Supporting Information

IMPROVED FULLY AUTOMATED METHOD FOR THE DETERMINATION OF MEDIUM TO HIGHLY POLAR PESTICIDES IN SURFACE AND GROUNDWATER AND APPLICATION IN TWO DISTINCT AGRICULTURE-IMPACTED AREAS.

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Table S1. Target pesticides, main physical-chemical properties, and current legislative status.

Analyte	Chemical class	Formula[‡]	MM (g/mol)[‡]	Solubility (mg/L)[‡]	K_{oc} (mL/g)[‡]	K_{ow} logP[‡]	GUS[‡]	DT50[‡] (days)	Legislative status[‡]	Currently used in Spain[‡]	EQS[Ω] (µg/L)	Method LODs[ε] (ng/L)
2,4-D	Alkylchlorophenoxy	$C_8H_6Cl_2O_3$	221.04	24300	39	-0.82	3.82	7.7	✓	✓		
Acetamiprid[ε]	Neonicotinoid	$C_{10}H_{11}ClN_4$	222.67	2950	200	0.80	0.94	4.7	✓	✓		8.3
Alachlor[×]	Chloroacetamide	$C_{14}H_{20}ClNO_2$	269.77	240	335	3.09	0.8	-	X		0.7	
Atrazine[×]	Triazine	$C_8H_{14}ClN_5$	215.68	35	100	2.70	2.57	-	X		2	
Azinphos-ethyl	Organophosphate	$C_{12}H_{16}N_3O_3PS_2$	345.38	4.5	1500	3.18	1.4	-	X			
Azinphos-methyl	Organophosphate	$C_{10}H_{12}N_3O_3PS_2$	317.32	28	1112	2.96	1.42	-	X			
Azinphos-methyl-oxon	Metabolite	$C_{10}H_{12}N_3O_4PS$	301.26	2604*	10 *	0.77*	-	-	-			
Bentazone	Benzothiazinone	$C_{10}H_{12}N_2O_3S$	240.30	7112	55	-0.46	1.95	80	✓	✓		
Bromoxynil	Hydroxybenzonitrile	$Br_2C_6H_2(OH)CN$	276.90	38000	302	0.27	1.71	13	✓	✓		
Chlorfenvinphos[×]	Organophosphate	$C_{12}H_{14}Cl_3O_4P$	359.60	145	680	3.80	1.72	7	X		0.3	
Chlorpyrifos[×]	Organophosphate	$C_9H_{11}Cl_3NO_3PS$	350.58	1.05	5509	4.70	0.58	5	✓	✓	0.1	
Chlortoluron	Phenylurea	$C_{10}H_{13}ClN_2O$	212.68	74	196	2.50	2.62	42	✓	✓		
Cyanazine	Triazine	$C_9H_{13}ClN_6$	240.69	171	190	2.10	2.07	-	X			
Clothianidin[ε]	Neonicotinoid	$C_6H_8ClN_5O_2S$	249.68	340	123	0.90	3.74	40.3	X	✓		8.3
Deisopropylatrazine	Metabolite	$C_5H_8ClN_5$	173.60	980	130	1.15	-	-	-			
Desethylatrazine	Metabolite	$C_6H_{10}ClN_5$	187.63	2700	110	1.51	4.37	-	-			
Diazinon	Organophosphate	$C_{12}H_{21}N_2O_3PS$	304.35	60	609	3.69	1.51	4.3	X			
Dichlorvos[×]	Organophosphate	$C_4H_7Cl_2O_4P$	220.98	18000	50	1.90	0.69	-	X		7×10^{-4}	
Diflufenican	Carboxamide	$C_{19}H_{11}F_5N_2O_2$	394.29	0.05	5504	4.20	1.19	-	✓	✓		
Dimethoate	Organophosphate	$C_5H_{12}NO_3PS_2$	229.26	25900	25*	0.75	2.18	12.6	X	✓[∞]		
Diuron[×]	Phenylurea	$C_9H_{10}Cl_2N_2O$	233.09	35.6	680	2.87	2.65	8.8	✓	✓	1.8	
Fenitrothion	Organophosphate	$C_9H_{12}NO_5PS$	277.23	19	2000	3.32	0.48	1.1	X	✓		
Fenitrothion oxon	Metabolite	$C_9H_{12}NO_6P$	261.17*	301 *	21*	1.69*	-	-	-			
Fenthion	Organophosphate	$C_{10}H_{15}O_3PS_2$	278.33	4.2	1500	4.84	1.26	-	X			
Fenthion oxon	Metabolite	$C_{10}H_{15}O_4PS$	262.26*	213.5*	57 *	2.31*	-	-	-			
Fenthion oxon sulfone	Metabolite	$C_{10}H_{15}O_6PS$	294.03*	7602*	13*	0.28*	-	-	-			
Fenthion oxon sulfoxide	Metabolite	$C_{10}H_{15}O_5PS$	278.26*	1222*	11*	0.15*	-	-	-			

