Electronic Supplementary Material

Simultaneous Testing of Multiclass Organic Contaminants in Food and Environment by Liquid Chromatography/Dielectric Barrier Discharge Ionization-Mass Spectrometry

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ABSTRACT: Additional information is provided, including a table with information related to the determination of pesticides and priority contaminants in olive oil extract by LC/DBDI-MS (**Table S1**), a table with information related to the determination of pesticides in orange extract by LC/DBDI-MS (**Table S2**), sample preparation procedures, detailed information on the DBDI set-up, and a figure (**Figure S1**) related to the determination of emerging contaminants in a wastewater extract by LC/DBDI-MS.

EXPERIMENTAL

Samples

Both virgin olive ion and oranges were obtained from the local market in Jaén, Spain. Wastewater samples used in this study were collected from a municipal sewage treatment plant located in El Ejido, Almería (southeast Spain). This plant treats urban wastewater with important contributions from greenhouses, plastic industry also related to greenhouses, and from a local hospital. Input wastewater undergoes a physical pre-treatment to remove coarse solids and greases, primary settling of particulates, and secondary treatment with activated sludge, after which the water is discharged to the sea.

Sample preparation

Sample treatment for oranges. The employed procedure was the so called "QuEChERS" method (acronym of "quick, easy, cheap, effective, rugged and safe") described elsewhere.[2] The proposed procedure comprised the following steps: A representative 15 g portion of previously crushed (including the peel), blended and homogenized sample was weighted in a 50 mL plastic centrifuge tube. Then 15 mL of

acetonitrile containing 1% acetic acid were added, and the tube was vigorously shaken for 1 minute. After this time, 6 g of anhydrous magnesium sulfate and 1.5 g of sodium acetate were added, and immediately the shaking process was repeated for 1 minute to prevent coagulation of $MgSO_4$. The extract was centrifuged (3700 rpm) afterwards for 1 minute. 5 mL of the supernatant (acetonitrile phase) was then collected with a pipette and transferred to a 15-mL graduated plastic centrifuge tube containing 250 mg of primary-secondary amine (Supelclean^{TM} PSA SPE Bulk packing, 50 µm) and 750 mg of $MgSO_4$, that was then energetically shaken for 20 s. The extract was then centrifuged again (3700 rpm) for 3 minutes. Finally, an extract containing the equivalent of 1 g of sample per mL in acetonitrile was obtained. Prior to LC/MS analysis the extract was filtered through a 0.45 µm PTFE filter (Millex FG, Millipore, Milford, MA, USA).

Sample treatment for olive oil. The employed procedure was the "QuEChERS" method modified for fatty food matrixes.[3,4] The procedure comprised the following steps: a representative 3 g portion of olive oil was weighed in a 50 mL centrifuge tube with 7 g of water. Then, 10 mL of acetonitrile were added, along with 4 g of anhydrous magnesium sulfate and 1 g of sodium chloride, and immediately the tube was vigorously shaken for 1 minute to prevent coagulation of $MgSO_4$. The extract was then centrifuged (3700 rpm) for 3 minutes. 5 mL of the supernatant (acetonitrile phase) was then taken with a pipette and transferred to a 15 mL centrifuge tube containing 250 mg of PSA sorbent, 250 mg of C_{18} sorbent, and 750 mg of $MgSO_4$. It was then energetically shaken for 30 seconds. The extract was then centrifuged again (3700 rpm) for 1 minute. 3 mL of supernatant were taken and evaporated near dryness under N_2 stream. The extract is reconstituted with 300 µL of ultrapure water plus 700 µL of MeOH, so that it finally contained the equivalent of 1 g of sample per mL. Prior to LC/MS analysis the

extract was filtered through a 0.45 μm PTFE filter (Millex FG, Millipore, Milford, MA, USA).

