A novel dynamic passive sampling approach for marine monitoring of emerging contaminants

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Introduction

Anthropogenic contaminants enter the marine environment directly from land-based sources, however they can also be emitted or re-mobilised in the marine environment.
The EU Marine Strategy Framework Directive (MSFD) is responsible for providing provisions against the pollution of marine waters by chemical substances. These contaminants are of great concern due to their known toxicological effects (i.e., endocrine disruption, immunotoxicity), with some known to accumulative in organisms and food webs. However, it is impossible to capture all contaminants that may be present in this dynamic marine environment.

As a result, many of these chemicals and chemical mixtures have been characterised as '***contaminants of emerging concern' (CECs***). Passive samplers can accumulate pollutants and concentrate sufficient amounts of pollutants from water for chemical analysis where spot sampling methods often fail. This study evaluates the use of a novel dynamic passive sampling approach for the determination of CECs in seawater.

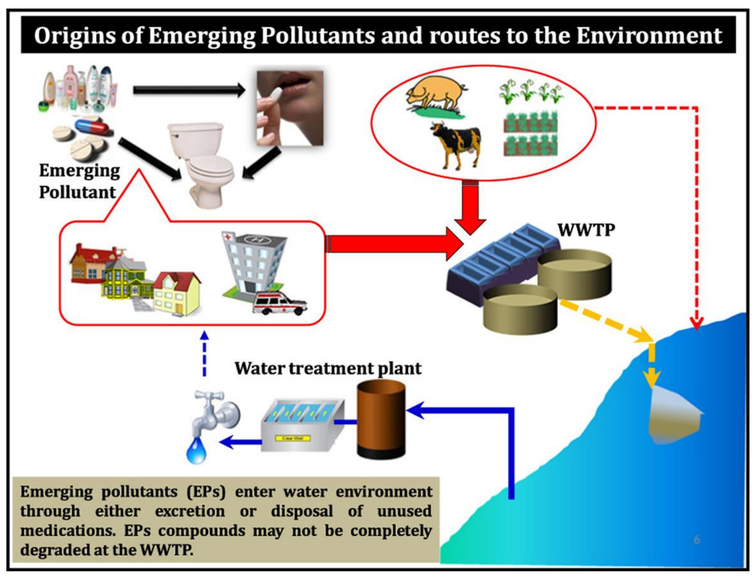

Fig 1. Origins of emerging pollutants and routes to the aquatic environment (Groundwater for Sustainable Development 6 (2018), 169 – 180).

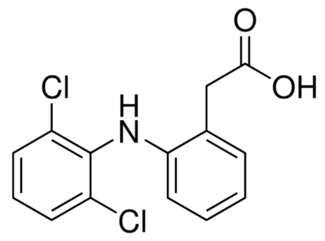

Fig 2. Structure of Diclofenac

The aim of this work is the develop a robust, sensitive and reliable method for the preconcentration of CECs in seawater using a novel dynamic passive sampling process.

Methods

1) Test tank set-up
The tank (46 x 30 x 30 cm) was cleaned with Decon 90 solution and MeOH. The tanks were filled with 30 L of deionized water, followed by spiking with a 1 ppm standard solution of diclofenac. The tank was in a continuous flow mode using two Jier submersible pumps (Amazon, UK).

2) Passive sampling material
C18 receiving phase (T.E. Laboratories, Co. Carlow, Ireland) sorbents were placed in the tank via a PMMA holder and suspended from a retort stand (Fig 3).

3) Extraction
3 mm sections of the C18 receiving phase membranes (n = 3) were collected from the tank via a sterilized hole puncher on days 0, 3, 6 and 9. These sections were placed in 2 mL Eppendorf tubes, and 1 mL of ACN was added to each to extract the diclofenac present on the C18 sorbent into solution.

4) Measurement of CECs in passive sampler
The extract was measured using LC-UV fitted with a C18 column (4.6 x 100 mm, 3.5 µm) was used to determine the uptake of the target analyte, diclofenac. The mobile phases of 10 mM ammonium Acetate in water (A) and acetonitrile (B) was used with a flow rate of 1 mL/min in a gradient separation. At starting conditions, B was set at 10%; 0-6 min: B increased to 50%; 6-8 min: another linear ramp of B increased to 90%; 8-10 min: B further increased to 100%; 10-13 min: B stayed at 100%; from 13-18 min: linear ramp decrease to 10% of B.