Fenthion sulfone	Metabolite	$C_{10}H_{15}O_5PS_2$	310.33*	190.4*	235	2.05*	-	-	-			
Fenthion sulfoxide	Metabolite	$C_{10}H_{15}O_4PS_2$	294.33*	3.72*	183	1.92*	-	-	-			
Fluroxypyr	Pyridine	$C_7H_5Cl_2FN_2O_3$	255.03	6500	10*	0.04	3.7	10.5	✓	✓		
Imidacloprid[ε]	Neonicotinoid	$C_9H_{10}ClN_5O_2$	255.66	610	6719	0.57	3.69	30	✓	✓		8.3
Irgarol[x]	Triazine	$C_{11}H_{19}N_5S$	253.37	7	1569	3.95	-	-	X		0.016	
Isoproturon[x]	Phenylurea	$C_{12}H_{18}N_2O$	206.28	70.2	251*	2.5	2.61	40	X	✓	1	
Linuron	Phenylurea	$C_9H_{10}Cl_2N_2O_2$	249.09	63.8	843	3	2.11	13	X	✓		
Malaoxon	Metabolite	$C_{10}H_{19}O_7PS$	314.29*	7500*	4650*	0.52*	-	-	-			
Malathion	Organophosphate	$C_{10}H_{19}O_6PS_2$	330.36	148	1800	2.75	0.00	0.4	✓	✓		
MCPA	Organophosphate	$C_9H_9ClO_3$	200.62	29390	29*	-0.81	2.98	13.5	✓	✓		
Mecoprop	Aryloxyalkanoic acid	$C_{10}H_{11}ClO_3$	214.65	250000	47	-0.19	2.29	37	X	✓		
Methiocarb[ε]	Carbamate	$C_{11}H_{15}NO_2S$	225.31	27	182*	3.18	1.82	1.6	✓	✓		2
Metolachlor	Chloroacetamide	$C_{15}H_{22}ClNO_2$	283.80	530	120	3.40	2.36	88	X			
Molinate	Thiocarbamate	$C_9H_{17}NOS$	187.30	1100	190	2.86	1.89	4	X	✓		
Pendimethalin	Dinitroaniline	$C_{13}H_{19}N_3O_4$	281.31	0.33	17491	5.40	-0.28	4	✓	✓		
Propanil	Anilide	$C_9H_9Cl_2NO$	218.08	95	149	2.29	-0.51	1.2	X	✓		
Quinoxyfen[x]	Quinoline	$C_{15}H_8Cl_2FNO$	308.13	0.05	23°	4.66	-0.8	5	✓	✓	2.7	
Simazine[x]	Triazine	$C_7H_{12}ClN_5$	201.66	5	130	2.30	2.2	46	X	✓	4	
Terbuthylazine	Triazine	$C_9H_{16}ClN_5$	229.71	6.6	329*	3.40	2.19	6	✓	✓		
Terbutryn[x]	Triazine	$C_{10}H_{19}N_5S$	241.36	25	2432	3.66	2.21	27	X		0.34	
Thiacloprid[ε]	Neonicotinoid	$C_{10}H_9ClN_4S$	252.72	184	615°	1.26	1.1	1000	✓			8.3
Thiamethoxam[ε]	Neonicotinoid	$C_8H_{10}ClN_5O_3S$	291.71	4100	56	-0.13	3.58	30.6	X	✓		8.3
Thifensulfuron methyl	Sulfonylurea	$C_{12}H_{13}N_5O_6S_2$	387.39	54.1	28	-1.65	3.05	22	✓	✓		
Triallate	Thiocarbamate	$C_{10}H_6Cl_3NOS$	304.70	4.1	3034	4.06	0.61	104	✓	✓		

[x] Compound included in the list of priority substances. EC Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regard priority substances in the field of water policy. Retrieved from: https://goo.gl/diHn8W.

[ε] Compound included in the European Watch List and corresponding maximum acceptable method detection limit (ng/L). EC Commission Implementing Decision (EU) 2018/840 of 5 June 2018 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council and repealing Commission Implementing Decision (EU) 2015/495 (notified under document C(2018) 3362). Retrieved from: https://goo.gl/nR4ezg.

