

Supplementary Materials

Optimization and Validation of a Method Based on QuEChERS Extraction and Gas Chromatographic-Mass Spectrometric Analysis for the Determination of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls in Olive Fruits Irrigated with Treated Wastewaters

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Table S1 – Mean values (n = 3) and standard deviations (in brackets) of physicochemical parameters of FW and TWWs in the period July-November 2021. Limits considered in the Italian regulations for wastewater reuse (D.M. 185/2003) are also shown.

Parameters	FW	TWW1	TWW2	TWW3	TWW4	D.M. 185
<i>Physicochemical parameters</i>						
TSS ^(a) [mg/L]	248 (67)	12 (3)	1.6 (0.2)	1.3 (0.2)	12 (4)	<10
pH	7.8 (0.3)	6.95 (0.07)	7.41 (0.03)	7.88 (0.09)	7.94 (0.05)	6.0-9.5
SAR ^(b)	0.37 (0.08)	9.1 (0.4)	9.6 (0.3)	9.2 (0.8)	9.6 (0.3)	<10
EC ^(c) [μ S/cm]	472 (64)	2442 (248)	1661 (434)	1322 (331)	1611 (385)	<3000
<i>Chemical parameters (mg/L)</i>						
COD ^(d)	22 (3)	40 (5)	21 (3)	15 (3)	67 (8)	<100
BOD ₅ ^(e)	13 (4)	11 (2)	3.5 (0.7)	4.3 (0.9)	13 (1)	<20
N-NH ₄ ⁺	<0.05	2 (1)	1.1 (0.6)	0.8 (0.4)	1.1 (0.4)	<2
N _{tot}	2.1 (0.3)	6 (1)	5 (1)	4.9 (0.9)	7.5 (1.8)	<15
P _{tot}	0.14 (0.04)	0.5 (0.1)	0.4 (0.2)	0.3 (0.2)	0.8 (0.3)	<2

^(a) TSS = total suspended solids. ^(b) SAR = sodium adsorption ratio. ^(c) EC = electrical conductivity. ^(d) COD = chemical oxygen demand (mg O₂/L); ^(e) BOD₅ = five-days biochemical oxygen demand (mg O₂/L). n.a. = not analysed.

Table S2 – Mean values and concentration ranges of PAHs in treated wastewaters waters (TWW) used for irrigation, sampled within July and November 2021. FW: control (freshwater). Results are expressed in ng/L. Naphtalene (NaPh), Acenaphthylene (AcPY), Acenaphtene (AcPh), Fluorene (Flu), Phenanthrene (Phe), Fluoranthene (Flth) Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chr), Benzo[b]fluoranthene (BbFL), Benzo[k]fluoranthene (BkFL), Benzo[a]pyrene (BaP), Indeno[1,2,3-cd]pyrene (Ind), Dibenzo[a,h]anthracene (DBA), Benzo[ghi]perylene (BP)

	FW	TWW1	TWW2	TWW3	TWW4
NaPh	142.8 (5.8-279.8)	14.2 (0.3-42)	321.1 (16.7-893.1)	16.5 (0.3-48.8)	14 (0.3-41.4)
AcPY	5.6 (1-10.2)	9.2 (0.6-21.7)	8.7 (0.2-22.9)	1 (0.2-2.5)	2.1 (0.2-5.3)
AcPh	26.3 (13.6-39)	57.6 (27.9-99.5)	6.7 (0.3-13.4)	4.7 (0.3-12.5)	9.8 (0.3-21.9)
Flu	61.8 (13.9-109.6)	93.6 (11.6-213.5)	91.9 (12.2-237.6)	25.4 (0.2-58.1)	16.1 (0.2-41.5)
Phe	37.3 (17.3-57.2)	40.7 (5.9-71.9)	37.8 (12.4-66.2)	5 (0.2-14.7)	8.4 (0.2-24.8)
Flth	5.4 (2.4-8.3)	6 (4-8.6)	4.8 (0.2-10.6)	0.2 (0.2-0.2)	2.8 (0.2-7.1)
Pyr	3.3 (1.9-4.6)	3.1 (2.3-4.1)	2.4 (0.2-4.9)	0.2 (0.2-0.2)	1.4 (0.2-3.9)

Table S3 – Mean values and concentration ranges of PCBs in treated wastewaters waters (TWW) used for irrigation, sampled within July and November 2021. FW: control (freshwater). Results are expressed in ng/L. Dioxin like PCBs are marked with an asterisk (*).

