Supporting Information

Fully Automated Water Sampling – Surfactant-Enhanced Membrane Bag Liquid-Phase Microextraction – Ultrahigh Performance Liquid Chromatography-Mass Spectrometry

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Abstract

This document consists of (i) detailed stepwise fabrication of the extraction device; (ii) figures of the optimisation parameters; (iii) chromatogram of the canal water sample; and (iv) properties of the analytes studied in this work.

Stepwise fabrication of the extraction device

The final extraction device was an assembly of two supporting devices, a metal ring, and the membrane bag. Supporting device 1 (a truncated 200 µL pipette tip of 1.5 cm in length) helped to secure the membrane bag. This was obtained by cutting off 1.4 cm and 2.9 cm, respectively from the base of the tip to obtain the mid-section for this purpose (see Figure S1). Supporting device 2 was acquired from the section at the top of a plastic insert (length of 1.0cm) as shown in Figure S2.

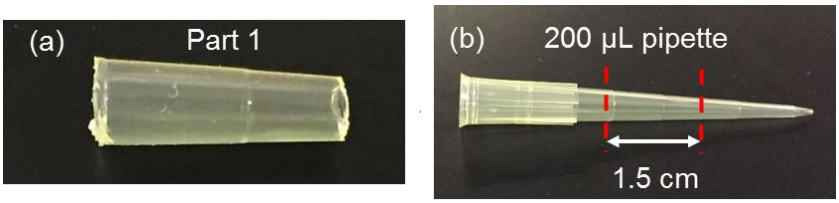


Figure S1. (a) Supporting device part 1 from (b) original 200 µL pipette tip

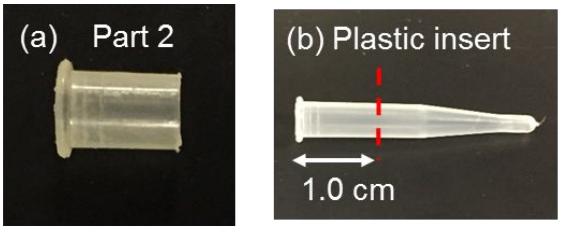


Figure S2. (a) Supporting device part 2 from (b) original plastic insert

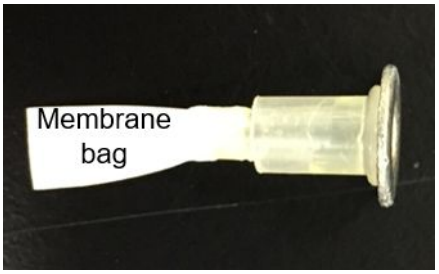


Figure S3. Complete assembly of the extraction device

The two supporting devices were assembled by fitting them successively into each other. A metal ring was mounted onto the top of two-part assembly using cyanoacrylate adhesive. The cylindrical membrane bag was subsequently attached to

the end of the supporting device 1 with Parafilm. The volume of the bag was estimated to be 70 µL. Figure S3 shows the final assembly of the extraction device.

Optimisation parameters

Figure S4: Effect of the agitation rate during extraction (n=3). Volume of extractant solvent: 30 µL of 0.1% SDS in n-octanol; aqueous sample: Glucocorticoids spiked into ultrapure water (5 ng/mL of each) (pH 7); extraction temperature: 35°C; extraction time: 30 min; post-extraction dilution: 60 µL MeOH added; 0% NaCl; flow rate: 0 mL/min