Solid-phase extraction procedure of effluent wastewater samples. The generic extraction method of wastewater matrices consisted of a solid-phase extraction with polymer based hydrophilic-lipophilic balanced SPE cartridges (Oasis^{TM} HLB, 200 mg, 6 mL) purchased from Waters (Milford, MA, USA). The cartridges were preconditioned with 4 mL of MeOH and 4 mL of milli-Q water at a flow rate of 2 mL min^{-1}. After the conditioning step, 100 mL of sample were loaded into the cartridge. Wastewater sample was passed through the cartridges at a flow rate of 3 mL min^{-1}. The retained analytes were eluted with 2 x 4 mL of MeOH at 1 mL min^{-1}. This eluate was then evaporated until near dryness by a gentle nitrogen stream in a concentration workstation (15 psi N_2, 30 ºC) and taken up with 200 μL of MeOH and 1800 μL of milli-Q water (final preconcentration factor 50:1). Then this extract was filtered through a 0.45 μm PTFE filter and transferred into a vial.

Dielectric Barrier Discharge Microplasma Ionization (DBDI) set-up. Mass spectrometric detection was carried out using an Exactive^{TM} orbitrap mass spectrometer equipped with an Ion Max^{TM} API source housing (Thermo Fisher Scientific, Bremen, Germany). This housing has an adjustable probe mount that allows the adjustment of the probe depth and also the exchange between APCI, APPI and ESI probes. Besides, this commercial housing has two windows (located in the left and front side) that can be removed to install the PEEK adapter for the capillary DBD plasma jet probe, being the HPLC eluent nebulized and vaporized in the same manner as for APCI. This PEEK adapter was manufactured at ISAS (Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V., Dortmund, Germany), as reported by Hayen *et al.*[4] Ionization was carried

out by a DBD with a plasma cone (plasma jet) outside the electrode region. The plasma was operated with helium 5.0 (99.999% purity) at a flow of 200 mL/min. The capillary DBD probe consisted of a 3-cm long glass capillary with an inner diameter of 500 μm and an outer diameter of 1.2 mm (that means 5 μL of gas capacity). Rings made of brass with an inner diameter of 600 μm are located around the capillary, forming electrodes with a separation distance of 12 mm. The distance of the electrode to the end of the capillary is 2 mm. A periodic positive voltage pulse (6.5 kV with a frequency of 20 kHz and a pulse width of 2 μs) is applied. The plasma electrodes are enclosed in a teflon tube not only for safety precautions but also to prevent a discharge between the electrodes outside the capillary. This teflon tube containing the DBD was located in the left side of the source housing, in radial position regarding to the MS inlet capillary (heated at 275 ºC). This ion source, like the unmodified APCI source, is working with a heated nebulizer maintained at 450 ºC. Nitrogen (99.999% purity) was used to nebulize the liquid eluent (sheath gas, flow rate set at 40.0 arbitrary units) and also to transport the finely dispersed sample droplets through the heated ceramic tube in which they were vaporized (auxiliary gas, flow rate set at 5.0 arbitrary units). Additionally, another nitrogen flow (sweep gas, flow rate of 2.0 arbitrary units) through the opposite direction of ions is used.

RESULTS

Multiclass detection of organic contaminants in virgin olive oil.

Table S1. LC/DBDI-MS analysis of multiclass pesticides and priority contaminants in an olive oil extract (QuEChERS, undiluted). Linearity and matrix effects (slope ratios matrix/solvent) are showed for 16 selected compounds. To evaluate the matrix effects, the slopes obtained in the calibration with matrix-matched standards were compared with those obtained with solvent-based standards, calculating slope ratios matrix/solvent for each compound.

