PERMOTOX: Detection of PMT Chemicals in Environmental Samples via SPE and HPLC Analysis

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Background: Persistent Mobile and Toxic (PMT) chemicals are described by their resistance to degradation, mobility in water and soil and toxicity to humans and the environment particularly posing a hazard to water. These chemicals mainly come from the agricultural and pharmaceutical industries, and many can pass through wastewater treatment plants unimpeded. These chemicals pose a danger as once they are released into the environment their persistence may allow them to start to accumulate over time. The mobility of PMT chemicals which make them pervasive in water ways make them difficult to remove during waste-water treatment, and to analyse in water samples. As such many PMT chemicals are in an "analytical and monitoring gap" whereby they are not able to be analysed in laboratories due limitations in available analysis equipment. Table 1 shows chemicals chosen for study from the UBA list of priority class A chemicals, those produced in the EU >10 tons per annum and with varying Koc values. Caffeine, a commonly found anthropogenic marker in municipal wastewater and surface waters, can serve as an analogue to pharmaceutical chemicals due to its structure and mobility.

Table 1: List of PMT chemicals chosen for study along with Mobility value Koc. *Dow instead of Koc[1]

Compound name	CAS No #	Log Koc
Climbazole	38083-17-9	3.8
Diphenylamine	122-39-4	3.4
Oxybenzone	131-57-7	3.2
Ametryn	0834-12-8	2.1
Sulisobenzone	4065-45-6	2
Dapsone	80-08-0	1.8
Cyanuric acid	108-80-5	1.7
Benzotriazole	95-14-7	1.5
Melamine	108-78-1	1.1
Losartan	114798-26-4	1*
Caffeine	58-08-2	-0.6
Salbutamol	18559-94-9	-0.9
Amoxicillin	26787-78-0	-3.6*
Methenamine	100-97-0	-6.6*

Objectives of PERMOTOX

1. Develop suitable analytical methods for determination of PMT chemicals
2. Assess the presence and quantify PMT chemicals in Irish waters.
3. Undertake an emissions review of PMT chemicals with details on industries and sectors that use or produce these chemicals.
4. Provide recommendations to inform monitoring programmes to identify chemicals of interest, as well as areas of concern where monitoring efforts might need to be concentrated.

Technical work packages

PERMOTOX has a number of technical WPs that will be followed.

WP 2 Scoping for potential pathways of PMT/vPvM chemicals;

WP 3 Develop analytical methods;

WP 4 Assess the presence of PMT/vPvM chemicals in water in Ireland;

WP 5 Innovative monitoring approaches using citizen science and surrogate monitoring;

WP 6 An emissions review of PMT/vPvM chemicals relating to emission sectors.

Methods: Water samples are prepared for analysis by using solid phase extraction (SPE). A polymeric "HLB" SPE cartridge was used to preconcentrate and isolate the target analytes. The samples where spiked with theobromine as an internal standard and then measured using High Performance Liquid Chromatography (HPLC) in 40:60 Methanol: water mobile phase. Detection was by UV at 272 nm. Each sample was measured in triplicate. A caffeine calibration curve (Figure 1) was created to quantify the caffeine found in surface water samples. Theobromine (Theo) and caffeine (Caff) elute at 3.2 min and 4.1 min respectively (Figure 2).

Results: The concentration of caffeine was measured in surface water samples (Figure 3) using the method described. Concentration of caffeine was measured in several samples ranging from 1.6 – 63.7 ppb. The concentration of each sample and the relative standard deviation (RSD) is shown in Table 2.

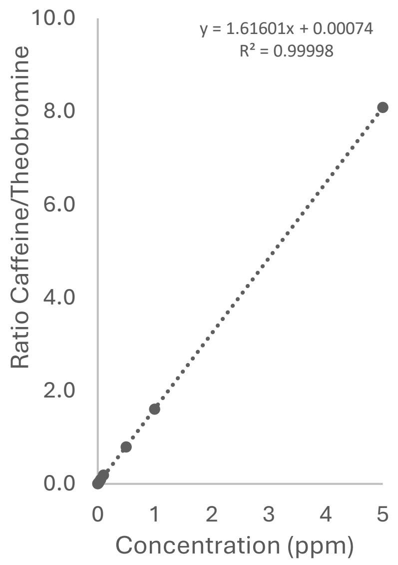

Figure 1: Caffeine Calibration curve
LOD = 0.1 ppb and LOQ = 0.5 ppb (n=3)

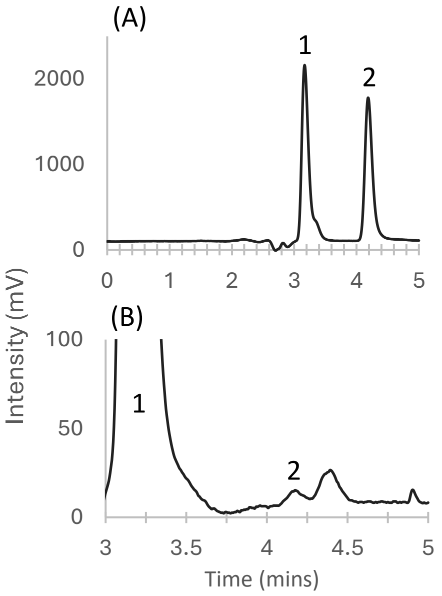

Figure 2: (A) Theo 0.5 ppm, Caff 0.5 ppm; (B) Theo 0.5 ppm, Caff 0.001 ppm, Peak ID = 1 Theo and 2 Caff.

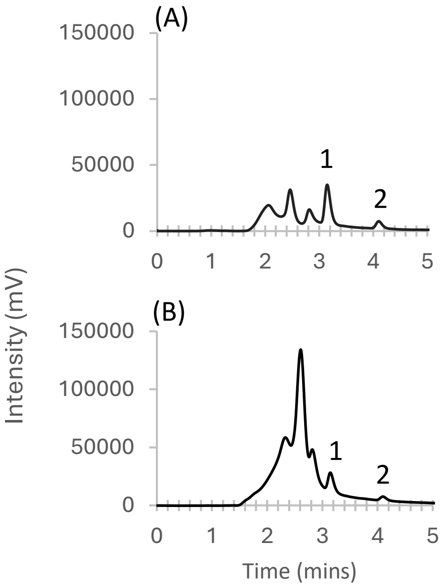

Figure 4: Sample analysis
(A) = sample 5, (B) = Sample 4

Table 2: Summary of surface water monitoring for caffeine as an indicator of anthropogenic inputs.

Sample number	Sample name	Caffeine Conc (µg L^{-1})	%RSD (n=3)
1	Lough Derg	1.6	5.7
2	Urban Effluent 1	2.6	10.6
3	Rural site 1	4.3	4.8
4	R. Liffey (Kildare)	38.7	0.3
5	R. Liffey	63.7	0.3
6	R. Nore	<LOQ	N/A
7	R. Dungloe	<LOQ	N/A
8	Final Effluent 1	<LOQ	N/A
9	R. Suir 1	<LOQ	N/A
10	R. Suir 2	<LOQ	N/A
11	Urban effluent 2	<LOQ	N/A

Conclusions: The results indicate that caffeine occurs in many surface waters sampled. This shows that it is a good indicator of anthropogenic inputs to water. Further work in PERMOTOX will involve investigations in further separation and analysis techniques and into the prioritised PMT chemicals to determine their presence in the aquatic environment.

References: 1 H. P. Arp, S. Hale and M. Neumann, PMT/vPvM assessment of REACH registered Substances Detected in Wastewater Treatment Plant Effluent, Freshwater Resources and Drinking Water, 2023.

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