a mixture of cover crops that contain grasses and broadleaves in the spring prior to planting (Legleiter et al. 2015).

Glyphosate is known to have low toxicity but there is increasing public health concerns due to reports of potential human health risks such as endocrine disruption and cancer from glyphosate levels lower.
than the current drinking water standard or approved for consumption (Guyton et al. 2015). There is limited data on glyphosate occurrence in the midwestern US surface waters. This is partially because it is difficult, expensive, and time consuming to measure glyphosate, due to presence of polar functional groups that makes glyphosate ‘sticky’ with strong sorption properties. This is a good characteristic of an herbicide to lower the potential for runoff, but it makes glyphosate particularly difficult to analyze. With the development of new generation anion exchange SPE cartridges and mixed mode HPLC columns that can be used on LC-MS/MS systems, it has become easier to extract and analyze glyphosate. We will take advantage of this new technology, to rapidly analyze glyphosate in the surface water samples using our newly developed method.

Due to the strong sorption properties of glyphosate, it is expected to sorb strongly to the soil and generally be immobile. The variability in transport properties with wide range of partition coefficients and half-lives makes it difficult to assess the expected transport pattern of glyphosate under different conditions. In this regard, our study will reveal the true nature of glyphosate transportation in the watershed by comparing its concentration trends to that of other chemicals such as P, nitrate, suspended sediments, and atrazine under similar conditions in those watersheds. **Hence our overall goal will be to understand the processes that influence runoff patterns and transport of glyphosate in the Lake Erie watershed.**

Our main hypotheses are:

1. Due to high usage in current row-crop agriculture and cover crops BMPs, we expect to find glyphosate in surface water samples
2. Because the properties of glyphosate are similar to P, we predict the runoff patterns will exhibit chemostatic behavior and will be transport limited rather than source limited

Our research goal aligns with Ohio Sea Grant’s mission of striving to improve environmental conditions in Lake Erie and Great Lakes ecosystems. Our study on glyphosate concentration trends will be the first of its kind and will help discern the occurrence and transport characteristics of glyphosate as well as improve recommendations for glyphosate application by clarifying the best application times, rates, amounts, and areas to prevent runoff into surface water. This project not only trains and supports 2 undergraduates in the NCWQR, but also supports training of an early-career postdoctoral scientist (lead PI, Biswas) in project management and completion under the advisement of co-PI Johnson. Near the completion of the project, we will conduct standard outreach activities (scientific conferences, regional conferences), but more importantly we will develop a video presentation for educational, environmental, or other organizations to “mythbust” some of the narrative on herbicides in the environment to help fight against pseudoscience. This video will be hosted on NCWQR.org and will be broadly disseminated starting with a press release and through presentations.

**REFERENCES:**