	FW	TWW1	TWW2	TWW3	TWW4
PCB11	<1.3 ^a	1.5 (1.3-2)	2.2 (1.3-4)	1.7 (1.3-2.6)	4.3 (1.3-6.4)
PCB15	14.2 (7-21.4)	8.5 (1.8-12.3)	2.2 (1.8-2.7)	2.6 (2.1-3.2)	5.8 (4.2-7.2)
PCB81*	<1.7 ^a	4.5 (1.7-10.1)	<1.7 ^a	1.9 (1.7-2.2)	2.8 (1.7-4.9)
PCB118*	<1.9 ^a	<1.9 ^a	<1.9 ^a	2.2 (1.9-2.8)	3 (1.9-5.2)
PCB123*	<0.7 ^a	<0.7 ^a	<0.7 ^a	1.2 (0.7-2.1)	3.1 (0.7-7.8)
PCB138	4.1 (1-7.2)	<1.0 ^a	<1.0 ^a	1.4 (1-2.1)	4.2 (1-6.4)
PCB167*	14.6 (1-28.1)	<1.0 ^a	<1.0 ^a	<1.0 ^a	<1.0 ^a
PCB169	18 (1.7-34.3)	<1.7 ^a	<1.7 ^a	<1.7 ^a	2.1 (1.7-3)