	Compound	Rt(min)	Ion	Formula ion	Linearity (r)	Matrix effects
1	Dimethoate	5.04	$[M+H]^+$	$C_5H_{13}NO_3PS_2$	0.99935	1.09
2	Diuron	7.88	$[M+H]^+$	$C_9H_{11}Cl_2N_2O$	0.99930	1.03
3	Terbuthylazine	8.99	$[M+H]^+$	$C_9H_{17}ClN_5$	0.99990	1.15
4	Malathion	9.73	$[M+H]^+$	$C_{10}H_{20}O_6PS_2$	0.99745	0.89
5	Acenaphtylene	10.80	$[M]^{\cdot+}$	$C_{12}H_8$	0.99970	0.87
6	Endosulfan sulfate	10.91	$[M-H]^-$	$C_9H_5Cl_6SO_4$	0.99965	0.91
7	Fluorene	11.65	$[M]^{\cdot+}$	$C_{13}H_{10}$	0.99875	0.75
8	Acenaphthene	11.88	$[M]^{\cdot+}$	$C_{12}H_{10}$	0.99935	0.70
9	Oxyfluorfen	11.97	$[M+H]^+$	$C_{15}H_{12}ClF_3NO_4$	0.99985	1.05
10	Phenanthrene	12.08	$[M]^{\cdot+}$	$C_{14}H_{10}$	0.99930	0.94
11	Anthracene	12.39	$[M]^{\cdot+}$	$C_{14}H_{10}$	0.99940	0.85
12	Fluoranthene	13.13	$[M]^{\cdot+}$	$C_{16}H_{10}$	0.99960	0.92
13	Pyrene	13.72	$[M]^{\cdot+}$	$C_{16}H_{10}$	0.99985	0.89
14	Benz[a]anthracene	14.70	$[M]^{\cdot+}$	$C_{18}H_{12}$	0.99960([a])	1.27([a])
15	Chrysene					
16	Benzo[b]fluoranthene	16.49	$[M]^{\cdot+}$	$C_{20}H_{12}$	0.99970	1.18

([a]) Sum of benz[a]anthracene and chrysene. Both compounds coelute in the same chromatographic peak.

Multiclass pesticide testing in orange. The proposed LC/DBDI-MS was also tested in orange matrix as a model of pesticide testing in non-fatty vegetable matrices. Matrix-matched standards using the QuEChERS procedure spiked with a mixture of representative pesticides were prepared. **Table S2** includes the data for the 33 studied

compounds. In most cases, $[M+H]^+$ was the observed ion. Only in the case of dimethoate, chlorpyrifos, prochloraz, metalaxyl, and krexosim methyl, the protonated molecule was not the most abundant ion in the mass spectrum. This might be attributed to in-source collisional-induced dissociation (CID) fragmentation, although some fragmentation events may occur in the plasma.[5] Further work on decoupling and elucidating the fragmentation origin should be accomplished.

Accurate mass measurements average errors were kept below 2 ppm in most cases, despite being undertaken at low concentration levels (10 µg kg^{-1}). The sensitivity attained was satisfactory in most cases. Signal-to-noise ratios obtained for the tested concentration level were distinctly higher than 50:1 in most cases. Actually, LODs are in general in the low µg kg^{-1} range, thus demonstrating a relative competitive performance when compared with electrospray ionization, and fulfilling the most stringent detectability requirements established by EU for this type of samples.

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Table S2. LC/DBDI-MS analysis of multiclass pesticides in an orange extract (QuEChERS) spiked at 10 µg kg^{-1}. All the compounds were detected in the positive ionization mode.

