Supplementary Materials

Detection of eight cannabinoids and one tracer in wastewater and river water by SPE-UPLC–ESI-MS/MS.

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Figure S1. Aerial view of the WWTP located in Vila Nova de Gaia, Porto (Photo courtesy of Águas de Gaia).

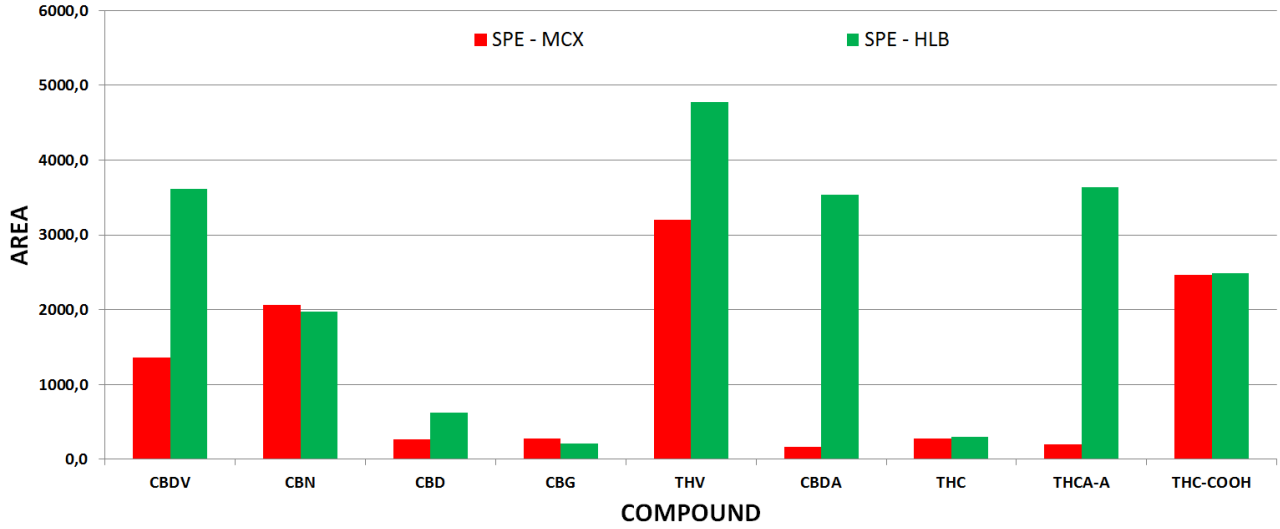


Figure S2. Comparison of solid-phase MCX (6 mL) and HLB (6 mL) sorbent types needed for the cartridge optimization.

