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Low-Cost 3D-Printed Passive Samplers for Emerging Contaminant Monitoring in River Waters

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1. Context of Work

The project seeks funds to monitor emerging contaminants in surface water using a low-cost 3D-printed passive sampler with an integrated porous membrane. Emerging contaminants such as pharmaceuticals, pesticides, and industrial chemicals pose significant human and ecological health risks due to their potential toxicity, extensive use, and ubiquity in surface water. Yet, they are not regulated or routinely monitored, although some are candidates for regulation.

1.1 Emerging contaminants in surface water

In 2018, carbamazepine, metazachlor, and bisphenol A were found to be the most frequently and abundantly detected emerging contaminants in surface water in England.[1] Carbamazepine is an anti-epileptic and psychiatric drug with an estimated annual consumption of around 1000 tons globally. It can bioaccumulate in aquatic species and cause reproductive impairment at concentrations as low as 0.01 μg L^{-1}.[2] Metazachlor is carcinogenic, endocrine disrupting, and plankton growth inhibiting chloroacetamide herbicide that mainly enters surface water *via* agricultural runoff. It is stable in surface water and has been detected at concentrations of up to 100 μg L^{-1} in surface water. Bisphenol A is a highly persistent, toxic, and bioaccumulative compound used in manufacturing plastics, and it has been detected in surface water at concentrations of up to 2,720 μg L^{-1}.[3] <u>Hence, there is a need for long-term monitoring of carbamazepine, metazachlor, and bisphenol A in surface water</u>.

1.2 Passive sampling of emerging contaminants

Passive sampling offers a cost-effective and highly sensitive approach for monitoring bioavailable contaminants over extended periods. Commercial passive samplers often come in limited sizes and configurations, making it difficult to deploy them for monitoring diverse contaminants with varying concentrations and physicochemical properties simultaneously.

Recently, a 3D-printed passive sampler holding six miniaturized membranes was used to monitor 193 emerging contaminants in surface water.[4] This study demonstrated that 3D printing has the potential for developing passive samplers for monitoring multiple classes of emerging contaminants.

2. Hypotheses and objectives

Black polylactic acid and Poro-Lay Lay-Felt filament were previously used to 3D print a passive sampler housing and integrated porous membrane for monitoring atrazine in aquatic environments.[5] The membrane was loaded with a hyper-crosslinked polystyrene sorbent (HCPS), MN150 to improve performance. However, the performance of 3D-printed integrated porous membranes in monitoring <u>diverse</u> emerging contaminants in <u>actual</u> surface water remains unknown.

<u>I hypothesize that since HCPS has multiple functional groups, a 3D printed passive sampler with an integrated porous membrane with HCPS sorbent is effective in sampling carbamazepine, metazachlor, and bisphenol A in river water.</u>

To build on previous work, the proposed study will: (i) compare the sampling rates of different sorbents (MN100, MN150, and MN200); (ii) assess the performance of the membrane in extracting different emerging contaminants (carbamazepine, metazachlor, and bisphenol A) in water samples; and (iii) evaluate the performance of the 3D printed passive sampler in monitoring contaminants in rivers.

3. Methodology

Using the method developed by Kalsoom et al.,[5] the proposed study will involve, chronologically: designing and fabricating the 3D printed passive sampler and integrated porous membrane (4 months); assessing the characteristics of the 3D printed devices (1 month); calibrating the extraction procedures in the laboratory (4 months); deploying the 3D printed passive sampler in the field in River Tyne, UK (1 month); and extracting and analyzing the samples using HPLC (2 months).

<u>3D printing</u>: the housing and membrane will be fabricated using black polylactic acid and Poro-Lay Lay-Felt filament on a 3D printer with extrusion temperatures set at 200 °C and 230 °C, respectively (Fig. 1). A membrane thickness of 0.5 mm will be used, and an HCPS (MN100, MN150, and MN200) will be added.

<u>Membrane characteristics</u>: The 3D printed membrane samples will be dried under nitrogen overnight first, after which their surface properties and porosity will be measured using scanning electron microscopy and Brunauer–Emmett–Teller method, respectively.