	Compound	RT (min)	ion	formula ion	theoretical m/z	Experim. m/z	Error ppm	Area
1	Difenoxuron	3.75	$[M+H]^+$	$C_{16}H_{19}N_2O_3$	287.13902	287.13794	-3.8	4.71E+05
2	Imidacloprid	5.87	$[M+H]^+$	$C_9H_{11}ClN_5O_2$	256.05958	256.05947	-0.4	9.01E+05
		5.85	Frg. 1	$C_9H_{10}ClN_4$	209.05885	209.05884	-0.1	2.96E+05
		5.84	Frg. 2	$C_9H_{11}N_4$	175.09782	175.09748	-2.0	2.35E+05
3	Dimethoate	6.06	$[M+H]^+$	$C_5H_{13}NO_3PS_2$	230.00690	n.d.	--	--
		6.06	Frg. 1	$C_4H_8O_3PS_2$	198.96470	198.96453	-0.8	1.59E+05
4	Imazalil	6.58	$[M+H]^+$	$C_{14}H_{15}Cl_2N_2O$	297.05559	297.05493	-2.2	4.42E+06
5	Thiacloprid	6.81	$[M+H]^+$	$C_{10}H_{10}ClN_4S$	253.03092	253.03023	-2.7	1.86E+06
6	Monuron	7.25	$[M+H]^+$	$C_9H_{12}ClN_2O$	199.06327	199.06285	-2.1	5.47E+05
7	Desethyl terbuthylazine	7.38	$[M+H]^+$	$C_7H_{13}N_5Cl$	202.08540	202.08515	-1.2	2.68E+06
		7.35	Frg. 1	$C_3H_5ClN_5$	146.02280	146.02246	-2.3	2.82E+05
8	Chlorotoluron	7.92	$[M+H]^+$	$C_{10}H_{14}N_2OCl$	213.07892	213.07872	-0.9	5.14E+05
9	Isoproturon	8.11	$[M+H]^+$	$C_{12}H_{19}N_2O$	207.14919	207.14903	<0.1	7.16E+05
10	Atrazine	8.15	$[M+H]^+$	$C_8H_{15}ClN_5$	216.10105	216.10073	-1.5	2.19E+06
11	Pyrimethanil	8.15	$[M+H]^+$	$C_{12}H_{14}N_3$	200.11822	200.11838	0.8	1.34E+06
12	Metalaxyl	8.16	$[M+H]^+$	$C_{15}H_{22}NO_4$	280.15433	280.15293	-5.0	5.74E+05
		8.12	Frg. 1	$C_{13}H_{18}NO_2$	220.13321	220.13283	-1.7	3.28E+05
		8.17	Frg. 2	$C_{12}H_{18}NO$	192.13829	192.13791	-2.0	2.86E+06
13	DEET (Diethyltoluamide)	8.17	$[M+H]^+$	$C_{12}H_{18}NO$	192.13829	192.13793	-1.9	2.86E+06
14	Ethoxyquin	8.17	$[M+H]^+$	$C_{14}H_{20}NO$	218.15394	218.15276	-5.4	3.79E+05
15	Diuron	8.18	$[M+H]^+$	$C_9H_{11}Cl_2N_2O$	233.02429	233.02375	-2.3	4.94E+05
16	Monolinuron	8.18	$[M+H]^+$	$C_9H_{12}ClN_2O_2$	215.05818	215.05782	-1.7	3.88E+05
17	Prochloraz	8.71	$[M+H]^+$	$C_{15}H_{17}Cl_3N_3O_2$	376.03809	376.03699	-2.9	3.32E+04
		8.71	Frg. 1	$C_{12}H_{13}NO_2Cl_3$	308.00064	308.00028	-1.2	2.31E+05
18	Propazine	8.90	$[M+H]^+$	$C_9H_{17}ClN_5$	230.11670	230.11619	-2.2	2.10E+06
19	Fenamiphos	9.00	$[M+H]^+$	$C_{13}H_{23}NO_3PS$	304.11308	304.11306	-0.1	1.46E+06
20	Terbuthylazine	9.07	$[M+H]^+$	$C_9H_{17}ClN_5$	230.11670	230.11624	-2.0	1.84E+06
		9.05	Frg. 1	$C_5H_9ClN_5$	174.05410	174.05386	-1.4	4.49E+05
21	Linuron	9.09	$[M+H]^+$	$C_9H_{11}Cl_2N_2O_2$	249.01921	249.01876	-1.8	3.40E+05
22	Bromuconazole isomer-1	9.09	$[M+H]^+$	$C_{13}H_{13}BrCl_2N_3O$	375.96285	375.96014	-3.2	1.18E+05
	Bromuconazole isomer-2	9.39	$[M+H]^+$	$C_{13}H_{13}BrCl_2N_3O$	375.96285	375.96213	2.1	1.74E+05
23	Triadimefon	9.17	$[M+H]^+$	$C_{14}H_{17}ClN_3O_2$	294.10038	294.09956	-2.8	1.35E+06
		9.18	Frg. 1	$C_{11}H_{14}OCl$	197.07277	197.07243	-1.7	1.30E+05
24	Fenhexamid	9.22	$[M+H]^+$	$C_{14}H_{18}Cl_2NO_2$	302.07091	302.07025	-2.2	1.02E+06
25	Tebuconazole	9.32	$[M+H]^+$	$C_{16}H_{23}ClN_3O$	308.15242	308.15169	-2.4	1.58E+06
		9.32	Frg. 1	$C_{16}H_{21}N_3Cl$	290.14185	290.14103	-2.8	3.12E+05
26	Chlorfenvinphos E-isomer	9.81	$[M+H]^+$	$C_{12}H_{15}Cl_3O_4P$	358.97680	358.97729	1.4	3.02E+05
		9.81	Frg. 1	$C_4H_{12}O_4P$	155.04677	155.04659	-1.2	9.22E+04
	Chlorfenvinphos Z-isomer	10.09	$[M+H]^+$	$C_{12}H_{15}Cl_3O_4P$	358.97680	n.d.	--	--
		10.09	Frg. 1	$C_4H_{12}O_4P$	155.04677	155.04655	-1.4	1.48E+04
27	Kresoxim-methyl	9.81	$[M+H]^+$	$C_{18}H_{20}NO_4$	314.13868	n.d.	--	--
		9.83	Frg. 1	$C_{17}H_{16}NO_3$	282.11247	282.11209	-1.3	1.32E+05
		9.81	Frg. 2	$C_{15}H_{12}NO$	222.09134	222.09123	-0.5	6.50E+04
28	Difenoconazole	9.96	$[M+H]^+$	$C_{19}H_{18}Cl_2N_3O_3$	406.07197	406.07110	-2.2	1.02E+06
29	Trifloxystrobin	10.48	$[M+H]^+$	$C_{20}H_{20}F_3N_2O_4$	409.13697	409.13653	-1.1	7.37E+05
		10.48	Frg. 1	$C_9H_7NF_3$	186.05251	186.05238	-0.7	3.58E+05
30	Diazinon	10.61	$[M+H]^+$	$C_{12}H_{22}N_2O_3PS$	305.10833	305.10788	-1.5	1.25E+06
		10.61	Frg. 1	$C_{10}H_{18}O_3N_2PS$	277.07703	277.07676	-1.0	1.09E+05
		10.61	Frg. 2	$C_8H_{13}N_2O$	153.10224	153.10201	-1.5	2.09E+05