^a: method quantitation limit

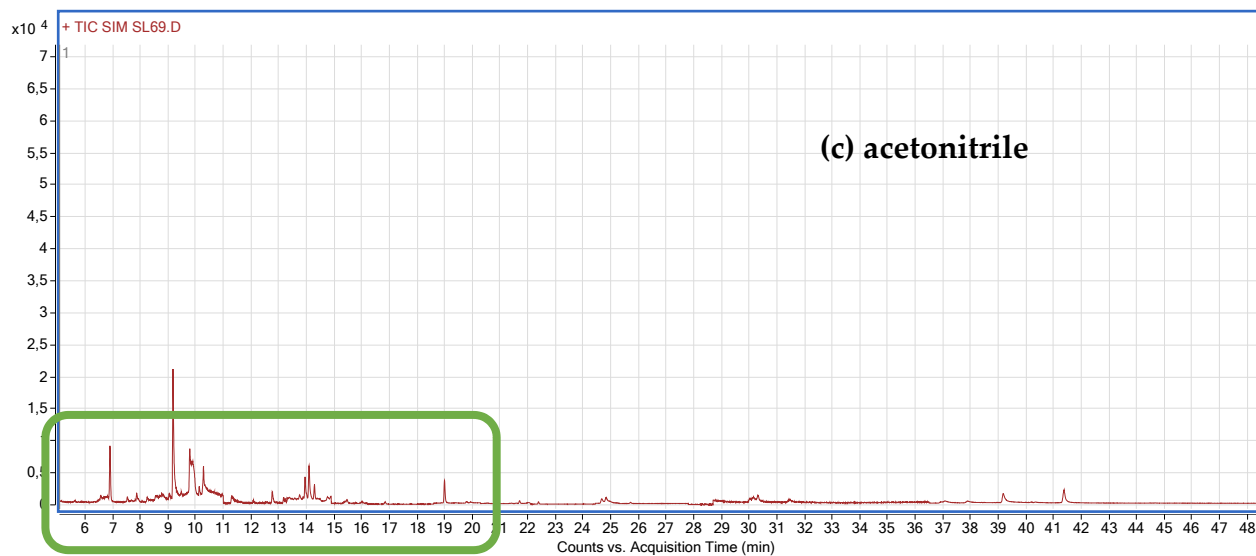
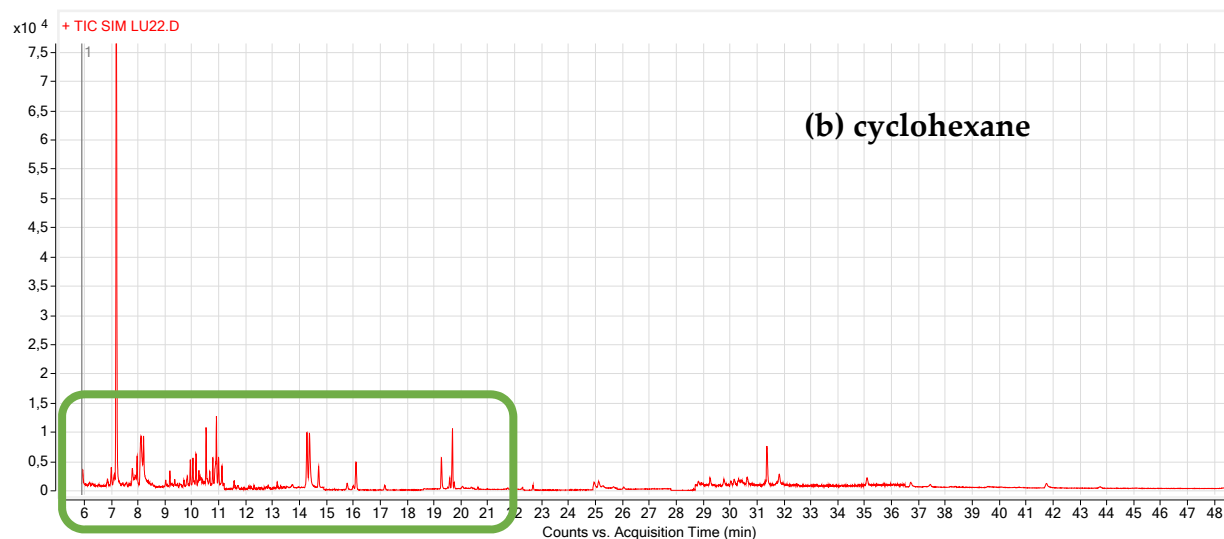
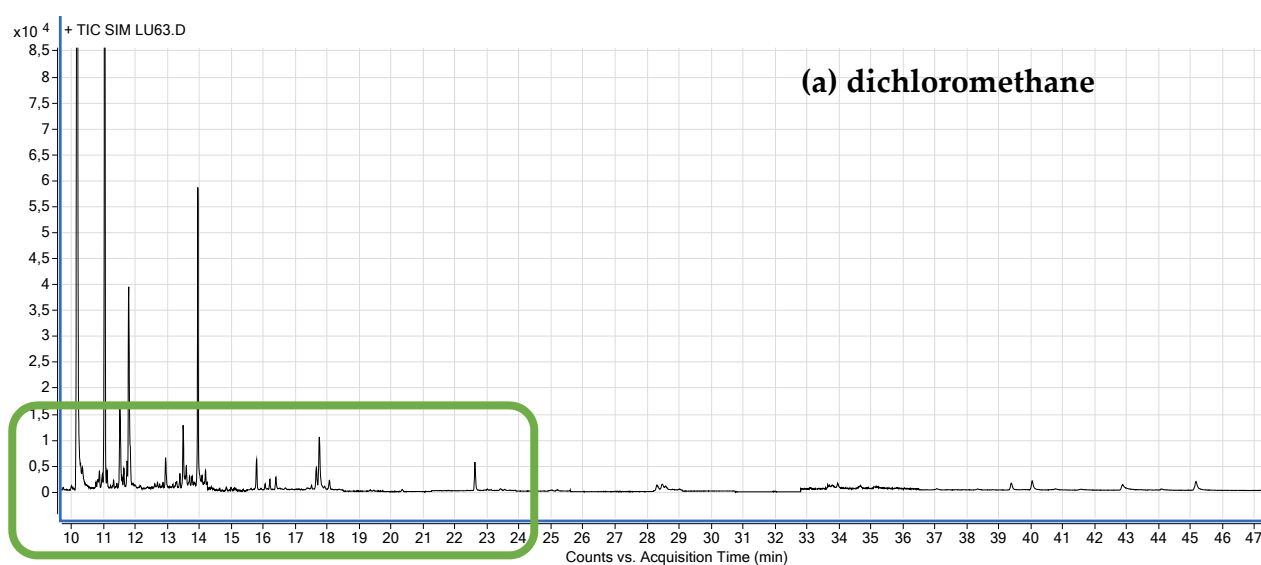


Figure S1. Effect of the extracting solvent on the GC background noise. Chromatogram tracks (scan mode) of not labelled olive samples extracted by (a) dichloromethane, (b) cyclohexane and (c) acetonitrile are shown. Instrumental conditions are reported in the manuscript.

