

Passive sampling for tyre chemical measurement in water

Sam Walker, School of Pharmacy, Applied Sciences and Public Health, Robert Gordon University, Aberdeen

Introduction

Tyre wear is a major source of microplastics to the aquatic environment. There are now concerns that additive chemicals which leach from tyres into water pose a significant risk to aquatic organisms. A recent study in China found 11 of 23 additive chemicals displayed mid to high ecological risks in surface water [1]. The vulcanization agent 1,3-diphenylguanidine was found at a maximum concentration of $59 \mu\text{g L}^{-1}$. Stormwater from newly constructed roads in the UK is treated by sustainable urban drainage systems (SuDS) such as retention ponds. These enable the settling of particulate matter before water is discharged to a nearby water course. However, there is a lack of information on the fate of additive chemicals in SuDS due to the lack of appropriate sampling methods for their monitoring. Only limited information can be obtained by grab or spot sampling which provides a 'snapshot' of pollutant concentration. Therefore, sampling methods need developed that can obtain average additive chemical concentrations for longer time periods (e.g. several days to weeks). Passive sampling, which relies on the diffusion of chemicals from the water phase onto an adsorbent material [2], is a suitable method for this purpose but needs optimised for tyre additive chemicals. Therefore, the aim of this ChromSoc summer studentship was to develop a passive sampling method for monitoring tyre additive chemicals in environmental waters.

Materials and methods

A key requirement for using passive samplers to quantify tyre chemicals in the environment is to calibrate the uptake of the chemicals from water into adsorbent disks. Ex-situ uptake studies were undertaken under controlled laboratory conditions (Figure 1). These studies were undertaken at a constant water velocity of 0.6 m/s at temperatures of 15°C and 5°C to replicate summer and winter temperatures, respectively. These were conducted in a glass tank containing 15 L of road runoff spiked with tyre chemicals at $1 \mu\text{g/L}$ (1,3-diphenylguanidine and hexamethoxymethylmelamine – HMMM). An overhead stirrer was used to control the flow velocity. Uptake to passive samplers was assessed over 14 days. The passive samplers consisted of a PTFE body containing a 47 mm hydrophilic-lipophilic balance disk. Following exposure, the disks were extracted in methanol and analysed by ultra-high performance liquid chromatography-triple quadrupole mass spectrometry (UHPLC-MS/MS). The UHPLC-MS/MS methodology has been previously validated (see [3]). Details on the MS/MS parameters and the chromatograms are shown (Table 1, Figure 2).

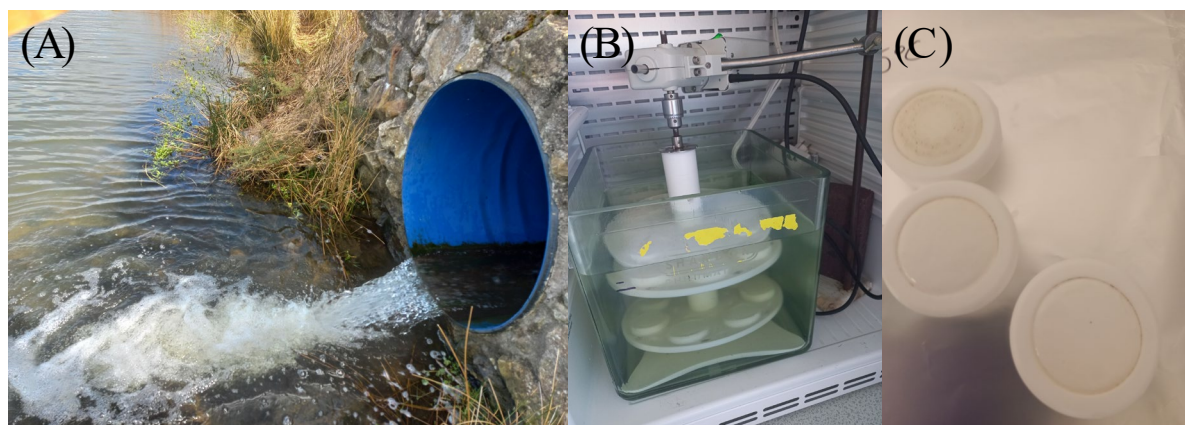


Figure 1. Retention pond showing road runoff entering the ponds that were used in laboratory calibration studies (A), 15 L calibration tank with overhead stirrer to control water velocity over

the passive samplers (B) and passive samplers following exposure in calibration tanks and ready for extraction (C).

Table 1. Mass spectrometry information used for the analysis of DPG and HMMM

Additive	Retention time \ min	ESI	Precursor ion \ m/z	Product ion \ m/z	Cone voltage \ V	Collision energy \ eV	Deuterated surrogate
DPG	4.1	+	212.3	119.1 94.1	20	25 26	5-MBTR-d ₆
HMMM	7.0	+	391.3	359.3 177.2	20	7 22	5-MBTR-d ₆