31	Pirimiphos-methyl	10.72	$[M+H]^+$	$C_{11}H_{21}N_3O_3PS$	306.10357	306.10317	-1.3	2.15E+06
32	Buprofezin	11.24	$[M+H]^+$	$C_{16}H_{24}N_3OS$	306.16346	306.16375	0.9	2.83E+05
		11.23	Frg. 1	$C_9H_{17}N_2OS$	201.10561	201.10581	1.0	9.92E+04
33	Hexythiazox	11.93	$[M+H]^+$	$C_{17}H_{22}ClN_2O_2S$	353.10850	353.10781	-2.0	1.66E+05
		11.92	Frg. 1	$C_{11}H_{12}N_2O_2SCl$	271.03025	271.03001	-0.9	3.06E+04
		11.94	Frg. 2	$C_{10}H_{11}ClNOS$	228.02444	228.02413	-1.4	1.98E+05
		11.94	Frg. 3	$C_9H_{11}NCl$	168.05745	168.05729	-1.0	6.05E+04

n.d.: not detected

Simultaneous multiclass detection of priority and emerging organic contaminants in effluent wastewater.

Figure S1. LC/DBDI-MS analysis of multiclass priority and emerging contaminants in an effluent wastewater sample extract spiked at 10 µg L^{-1} (each). Simultaneous detection of positive and negative ions was accomplished using polarity switching acquisition mode. EICs corresponding to the following selected contaminants: a) cocaine, b) delta-9-THC, c) ethoxyquin, d) propanolol, e) sulfathiazole, f) fenofibrate, g) pentachlorobenzene, h) alachlor, i) chlortoluron, j) diazinon, k) malathion, l) monuron, m) propazine and terbuthylazine, n) linuron, o) hexachlorobenzene.

