

Time-integrated Sensing to Study Extreme Weather Events in Pulsed Pesticide Contamination

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Summary:

This study highlights the impact of hydrometeorological extreme events on pesticide contamination in surface and groundwater resources in Ireland and Denmark. Using passive and grab sampling, the study compares pesticide levels before, during, and after such events. Solid-phase extraction (SPE) followed by LC-MS quantification will be used to analyze target pesticides. Passive sampling, a cost-effective and time-integrated technique, allows for better detection of episodic contamination events. The findings aim to improve understanding of how climate change-driven weather extremes influence pesticide loads in the water bodies. This research could enhance monitoring strategies for water quality management in the face of climate change.

Keywords: Climate Change, Pesticides, Passive Sampling, Liquid Chromatography-Mass-Spectrometry, Water Quality Assessment

Background, Motivation an Objective

Climate Change is acting as a driving force in the fundamental transformation of the hydrological systems across the globe, resulting in the exacerbation of water scarcity issue, degradation of water quality and causing an amplification in flood risks. The hydrological cycle greatly depends upon the fluctuations in the climatic variables especially Temperature and Precipitation [1]. Torrential rainstorms and floods tend to increase the mobility of suspended solids, metallic substances, nutrients, plastics and agricultural pollutants into the water bodies resulting in severe contamination of the drinking water reservoirs [4]. The sudden surge in the levels of current and emerging contaminants in the water bodies has caused significant damage to the ecosystem health and sustainability [5].

Passive sampling is an emerging technique for the preconcentration of pesticides from aquatic environments, achieved by deploying a sorbent-based device in situ for extended periods, typically ranging from 4 to 6 weeks. Despite its proven efficacy, the application of passive sampling for the screening and detection of priority pesticides in natural surface waters and groundwater remains relatively limited in the scientific literature. This method functions as a cost-effective, time-integrated sensor, capable of providing time-weighted average (TWA) concentrations of target analytes. Such an approach is particularly advantageous for capturing episodic contamination events and mitigating the limitations associated with conventional spot sampling, which often fails to detect transient pollutant occurrences.

The present study aims to investigate the intensification of pesticide contamination in surface and groundwater systems associated with the occurrence of hydrometeorological extreme events. This will be achieved through a comparative assessment of pesticide levels before, during, and after such events at selected sites in Ireland and Denmark, employing both passive sampling and grab sampling approaches. To isolate target analytes, water samples will undergo solid-phase extraction (SPE), followed by quantitative analysis using Liquid Chromatography coupled with Mass Spectrometry (LC-MS). This analytical workflow is designed to determine the concentrations of selected pesticides and assess temporal variations in contaminant loads in response to extreme weather conditions.

Description of the New Method or System

Passive Sampling is a cost-effective, time-saving, power-free and highly reliable method to accurately detect the pollution levels by determining the time weighted average (TWA) concentrations in an aquatic environment. Polar organic chemical integrative sampler (POCIS) and DGT passive samplers are highly robust and reliable passive samplers used for determining the levels of pesticides and pharmaceuticals in natural waters [2]. In the recent studies, use of Chemcatcher and LC/MS targeted analysis has been very helpful in quantifying 121 polar organic compounds in two sensitive rivers in UK, ranging in concentration $< \text{ng L}^{-1}$ to $> 500 \text{ ng L}^{-1}$ over a 12 month deployment period [3]. In the past, a wide range of passive samplers have been developed by using various sorbents and barriers in order to regularize the uptake rate. A recent study that compared three co-deployed passive samplers

(Speedisk, Hydrogel based passive sampler and POCIS) suggested that all samplers showed high accumulation of compounds with a consistent surface-specific uptake with a significant co-relation ($r \geq 0.76$) among all [6]. In the present study, different types of passive samplers shall be deployed at three locations in river Tolka (Ireland) and a water treatment plant in Denmark for the detection of contamination level of hazardous pesticides such as Clotrimazole, Thiamethoxam, Cypermethrin, Permethrin, Bifenthrin, Thiabendazole, Tebuconazole, Tetraconazole etc. in these drinking water resources. Moreover, the results obtained from passive sampling shall be compared with grab sampling in order to get a better image of the contamination levels of these substances. Furthermore, this shall be followed by the use of solid phase extraction and Liquid Chromatography Mass Spectrometry for identification and quantification of the targeted analytes. Moreover, these substances shall be regularly monitored for identifying the direct impact of torrential rains, flood and drought on their occurrence and prevalence.