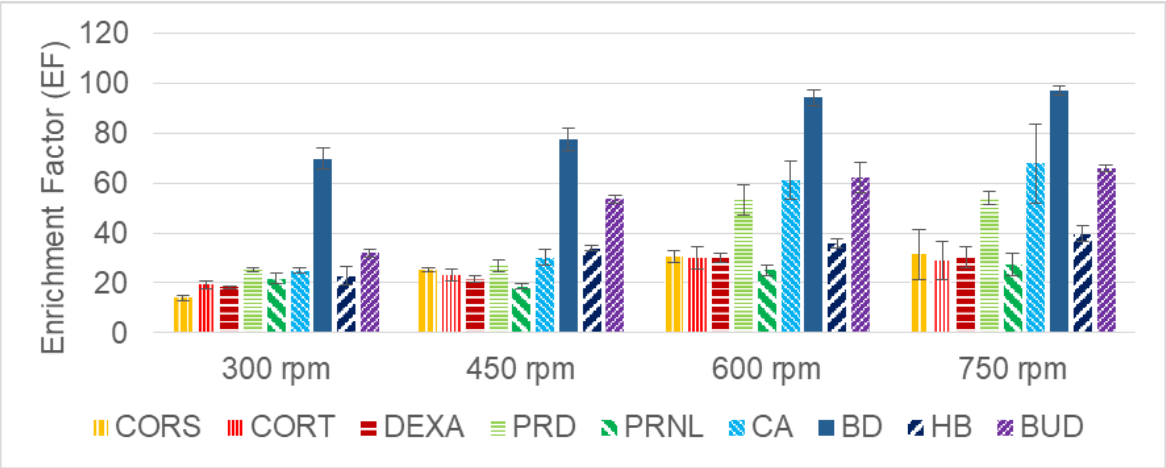


Figure S5: Effect of the duration of extraction (n=3). Volume of extractant solvent: 30 µL of 0.1% SDS in n-octanol; aqueous sample: Glucocorticoids spiked into ultrapure water (5 ng/mL