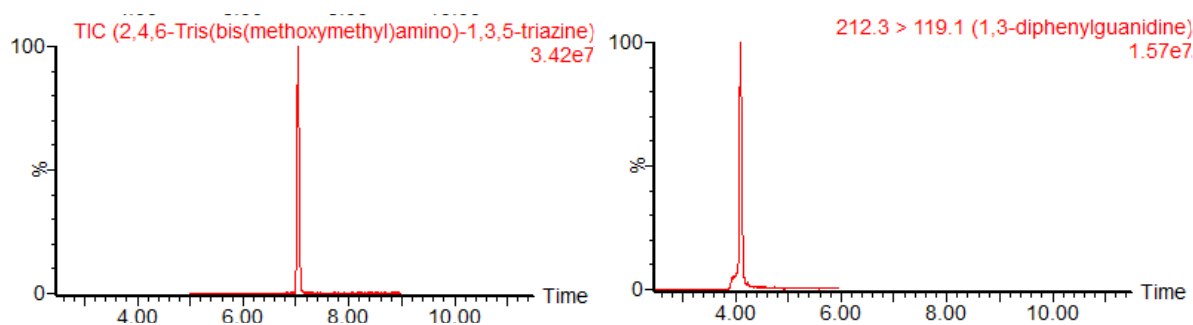


Figure 2. Representative chromatograms of HMMM(left) and 1,3-diphenylguanidine (right).

Results and discussion

Linear uptake of tyre chemicals to passive samplers was established over 14 days at both 15 °C and 5 °C (Figure 3). The sampling rates were in the range of 0.0253 to 0.0448 L/d and r^2 values were in the range 0.9628 to 0.9744 for both HMMM and 1,3-diphenylguanidine. The determined sampling rates were similar to those previously found for other polar organic pollutants (e.g., pharmaceuticals, personal care products and pesticides) using the same passive sampling configuration [2,4]. The sampling rates of HMMM were higher at 15 °C (0.0448 L/d) compared to 5 °C (0.0287 L/d). Previous research of other polar organic pollutants found that sampling rates increased with water temperature, up to twofold where temperature increased from 5 °C to 25 °C [5]. This is attributed to the increase mobility of pollutants and accelerated mass transfer from water to the receiving phase of the passive sampler. Interestingly, 1,3-diphenylguanidine showed similar sampling rates of 0.0253 L/d and 0.0281 L/d at 5 °C and 15 °C, respectively (Figure 3). This tyre chemical has lower stability in the environment, and it is postulated to be less stable in the passive sampler disks at 15 °C. Therefore, any increased uptake at 15 °C is reduced by the poorer stability on the extraction disk. However, further work is needed to confirm this.

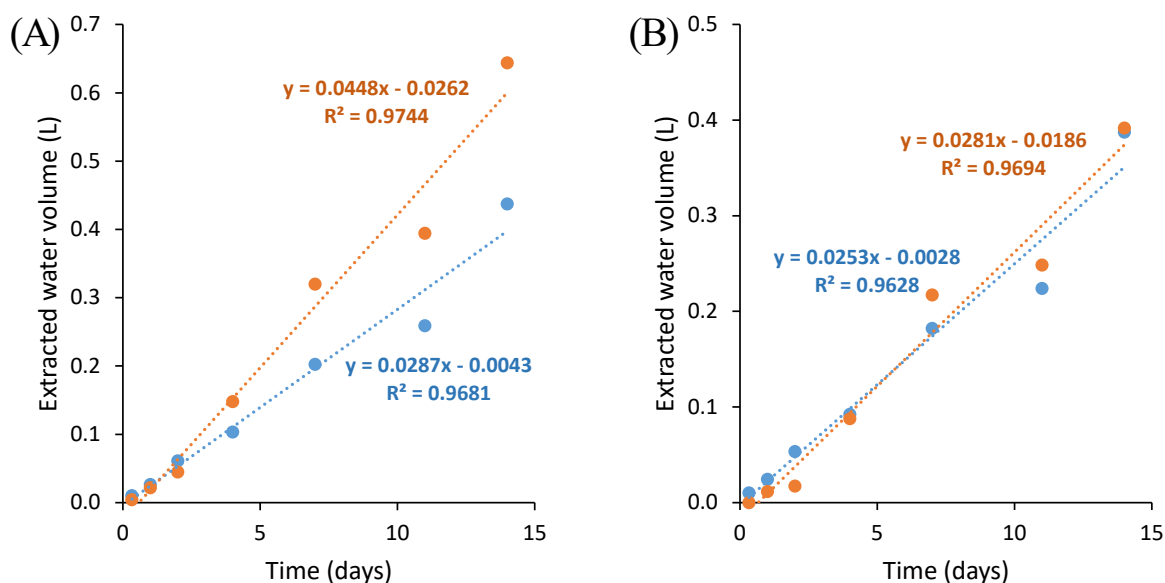


Figure 3. Equivalent extracted water volumes of HMMM(A) and 1,3-diphenylguanidine (B) for passive samplers over 14 days exposure at 15 °C (orange data points) and 5 °C (blue data points) at 60 m/s.

Conclusions

This study is the first to determine the uptake rates of tyre chemicals to passive samplers. Uptake was considered linear up to 14 days. These uptake rates will be used in future field studies to quantify tyre chemicals in road runoff and retention ponds. The mass of tyre chemicals accumulated on passive samplers, their deployment time and predetermined uptake rate from this study can be used to determine the average concentration of tyre chemicals in water. This will provide more representative data on tyre chemicals entering retention ponds and their removal during transport through the ponds themselves.

References

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