Matrix background, depicted in the selected area, decreases from (a) to (c) due to the reduced co-extracted species

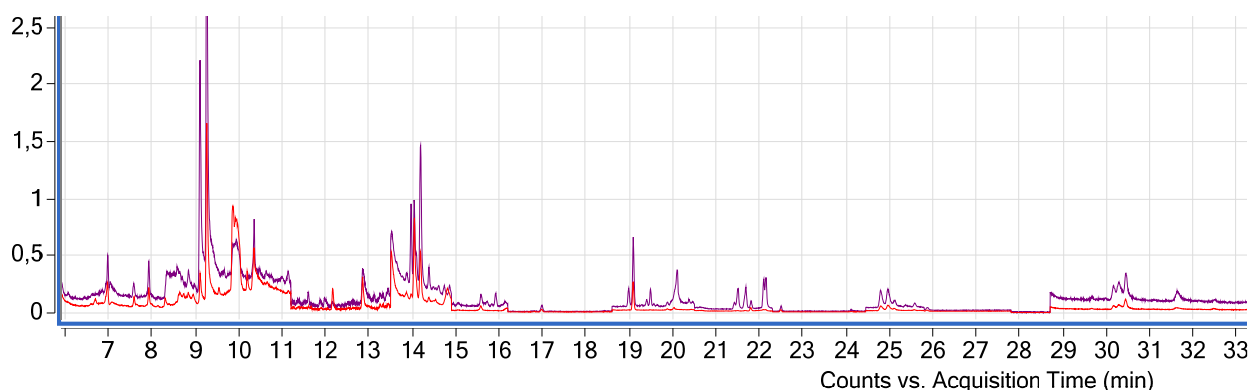


Figure S2. Effect of single (purple line) and double (red line) purification with 100 mg PSA + 50 mg Florisil, after extraction with acetonitrile on the background noise. Chromatogram tracks (scan mode) are reported.

Matrix background decreases using a double purification step with the same d-SPE phases, as a result of a better removal efficiency.

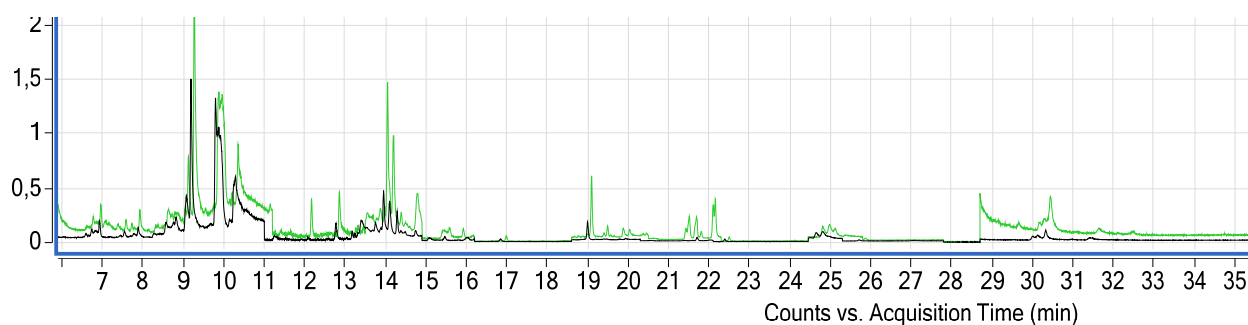


Figure S3. Comparison of chromatogram tracks (scan mode) after extraction with acetonitrile and a double step of purification with 100 mg PSA + 50 mg Florisil (green line) and 100 mg Z-Sep + 50 mg Florisil (black line).

Under a double purification step, matrix background decreases using Z-Sep in respect to PSA as a result of a better affinity of (mainly non-polar) coextracted compounds with Florisil.