Figure S1

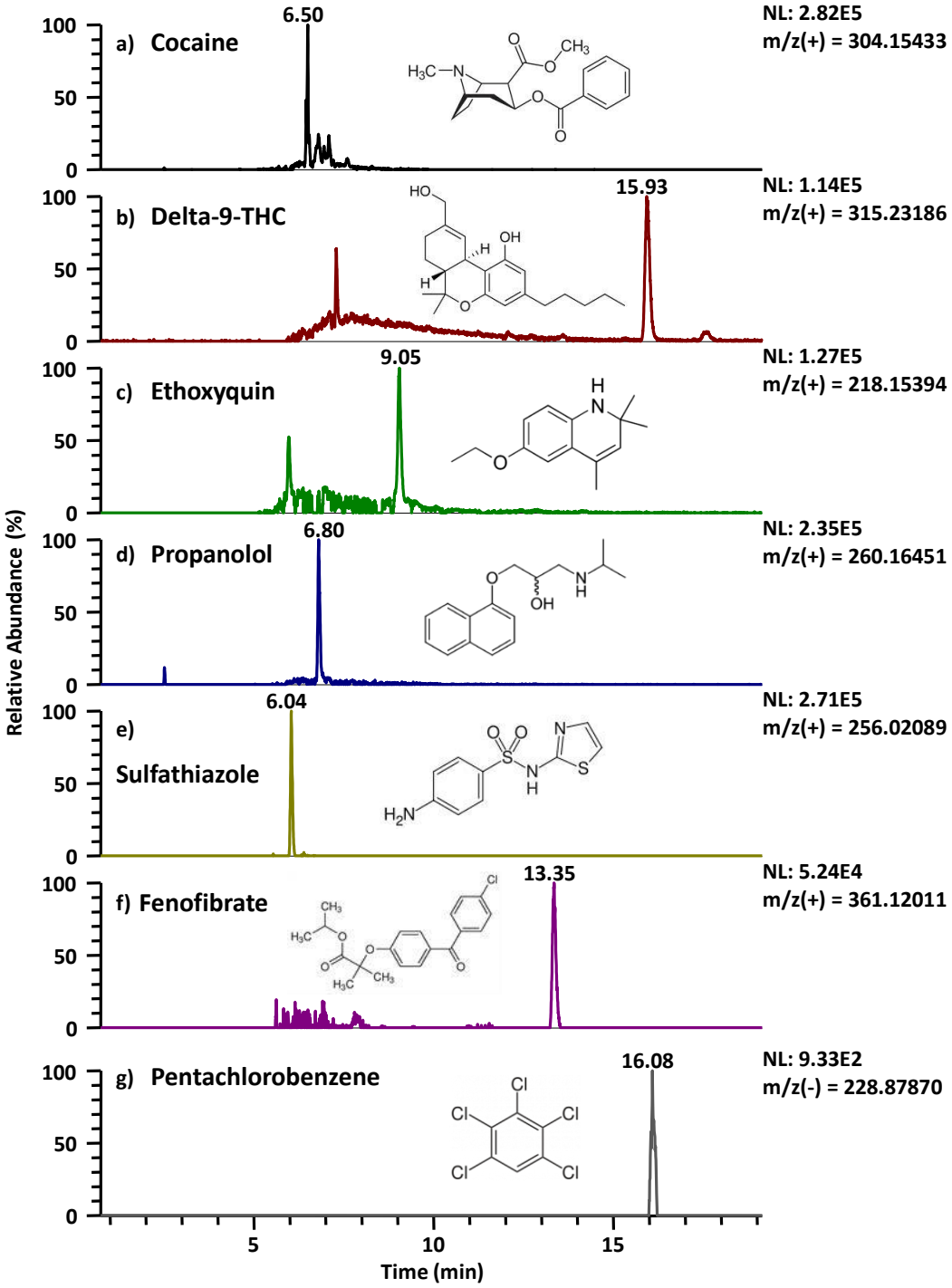
a) Cocaine
6.50
NL: 2.82E5
m/z(+) = 304.15433
b) Delta-9-THC
15.93
NL: 1.14E5
m/z(+) = 315.23186
c) Ethoxyquin
9.05
NL: 1.27E5
m/z(+) = 218.15394
d) Propanolol
6.80
NL: 2.35E5
m/z(+) = 260.16451
e) Sulfathiazole
6.04
NL: 2.71E5
m/z(+) = 256.02089
f) Fenofibrate
13.35
NL: 5.24E4
m/z(+) = 361.12011
g) Pentachlorobenzene
16.08
NL: 9.33E2
m/z(-) = 228.87870
Relative Abundance (%)
Time (min)

Figure S1 (cont)