DEVELOPMENT OF A NON-TARGET ANALYSIS METHOD FOR THE DETECTION OF "UNKNOWN" CONTAMINANTS AND A SIMPLE POLYDIMETHYLSILOXANE (PDMS) SPONGE FOR THE REMOVAL OF ENVIRONMENTAL ORGANIC CONTAMINANTS

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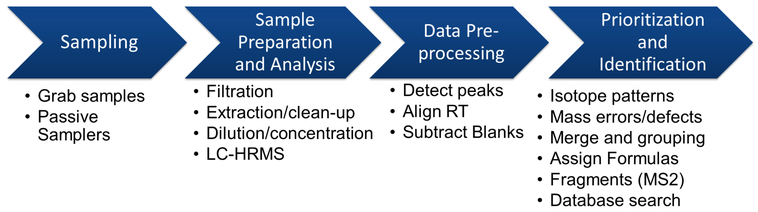
OBJECTIVES

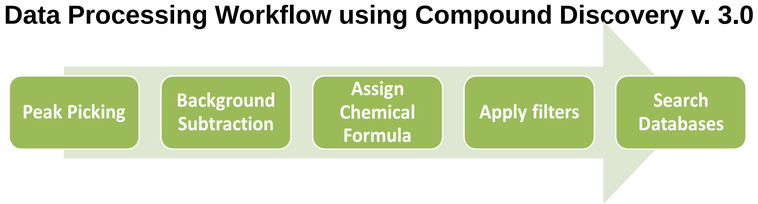
- Establish a non-targeted screening workflow for the tentative identification of "unknown" compounds using quality control (QC) mixtures based on HPLC-ESI/HRMS and Compound Discoverer
- Development of PDMS-based sponges and to evaluate their performance towards removal of organic compounds of different polarities (Log K_{ow}).
- The main goal is to establish the rates of absorption between the sponge and the selected compounds in order to evaluate the applicability of PDMS sponges in the remediation of contaminated water bodies.

MATERIALS AND METHODS

Non-target analysis workflow for environmental analysis adopted from Hollender *et. al*.[1]



Data Processing Workflow using Compound Discovery v. 3.0



The data analysis usually includes steps such as peak-picking, blank subtraction, componentization, molecular formula generation, isotopic pattern comparison, evaluation of adducts, and the assessment and comparison of fragmentation patterns.

PDMS sponge fabrication

1. Sugar cubes were added to commercially available PDMS pre-polymer and degassed for 4 hours under vacuum. During this degassing, PDMS infiltrates the sugar cube template via capillary action.
2. The sugar cubes were then heat treated (cured) at 120°C for 12 minutes, followed by dissolving of the the sugar template.[2]

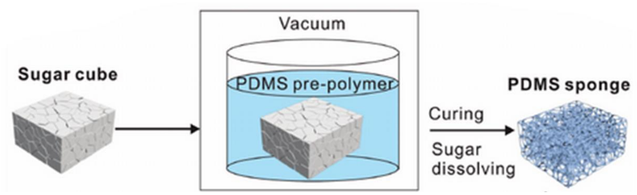


Figure 1. Schematic illustration of the PDMS sponge fabrication using a sugar template. This schematic was adapted from Zhou *et. al*.[3]

Figure 2. Resulting PDMS sponges from the above illustrated process.

Experimental analysis

1. The developed PDMS sponge was added to a mixture containing compounds covering a wide range of polarity (caffeine, lincomycin, sulfamethoxazole, trimethoprim, norcocaine, carbamazepine, diltiazem, atrazine, diphenhydramine, fluoxetine, sertraline and clotrimazole) at a concentration of 1 µg/L each and samples were taken from the mixture containing the sponge at different time intervals (0, 0.5, 1, 2, 4, 8, 12 and 24 hours) and analyzed.
2. Analysis was done in electrospray ionization (ESI) positive by online solid phase extraction (SPE), liquid chromatography coupled to a high resolution Q-Exactive for the determination of the compounds in water.