‡ The PPDB, Pesticide Properties Database. http://sitem.herts.ac.uk/aeru/footprint/index2.htm. - Lewis, K.A., Tzilivakis, J., Warner, D. and Green, A. (2016). An international database for pesticide risk assessments and management. Human and Ecological Risk Assessment: An International Journal, 22(4), 1050-1064.

* Data estimated using the US Environmental Protection Agency EPISuite™ http://www.Chemspider.com.

° Kegley, S.E., Hill, B.R., Orme S., Choi A.H., PAN Pesticide Database, Pesticide Action Network, North America (Oakland, CA, 2016), http://www.pesticideinfo.org.

^ Calculated using the mathematical formula: GUS = log10 (half-life) x [4 - log10 (Koc)].

Ω Environmental Quality Standards (EQS) for priority substances in surface waters.

∞ Commission implementing regulation (EU) 2019/1090 of 26 June 2019 concerning the non-renewal of approval of the active substance dimethoate. Member States shall withdraw authorizations for plant protection products containing dimethoate as active substance by 17 January 2020 at the latest.

MM: molecular mass; Solubility: solubility in water at 20 ^{o}C; K_{oc}: organic carbon partition coefficient; K_{ow}: octanol-water partition coefficient; GUS: leaching potential index; DT50: biodegradability, water phase only, expressed as *half-life* in days; Legislative status: ✓ approved, **X** not approved.

Table S2. Recovery and repeatability (RSD, relative standard deviation) obtained from the replicate (n=5) analysis of groundwater and surface water fortified with the target analytes at concentration levels of 10 and 1000 ng/L.

Analyte	**Groundwater**		**Surface water**	
	Analyte recovery ± RSD (%)		**Analyte recovery ± RSD (%)**	
	10 ng/L	**1000 ng/L**	**10 ng/L**	**1000 ng/L**
2,4-D	91 ± 15	95 ± 9	126 ± 7	127 ± 4
Acetamiprid	80 ± 19	101 ± 14	93 ± 5	80 ± 5
Alachlor	82 ± 11	80 ± 16	125 ± 5	98 ± 6
Atrazine	118 ± 10	119 ± 4	89 ± 5	94 ± 8
Azinphos ethyl	112 ± 17	92 ± 13	118 ± 17	85 ± 8
Azinphos methyl	114 ± 20	112 ± 18	113 ± 9	100 ± 10
Azinphos methyl oxon	121 ± 3	90 ± 5	BLOD	83 ± 23
Bentazone	107 ± 15	86 ± 16	104 ± 5	81 ± 8
Bromoxynil	82 ± 6	82 ± 18	121 ± 4	90 ± 5
Chlorfenvinphos	113 ± 17	90 ± 4	120 ± 14	93 ± 6
Chlorpyrifos	116 ± 11	89 ± 4	105 ± 7	122 ± 3
Chlortoluron	123 ± 16	88 ± 14	114 ± 11	87 ± 18
Clothianidin	BLOD	99 ± 7	BLOD	90 ± 12
Cyanazine	127 ± 24	120 ± 20	126 ± 4	120 ± 13
DEA	81 ± 6	93 ± 4	90 ± 6	102 ± 8
DIA	BLOD	104 ± 8	125 ± 3	112 ± 6
Diazinon	106 ± 10	104 ± 9	125 ± 18	106 ± 4
Dichlorvos	BLOD	87 ± 3	123 ± 7	95 ± 5
Diflufenican	BLOD	84 ± 20	BLOD	80 ± 17
Dimethoate	BLOD	84 ± 5	BLOD	110 ± 9
Diuron	111 ± 16	121 ± 4	85 ± 17	86 ± 11
Fenitrothion	BLOD	98 ± 3	BLOD	81 ± 5
Fenitrothion oxon	82 ± 17	88 ± 5	118 ± 8	91 ± 3
Fenthion oxon	107 ± 4	124 ± 20	102 ± 8	115 ± 6
Fenthion oxon sulfone	83 ± 5	106 ± 8	BLOD	94 ± 17
Fenthion oxon sulfoxide	99 ± 12	110 ± 16	98 ± 7	89 ± 8
Fenthion sulfone	116 ± 4	120 ± 4	BLOD	83 ± 11
Fenthion sulfoxide	84 ± 3	104 ± 8	95 ± 5	107 ± 11
Fluroxypyr	BLOD	97 ± 6	BLOD	79 ± 20
Imidacloprid	84 ± 4	83 ± 4	112 ± 15	118 ± 5
Irgarol	110 ± 15	122 ± 16	116 ± 10	102 ± 11
Isoproturon	104 ± 5	83 ± 5	107 ± 7	119 ± 13
Linuron	92 ± 4	106 ± 12	109 ± 6	86 ± 20
Malaoxon	120 ± 11	124 ± 10	125 ± 12	121 ± 13
Malathion	BLOD	80 ± 20	BLOD	88 ± 5
MCPA	115 ± 19	86 ± 13	93 ± 20	113 ± 13
Mecoprop	99 ± 16	86 ± 18	105 ± 14	106 ± 15
Methiocarb	111 ± 15	116 ± 19	88 ± 11	104 ± 12
Metolachlor	122 ± 10	114 ± 13	122 ± 19	118 ± 4
Molinate	BLOD	81 ± 8	BLOD	88 ± 7