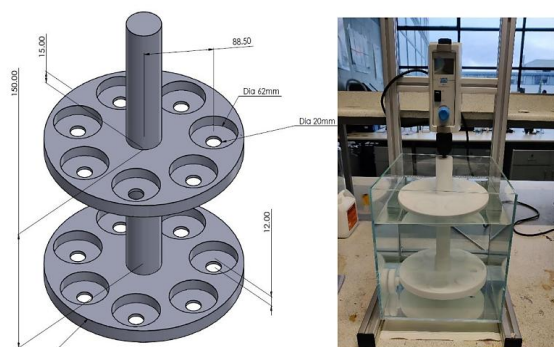


Fig. 2. PTFE Passive sampling carousel and dimensions

Results

A recent study at DCU was conducted on eleven selected pharmaceuticals highlighted that passive sampling showed higher number and concentration of these substances than grab sampling. This was due to the higher volumes of water gathered by passive samplers that would otherwise be overlooked by grab sampling. The presence of pharmaceuticals trimethoprim, diclofenac, clarithromycin, azithromycin, carbamazepine, venlafaxine, etc. were detected in river Liffey by passive sampling. The Chemcatcher device can measure the micropollutants in their freely dissolved concentration in the surface water bodies. Hence, the detection of pesticides by Passive Samplers is highly essential to reflect the bioavailability of these contaminants as well as their immediate impact on aquatic life. Current study shall focus on similar methodology to determine the pesticide contamination in selected sites by drawing a comparison between various passive samplers deployed in selected sites over a certain period.

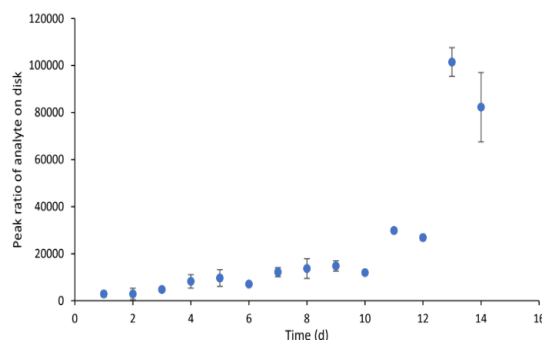


Fig. 2. Graph of Uptake of Trimethoprim in Chemcatcher HLB-L passive sampling disks during a 14-day exposure study at 1000 ng/L.

References

- [1] S. Wang, L. Zhang, G. Wang, D. She, Q. Zhang, J. Xia, Y. Zhang, More intense and longer torrential rain and flood events during the recent past decade in Eurasia, *Water Resources Research* 59(8), e2022WR033314 (2023); doi: 10.1029/2022WR033314
- [2] Y. Li, Z. Wang, X. Zhang, Z. Chen, Z. Zhao, X. Li, L. Wang, Application of passive sampling device for exploring the occurrence, distribution, and risk of pharmaceuticals and pesticides in surface water, *Science of the Total Environment* 901, 168393 (2023); doi: 10.1016/j.scitotenv.2023.168393
- [3] R. F. Robinson, G. A. Mills, R. Grabic, A. Bořík, G. R. Fones, Quantification and risk assessment of polar organic contaminants in two chalk streams in Hampshire, UK using the Chemcatcher passive sampler, *Science of the Total Environment* 939, 173316 (2024); doi: 10.1016/j.scitotenv.2023.173316
- [4] M. T. Van Vliet, J. Thorslund, M. Stokal, N. Hofstra, M. Flörke, H. Ehalt Macedo, ... & L. M. Mosley, Global river water quality under climate change and hydroclimatic extremes, *Nature Reviews Earth & Environment* 4(10), 687-702 (2023); doi: 10.1038/s41586-023-00669-6
- [5] N. Ntsasa, A. Mkhohlakali, T. Mogashane, J. Tshilongo, M. R. Letsoalo, Trends in Systematic Techniques for Pollutants Monitoring in the Environmental Water Systems (2024); doi: 10.5772/intechopen.1007099
- [6] P. Fialová, K. Šverclová, K. Grabicová, R. Grabic, H. Švecová, P. Nováková, B. Vrana, Performance comparison of three passive samplers for monitoring of polar organic contaminants in treated municipal wastewater, *Science of the Total Environment* 908, 168153 (2024); doi: 10.1016/j.scitotenv.2023.168153

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