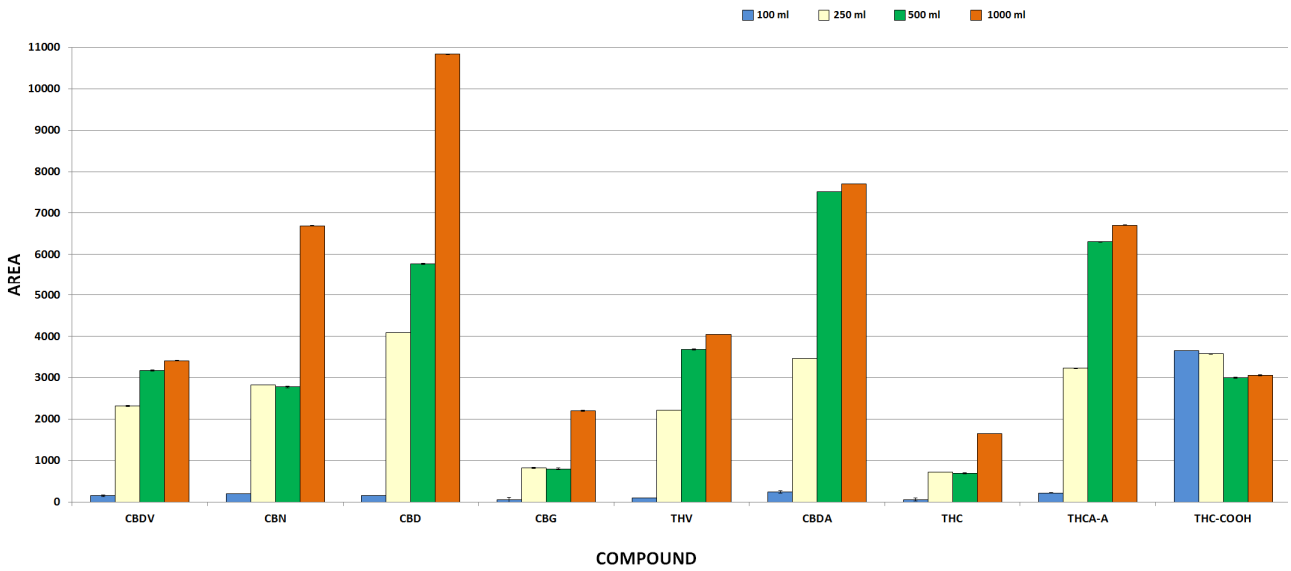
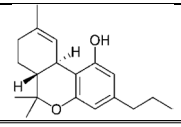
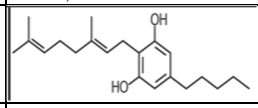
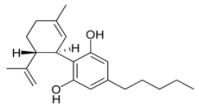
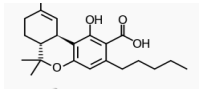
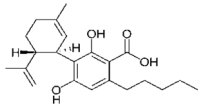
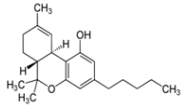
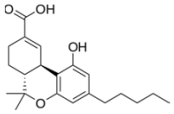
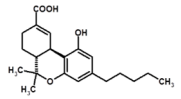
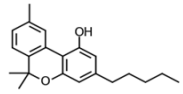


Figure S3. Breakthrough volume defining the optimal volume of environmental water sample to pre-concentrate/enrich via the developed offline SPE method using HLB cartridges (6 mL).

Table S1. Optimized SPE-UPLC-MS/MS parameters: working range, determination coefficient (R^2), molecular mass (MM), ionization mode (ESI), limit of quantification (LOQ), limit of detection (LOD), intermediate precision (IP) and repeatability (REP).

Compound	Range ($\mu g\ L^{-1}$)	R^2	MM	ESI	LOQ (S/N=10)	LOD (S/N=3)	IP (RSD%)	REP (%)
CBDV	0.050-0.500	0.9995	286.41	-p	0.046	0.015	6.1	6.8
CBN	0.050-0.500	0.9953	310.43	-p	0.147	0.048	10.0	5.3
CBD	0.050-0.500	0.9991	314.45	+p	0.065	0.021	2.6	8.8
CBG	0.050-0.500	0.9995	316.48	+p	0.047	0.016	8.0	24.8
THV	0.050-0.500	0.9990	286.41	-p	0.070	0.023	8.2	7.2
CBDA	0.050-0.500	0.9986	358.47	+p	0.080	0.026	5.9	17.1
THC	0.050-0.500	0.9991	314.45	+p	0.063	0.021	5.8	21.8
THCA-A	0.050-0.500	0.9980	358.47	-p	0.098	0.032	4.9	11.2
THC-COOH	0.050-0.150	0.9987	344.45	+p	0.019	0.006	3.8	13.8

Table S2. Summary of the standard solutions considered and electrospray ionization optimization (grey) through IntelliStart™ (CE = Collision energy; CV =Cone voltage).

