**PROJECT TITLE: Time-integrated sampling of chemical contaminants in Minnesota’s streams**

**PROJECT STATEMENT**

The occurrence of synthetic chemical contaminants will be assessed in streams throughout the State using time-integrated samplers to provide a better understanding of the degree of contamination of Minnesota waters. Efforts to improve stream water quality are partially dependent on understanding the timing and mixtures of the chemicals present in the water. Chemical contaminants frequently occur in pulses and mixtures as water flows downstream, which can be difficult to detect using traditional sampling methods. In this study, time-integrated sampling, through the use of passive samplers, will be performed. These samplers, which accumulate chemicals over periods of days to months, complement the traditional point-in-time stream sampling used in monitoring studies, which only capture a snapshot in time. They also allow for sampling of larger volumes of water, which permits the analysis of chemicals present at low concentrations in the stream. These lower concentration limits create the ability to search for previous unknown chemicals that are contaminating the stream, which may be present at extremely low, but environmentally and toxicology significant concentrations. This project will develop a time-integrated field sampling method and write standard operating procedures. The project will deploy these methods in streams across Minnesota in cooperation with the state agencies, to provide a comparison to the traditional sampling strategy. This will result in a better understanding of the mixture of organic chemical contaminants that occur in Minnesota streams, as well as a new tool for State and local monitoring programs.

Knowledge of the full extent of chemical contamination in Minnesota waters is vital to both maintaining and protecting our waters for future use, as well as the health and safety of the people and ecosystems which interact with these waters. A time-integrated sampling method has not yet been incorporated in Minnesota monitoring programs. This method will provide information on specified (targeted) organic chemicals, plus the identification of chemicals that are present, but not routinely screened for (unspecified chemicals) in current monitoring program. The time-integrated samplers are an established family of technologies that have been used in streams, lakes, sediments, and other environments. The samplers, deployed for weeks at a time, passively collects and concentrates the chemicals within the sampler from the stream water. Different materials within the samplers attract and capture different types of synthetic chemicals to provide a broad perspective on their occurrence in the stream. Time-integrating sampling could be a lower cost alternative sampling technique, due to the need for less frequent travel compared to traditional samples.

The goals of this study are to investigate Minnesota streams for specific and unspecified synthetic chemical contaminants in streams transported through surface runoff and groundwater using passive sampling techniques, as well as to develop a standard time-integrated sampling method. The insights and standard operating procedures for passive samplers developed in this study could supplement and expand the outcomes of the existing stream monitoring programs conducted by State agencies.

**II. PROJECT ACTIVITIES AND OUTCOMES**

**ENRTF BUDGET:**

**$116,000**

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| **Activity 1:** Development of procedures for the deployment and analysis of time-integrating  samplers for selected pesticides, pharmaceuticals, and unspecified chemical contaminants  **Description:** Two commercially-available, time-integrating sampling devices will be employed in this study; one that efficiently collects chemicals with low water solubilities (SPMD) and one that efficiently collects chemicals with high water solubilities (POCIS). A broad range of organic chemicals will be targeted, using the compounds specified in the Minnesota Department of Agriculture (155 pesticide and pesticide transformation products) and the Minnesota Pollution Control Agency’s (146 pharmaceuticals and personal care products (PPCPs)) surface water monitoring programs. In addition, the extracts of the passive samplers will be analyzed for other un-specified organic chemicals that may be present in streams at detectable levels. An initial deployment of the passive samplers will occur in the late summer and fall of 2020 to provide validation of field deployment and collection procedures, extraction method of the chemicals in the laboratory from the samplers, and provide initial samples for the analysis of specified and non-specified organic chemicals. | |  |
| **Outcome** | **Completion Date** |
| *1. Development of sampler extraction and analytical methods for specific organic chemicals* | *04/01/21* |
| *2. Initial deployment of samplers to be used for field and laboratory method validation and early field testing* | *04/01/21* |
| *3. Identification of non-specific organic chemicals found in samples* | *03/01/23* |

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| **Activity 2:** Investigations of organic chemical contaminants in selected urban and  agricultural streams using passive samplers  **Description:** The time-integrated samplers will be deployed during the spring/summer seasons and winter seasons for two years. The spring/summer growing season will be during active pesticide use and stream flow frequently dominated by runoff. These data will provide an understanding of the chemicals transported through surface runoff (over the landscape). In the winter season, groundwater dominates many streams. Data from this time will provide an understanding of the chemicals transported through the subsurface. Two strategies will be used for deployment, aimed at understanding the information gained from passive sampling across time (time series sampling of the same stream) and space (multiple stream sampling). Samples will be collected from small streams, one in a predominately urban watershed and one in a predominately agricultural watershed, at two-week intervals throughout the year. These will serve as the time-series investigation samples. Samples will also be collected from 20 different streams in different hydrologic and land use settings during the warm weather growing season and during the winter. These will serve as the spatial investigation samples. The location and timing of these samples will be coordinated with the State’s surface water monitoring activities, so that the results of the passive samplers can be directly compared to the agencies’ discrete samples. | |
| **Outcome** | **Completion Date** |
| *1. Spatial investigations using passive samplers in selected streams draining predominately agricultural and/or urban watersheds during the growing season* | *11/01/22* |
| *2. Spatial investigations using passive samplers in selected streams draining predominately agricultural and/or urban watersheds during the winter season under base flow conditions* | *3/01/23* |
| *3. Time-series deployment of passive samplers in selected streams throughout a year* | *3/01/23* |

**ENRTF BUDGET:**

**$175,000**

**ENRTF BUDGET:**

**$58,383**

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| Activity 3: Transfer of passive sampling techniques to Minnesota stream monitoring  programs  Description: The understanding developed in this study on the deployment and use of time-  integrated samplers for organic chemicals will be shared with State and local agencies. A standard sampler configuration and its standard operating procedure (SOP) will be developed and made available, as will protocols for sampling streams in the warm growing season during a range of streamflows and during the winter, with base flow conditions. The use of these samplers will complement the traditional point-in-time stream sampling used in monitoring studies by identifying the mixtures of chemicals moving through the stream in short pulses that are not captured by traditional sampling methods. | |  |
| **Outcomes** | **Completion Date** |
| *1. Development of field and laboratory standard operating protocols for the samplers* | *6/01/23* |

**III. PROJECT PARTNERS AND COLLABORATORS:**

**A. Partners receiving ENRTF funding**

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| **Name** | **Title** | **Affiliation** | **Role** |
| Meghan O’Connor | Post-Doctoral Researcher | University of Minnesota | Post-Doctoral Researcher |

**IV. LONG-TERM IMPLEMENTATION AND FUNDING:**

This study will provide a better understanding of the contamination of Minnesota’s streams by specified organic chemicals, as well as potentially find other contaminants not currently specified by the current State monitoring programs. This project will also create a standard sampling procedure that could be integrated by State and local agencies into their existing monitoring program. All results of this work will be shared through open access articles, and will be shared with state agencies and the public.

**V. TIME LINE REQUIREMENTS:** The project will be completed in a three year period. The sampler development, adaption of analytical methods, deployment of the samplers over multiple seasons, and development of a standard operating procedure are sequential activities that will require multiple years.