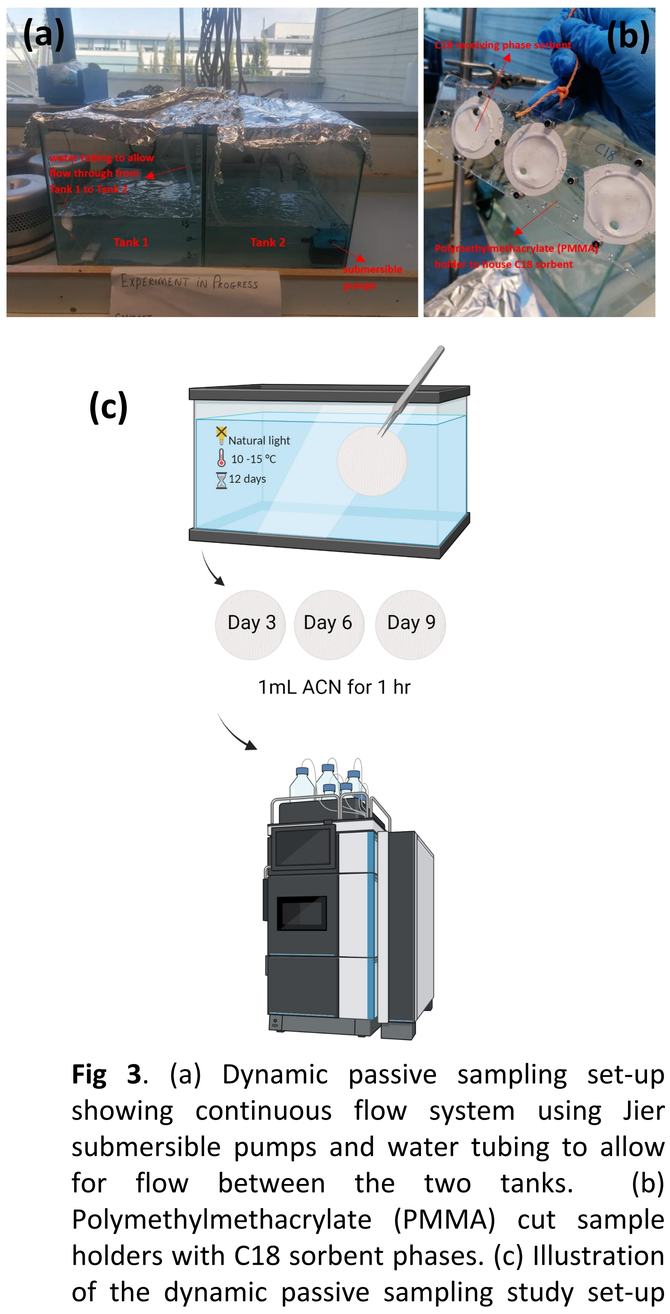

Fig 3. (a) Dynamic passive sampling set-up showing continuous flow system using Jier submersible pumps and water tubing to allow for flow between the two tanks. (b) Polymethylmethacrylate (PMMA) cut sample holders with C18 sorbent phases. (c) Illustration of the dynamic passive sampling study set-up and conditions.

Results and Discussion

Figure 4 illustrates the chromatographic peak for diclofenac following extraction from the C18 sorbent after a period of days under the dynamic passive sampling study.

The concentration of diclofenac present in C18 receiving phase sorbents was found to increase throughout the course of the uptake study (Day 3 to Day 9), illustrating it's effectiveness as a preconcentration method for the extraction of diclofenac in seawater samples. The flow rate of the water can be controlled to optimise the uptake of target analytes into the sorbent and maximise the concentration factor.

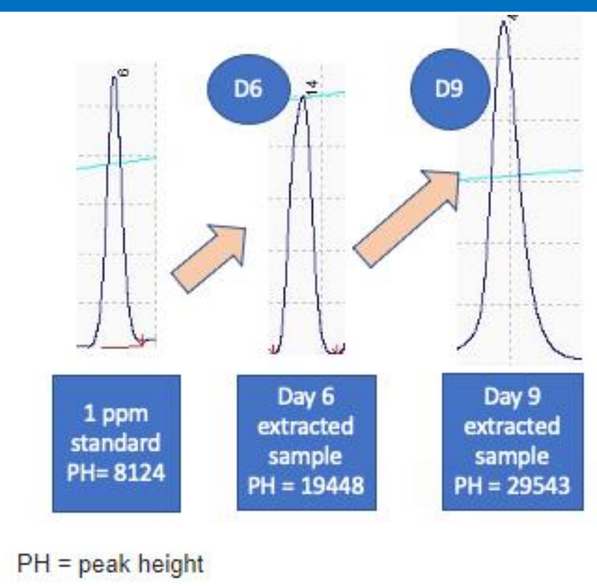

Fig 4. Chromatograms showing the uptake of diclofenac by peak height on Day 6 and Day 9 in comparison to a 1 ppm standard of this compound.

Conclusions

There is a need to be able to sample large volumes of seawater (>100 L) to enable detection of CECs in the marine environment. This study demonstrates the development of a ***proof of concept dynamic passive sampling method*** for the determination of CECs in seawater where concentrations are in the ngL^{-1} range. Diclofenac is used as an example of a frequently measured CEC to demonstrate the potential of the method. Water volumes in the region of 100s of litres can be sampled in order to reach the concentrations in the environment.

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