Compound name	Standard solution		Molecular formula	MM	Abbreviation	Structural formula	ESI POSITIVE			ESI NEGATIVE		
	Conc.	Unit					1ª	2ª	3ª	1ª	2ª	3ª
(-)-delta-9-Tetrahydrocannabinol-C3	1000	µg/mL	$C_{19}H_{26}O_2$	286.41	**THCV or THV**		**287.16(CV42) >165.05 (CE22)**	**287.16(CV42) >93.05 (CE22)**	**287.16(CV42) >135.17 (CE14)**	**285.16(CV60) >217.12 (CE26)**	**285.16(CV60) >163.17 (CE26)**	**285.16(CV60) >151.00 (CE20)**
Cannabigerol	1000	µg/mL	$C_{21}H_{32}O_2$	316.48	**CBG**		**317.21(CV22) >193.13 (CE22)**	**317.21(CV22) >123.05 (CE34)**	**317.21(CV22) >76.96 (CE22)**	**315.21(CV48) >136.01 (CE26)**	**315.21(CV48) >191.37 (CE24)**	**315.21(CV48) >177.13 (CE24)**
Cannabidiol	1000	µg/mL	$C_{21}H_{30}O_2$	314.45	**CBD**		**315.13(CV12) >168.99 (CE6)**	**315.13(CV12) >183.05 (CE6)**	**315.13(CV12) >283.11 (CE12)**	**313.19(68CV) >245.12 (CE26)**	**313.19(68CV) >191.12 (CE26)**	**313.19(68CV) >179.02 (CE22)**
Tetrahydrocannabinolic acid	1	µg/mL	$C_{22}H_{30}O_4$	358.4733	**THCA-A**		**-**	**-**	**-**	**357.18(CV48) >245.15 (CE32)**	**357.18(CV48) >191.14 (CE32)**	**357.18(CV48) >179.04 (CE28)**
Cannabidiolic Acid	1	µg/mL	$C_{22}H_{30}O_4$	358.47	**CBDA**		**359.12(CV14) >196.54 (CE18)**	**359.12(CV14) >213.13 (CE8)**	**359.12(CV14) >227.77 (CE10)**	**357.18(54CV) >245.16 (CE34)**	**357.18(54CV) >191.14 (CE34)**	**357.18(54CV) >107.05 (CE46)**
Tetraidrocanabinol	100	µg/mL	$C_{21}H_{30}O_2$	314.45	**THC**		**315.26(CV38) >193.16 (CE24)**	**315.26(CV38) >123.07 (CE32)**	**315.26(CV38) >93.06 (CE24)**	**313.19(66CV) >245.12 (CE28)**	**313.19(66CV) >191.12 (CE28)**	**313.19(66CV) >179.0 9 (CE24)**
Cannabidivarin	1000	µg/mL	$C_{19}H_{26}O_2$	286.41	**CBDV**		**287.10(CV12) >155.03 (CE12)**	**-**	**-**	**285.16(44CV) >151.06 (CE18)**	**285.16(44CV) >217.12 (CE22)**	**285.16(44CV) >107.05 (CE30)**
11-nor-9-Carboxy-THC	100	µg/mL	$C_{21}H_{28}O_4$	344.445	**THC-COOH**		**345.17(CV36) >289.09 (CE16)**	**345.17(CV36) >313.16 (CE8)**	**345.17(CV36) >143.10 (CE10)**	**343.23(CV14) >283.25 (CE10)**	**343.23(CV14) >255.14 (CE10)**	**-**
Cannabinol	1000	µg/mL	$C_{21}H_{26}O_2$	310.43	**CBN**		**311.23(CV38) >223.10 (CE20)**	**311.23(CV38) >43.05 (CE30)**	**311.23(CV38) >161.08 (CE24)**	**309.16(CV64) >279.14 (CE32)**	**309.16(CV64) >222.16 (CE44)**	**309.16(CV64) >171.08 (CE28)**