RESULTS

Quality Control

Compound	Log K_{ow}	Molecular formula	Monoisotopic mass	Monitored ions	Retention time (mins)
Sucralose	-1.00	$C_{12}H_{19}Cl_3O_8$	396.0146	395.0073[b]	11.16
Hydrochlorothiazide	-0.10	$C_7H_8ClN_3O_4S_2$	296.9645	295.9572[b]	11.39
Caffeine	0.16	$C_8H_{10}N_4O_2$	194.0804	195.0877[a]	11.01
Lincomycin	0.29	$C_{18}H_{34}N_2O_6S$	406.2137	407.2210[a]	10.60
Sulfamethoxazole	0.48	$C_{10}H_{11}N_3O_3S$	253.0521	254.0594[a]	12.42
Trimethoprim	0.73	$C_{14}H_{18}N_4O_3$	290.1379	291.1452[a]	11.11
Norcocaine	1.96	$C_{16}H_{19}NO_4$	289.1314	290.1387[a]	12.05
Carbamazepine	2.25	$C_{15}H_{12}N_2O$	236.0950	237.1022[a]	13.11
Diltiazem	2.79	$C_{22}H_{26}N_2O_4S$	414.1613	415.1686[a]	12.80
Atrazine	2.82	$C_8H_{14}ClN_5$	215.0938	216.1010[a]	13.66
Diphenhydramine	3.11	$C_{17}H_{21}NO$	255.1623	256.1696[a]	12.86
Diclofenac	4.02	$C_{14}H_{11}Cl_2NO_2$	295.0167	294.0094[b]	14.14
Fluoxetine	4.65	$C_{17}H_{18}F_3NO$	309.1341	310.1413[a]	13.46
Gemfibrozil	4.77	$C_{15}H_{22}O_3$	250.1569	249.1496[b]	14.48
Mefenamic acid	5.28	$C_{15}H_{15}NO_2$	241.1103	240.1030[b]	14.44
Sertraline	5.29	$C_{17}H_{17}Cl_2N$	305.0738	306.0811[a]	13.57
Clotrimazole	6.26	$C_{22}H_{17}ClN_2$	344.1080	345.1153[a]	13.68

[a]Ions were monitored in ESI positive (70.6%), [b]Ions were monitored in ESI negative (29.4%)
Table 1. List of quality control compounds and their respective log K_{ow} , molecular formula, monoisotopic mass and monitored ions.

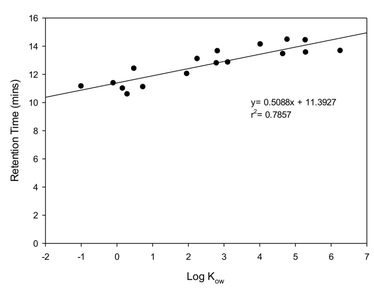


Figure 3 (right). Retention time vs Log K_{ow} model based on the QC mixtures for quality control and data reduction in non-target analysis.

B. Ng, *et. al*, Sci. Total Environ., **2020**, 713, doi.org/10.1016/j.scitotenv.2020.136568[4]

The PDMS sponge with compounds of varying Log K_{ow}

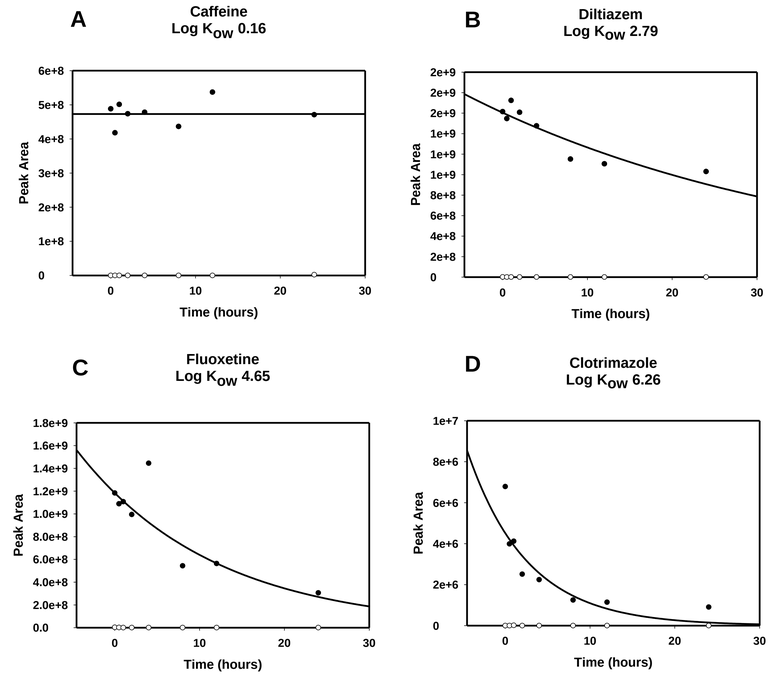


Figure 4. Measured peak area in water over time for four of the studied compounds. A: caffeine, B: diltiazem, C: fluoxetine, D: clotrimazole.

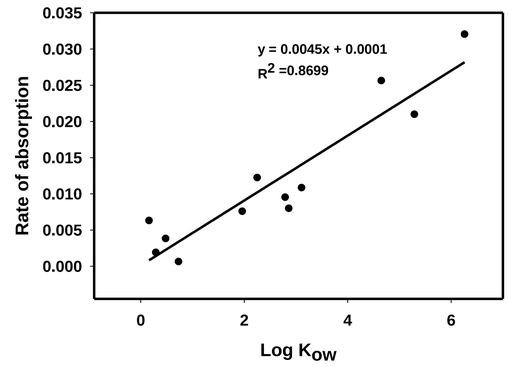


Figure 5. Correlation between absorption rate and Log K_{ow}.

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