of each) (pH 7); agitation speed: 600 rpm; extraction temperature: 35°C; post-extraction dilution: 60 µL MeOH added; 0% NaCl; flow rate: 0 mL/min

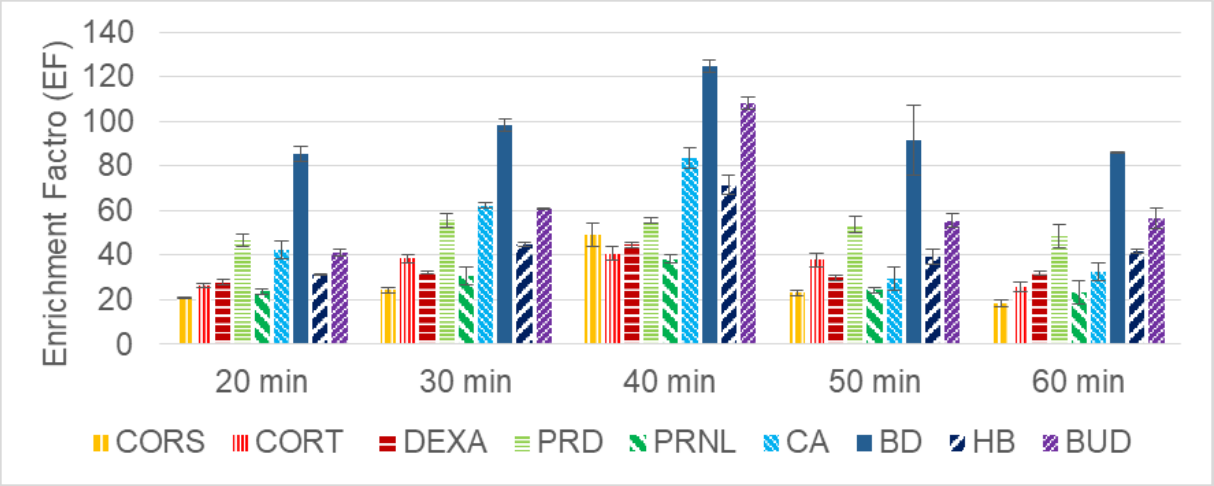
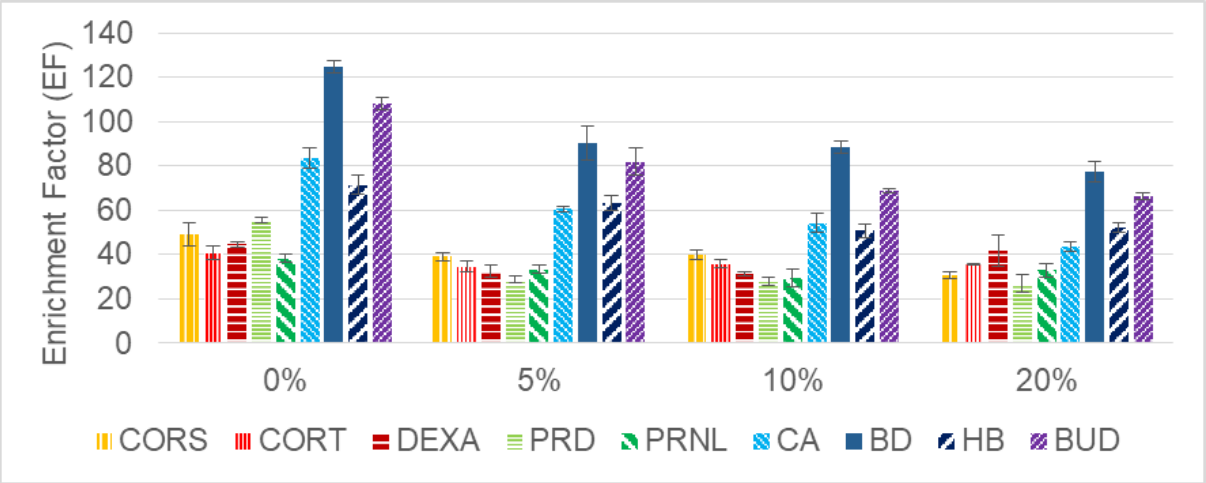