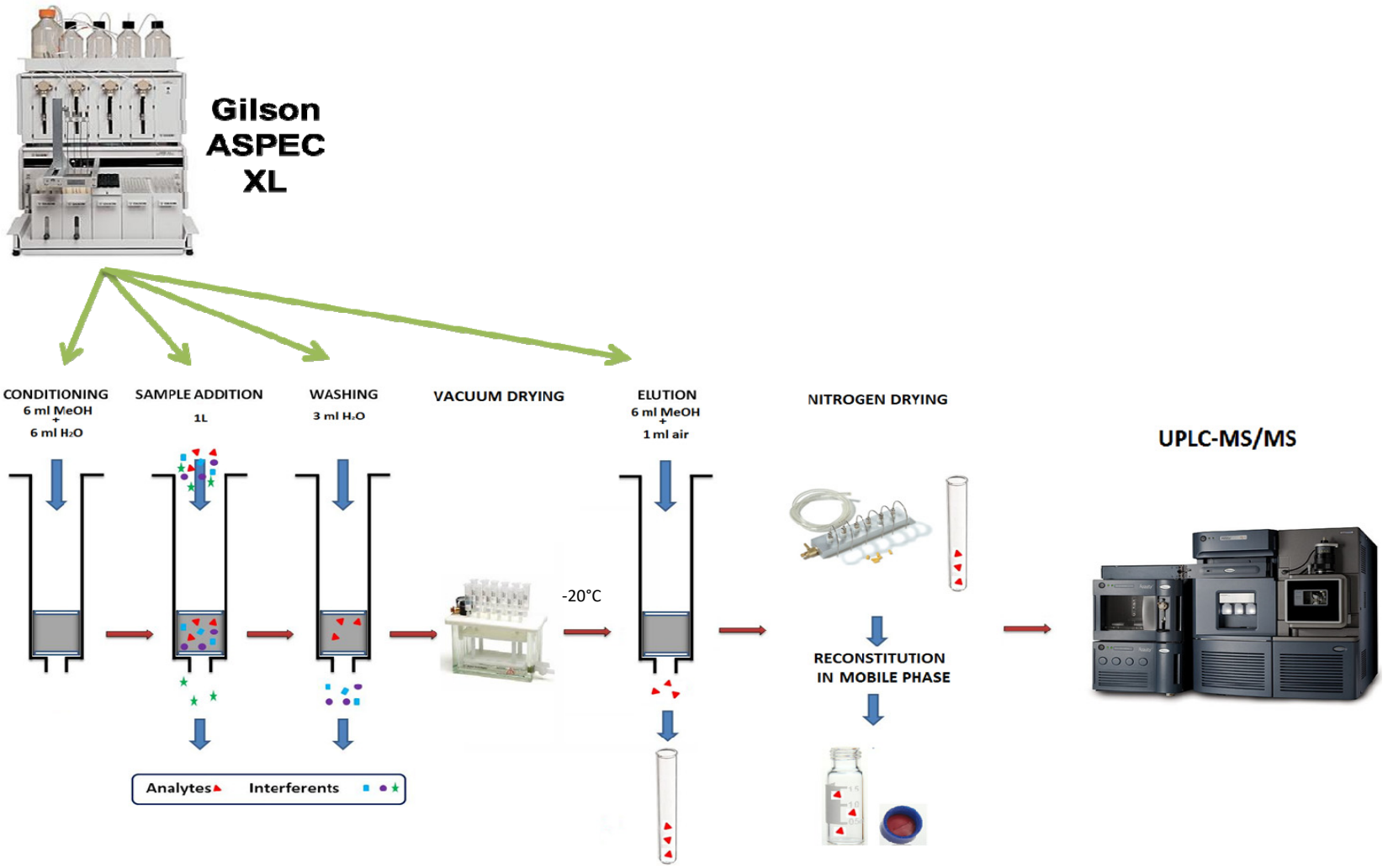


Figure S4. Scheme of the offline SPE method developed and applied for the enrichment / pre-concentration on standard solutions for calibration and on environmental water samples for quantification, prior to the UPLC-MS/MS analysis.