<u>Calibration</u>: UV/vis absorbance spectroscopy will be used to assess the adsorption of test probes such as copper sulphate and potassium permanganate on the membrane in distilled water. Imidacloprid and diclofenac will be spiked to distilled water, and the adsorption rate on the membrane will be determined using a static renewal approach, whereby distilled water is replaced every 24 hrs and re-spiked.

<u>Field deployment</u>: the 3D printed passive sampler will be placed in a mesh bag with weights, deployed in River Tyne, UK, and secured on the banks. The passive samplers will be deployed for a period ranging from 1 to 6 weeks, depending on the equilibrium rates obtained in the previous step.

<u>Extraction and Analysis</u>: carbamazepine, metazachlor, and bisphenol A were washed off the membranes using methanol under gravity. The extractants were then analyzed using HPLC with a multiwavelength detector and a C18 column to determine the time-weighted concentration.

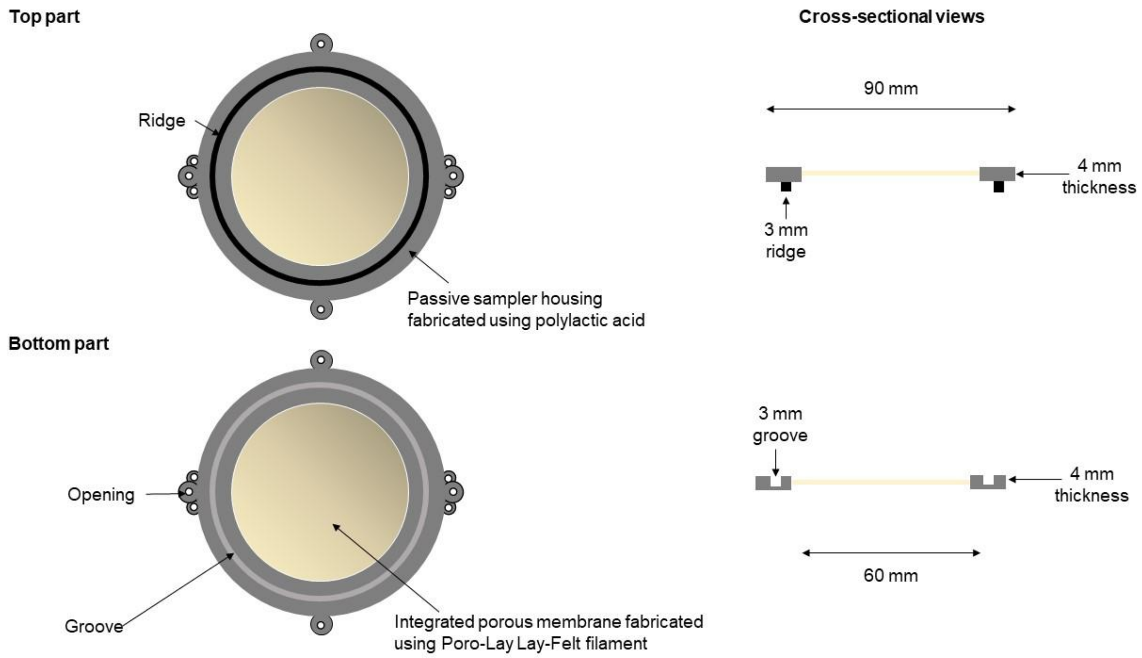

Fig. 1 Schematic of the proposed 3D printed passive sampler with an integrated porous membrane.

4. Outcomes

<u>The proposed 3D-printed passive sampler with an integrated porous membrane will provide a cost-effective approach for long-term monitoring of emerging contaminants to support environmental regulations and mitigation efforts</u>.

Results of this work will be published in a reputable international journal and the data thereof will be used to apply for a NERC Pushing the frontiers of environmental science research. My future work will focus on increasing the sampling rates while broadening the spectrum of emerging contaminants that could be sampled by the same sorbent.

5. References

1. Lapworth, D. *et al. British Geological Survey Open Report* vol. OR/18/052 https://nora.nerc.ac.uk/id/eprint/524322/1/OR18052.pdf (2018).

2. Srain, H. S., Beazley, K. F. & Walker, T. R. *Environmental Reviews* **29**, 142–181 (2021).

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