Figure S6: Effect of salting out with NaCl (n=3). Volume of extractant phase: 30 µL of 0.1% SDS in n-octanol; aqueous sample: Glucocorticoids spiked into ultrapure water (5 ng/mL of each) (pH 7); agitation speed: 600 rpm; extraction temperature: 35°C; extraction time: 30 min; post-extraction dilution: 60 µL MeOH added; flow rate: 0 mL/min.



Example Chromatogram

Figure S7: Typical extracted total ion chromatograms of the extracts of water samples (collected at the start of the canal) for the LC-MS/MS determination of glucocorticoids.

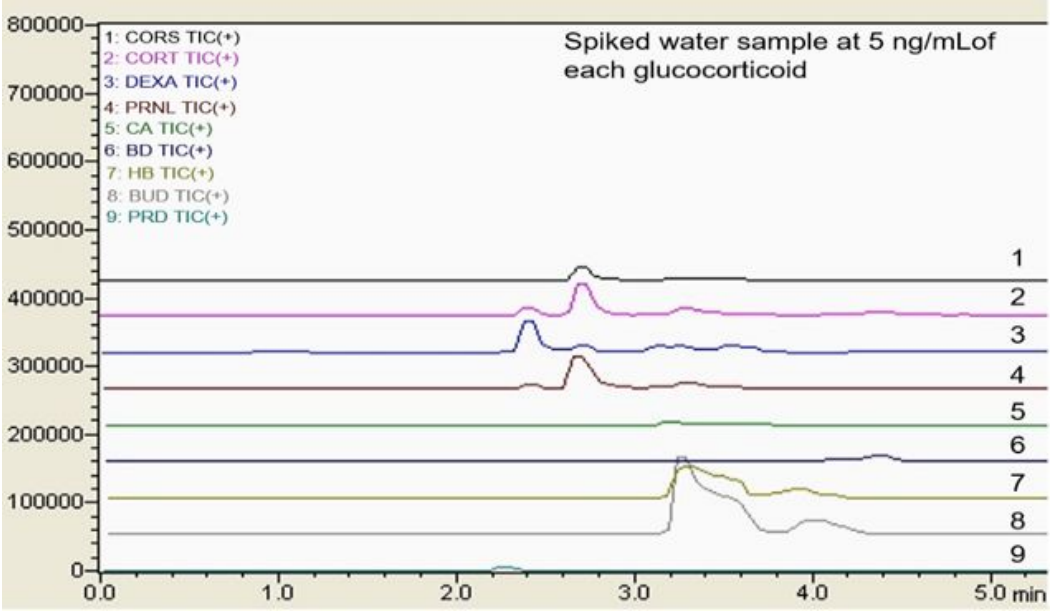


Table S1: Chemical structures and properties of glucocorticoids considered in this work

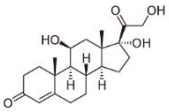
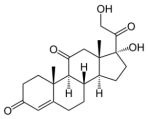
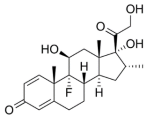
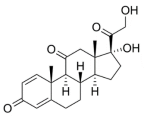
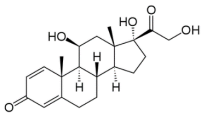
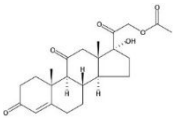
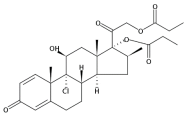
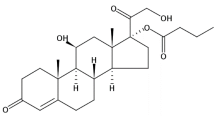
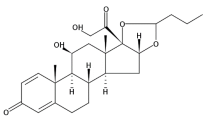
Analyte	Structure	pK_a	log P
CORS		12.5	1.76
CORT		12.4	1.43
DEXA (Synthetic)		12.1	2.03
PRD (Synthetic)		12.4	1.57
PRNL (Synthetic)		12.5	1.64
CA (Synthetic)		12.0	1.05
BD (Synthetic)		12.3	1.96
HB (Synthetic)		12.7	1.80
BUD (Synthetic)		12.8	1.51

Table S2: Optimised MS parameters for glucocorticoids under positive ESI mode

Analyte	Retention time (min)	Precursor Ion	Product Ions	Q1 pre bias (V)	CE (mV)	Q3 pre bias (V)
CORS	2.91	363.10	121.00 [1]	-19.0	-30.0	-27.0
			97.05 [2]		-32.0	-21.0
CORT	2.92	361.10	147.50 [1]	-19.0	-24.0	-15.0
			163.10 [2]		-28.0	-16.0
DEXA	2.61	393.10	361.20 [1]	-22.0	-7.0	-26.0
			373.20 [2]		-11.0	-28.0
PRD	2.52	359.10	341.15 [1]	-14.0	-13.0	-25.0
			147.00 [2]		-31.0	-28.0
PRNL	2.88	361.10	343.15 [1]	-20.0	-11.0	-25.0
			147.15 [2]		-25.0	-15.0
CA	3.40	403.2	162.90 [1]	-16.0	-30.0	-13.0
			343.00 [2]		-20.0	-13.0
BD	4.49	522.1	115.00 [1]	-21.0	-27.0	-20.0
			338.20 [2]		-23.0	-30.0
HB	3.93	433.3	345.30 [1]	-23.0	-11.0	-25.0
			120.80 [2]		-30.0	-25.0
BUD	4.09	431.3	413.20 [1]	-17.0	-12.0	-30.0
			173.20 [2]		-31.0	-18.0

Product ion[1] refers to the quantifier of the analyte and product ion[2] is its corresponding qualifier.; Q1 ionisation: ESI; Q2 fragmentation: CID; scan mode: positive; nebulising gas (N_2) flow: 3 L/min; drying gas (N_2) flow: 15 L/min; interface voltage: 4.5 kV; desolvation temperature: 250 ºC; heat block temperature: 400 ºC; detector voltage: 1.98 kV; collision-induced dissociation gas pressure: 230 kPa; dwell time: 100 ms.