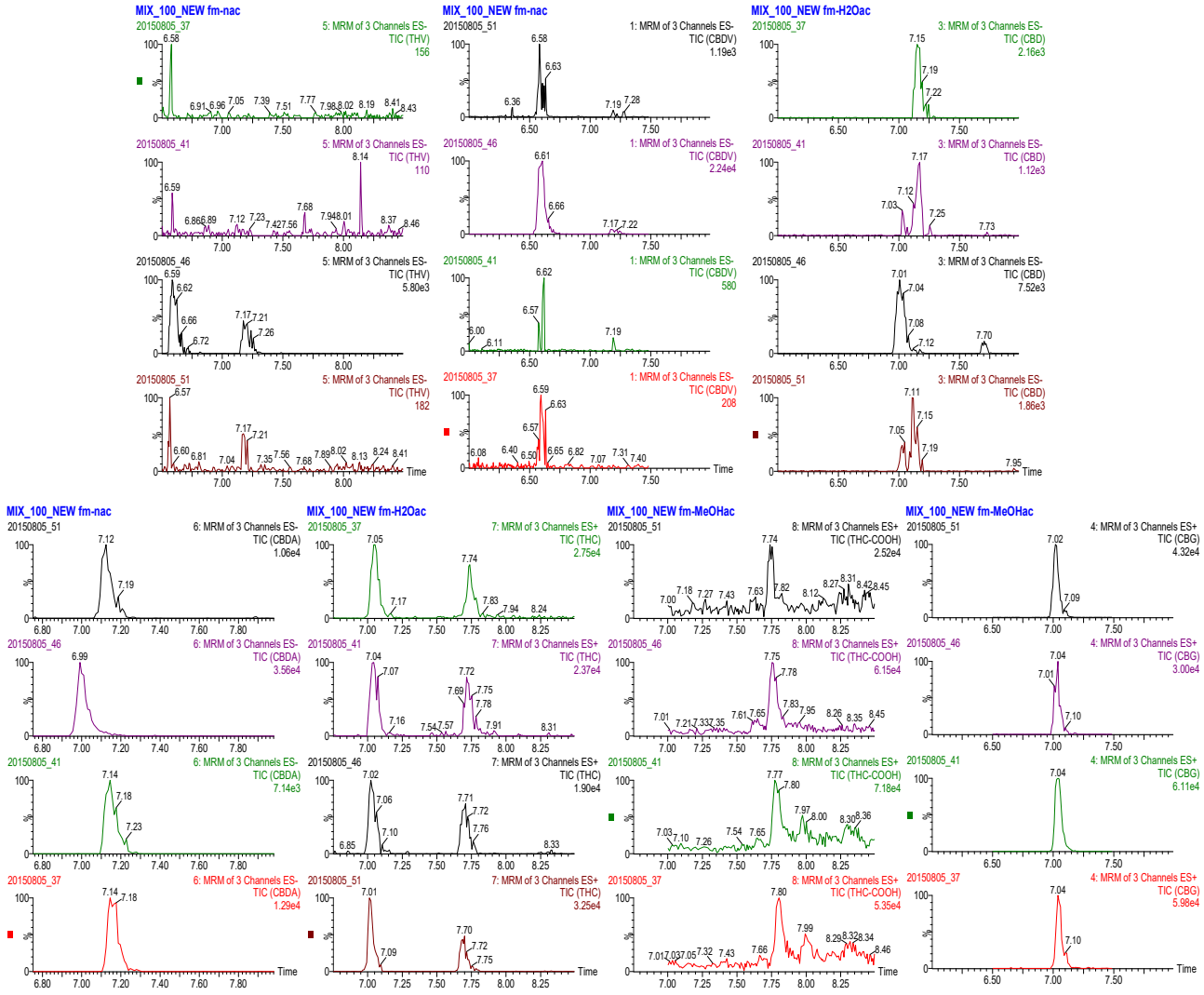


Figure S5. Improvement of chromatographic conditions for compounds THV, CBDV, CBD, CBDA, THC, THC-COOH, CBG obtained with the optimized chromatographic mobile phase (grey), compared to other mobile phases (other colors).