Oxadiazon	BLOD	109 ± 20	BLOD	104 ± 7
Pendimethalin	BLOD	99 ± 4	BLOD	121 ± 4
Propanil	120 ± 4	85 ± 17	103 ± 19	110 ± 9
Quinoxyfen	95 ± 3	88 ± 21	73 ± 5	106 ± 19
Simazine	123 ± 12	86 ± 20	96 ± 4	79 ± 19
Terbuthylazine	115 ± 19	111 ± 13	111 ± 7	83 ± 4
Terbutryn	99 ± 3	100 ± 3	117 ± 13	95 ± 8
Thiacloprid	112 ± 15	99 ± 6	122 ± 3	81 ± 18
Thiamethoxam	BLOD	80 ± 6	88 ± 12	98 ± 12
Thifensulfuron methyl	108 ± 14	84 ± 19	115 ± 3	91 ± 11
Triallate	75 ± 19	113 ± 19	106 ± 20	87 ± 14

BLOD: Below limit of detection

Table S3. Recovery and repeatability (RSD, relative standard deviation) obtained from the replicate (n=5) analysis of LC-grade water fortified with the target analytes at concentration levels of 10, 100 and 1000 ng/L, and limits of detection (LOD) and determination (LODet) achieved.

Analyte	Analyte recovery ± RSD (%)			Sensitivity	
	10 ng/L	100 ng/L	1000 ng/L	LOD ng/L	LODet ng/L
2,4-D	79 ± 14	81 ± 12	88 ± 5	6.1	20
Acetamiprid	106 ± 9	81 ± 19	95 ± 9	0.16	0.53
Alachlor	93 ± 15	105 ± 1	97 ± 3	1.2	3.8
Atrazine	102 ± 5	123 ± 14	92 ± 2	0.14	0.88
Azinphos ethyl	113 ± 14	85 ± 6	98 ± 12	0.42	1.4
Azinphos methyl	81 ± 6	92 ± 13	121 ± 13	0.38	1.3
Azinphos methyl oxon	126 ± 10	100 ± 7	108 ± 11	3.1	10
Bentazone	76 ± 20	88 ± 20	113 ± 10	4.3	14
Bromoxynil	111 ± 5	99 ± 5	121 ± 8	2.6	8.6
Chlorfenvinphos	112 ± 11	106 ± 4	112 ± 15	0.24	0.80
Chlorpyrifos	123 ± 18	120 ± 10	104 ± 18	0.44	1.5
Chlortoluron	125 ± 20	98 ± 5	107 ± 14	0.13	0.42
Clothianidin	113 ± 11	100 ± 4	80 ± 5	2.3	7.5
Cyanazine	115 ± 7	112 ± 5	124 ± 3	0.081	0.28
DEA	90 ± 6	100 ± 26	102 ± 8	2.3	7.9
DIA	105 ± 21	120 ± 5	116 ± 13	4.4	15
Diazinon	82 ± 3	103 ± 5	125 ± 6	0.042	0.16
Dichlorvos	94 ± 20	120 ± 15	113 ± 14	5.4	18
Diflufenican	121 ± 11	96 ± 13	100 ± 19	1.2	4.0
Dimethoate	120 ± 9	117 ± 17	84 ± 19	0.76	2.6
Diuron	109 ± 4	127 ± 12	124 ± 3	0.13	0.43
Fenitrothion	106 ± 12	123 ± 5	120 ± 17	2.6	8.8
Fenitrothion oxon	120 ± 4	85 ± 8	112 ± 6	0.79	2.6
Fenthion oxon	110 ± 12	119 ± 3	122 ± 7	0.17	0.59
Fenthion oxon sulfone	99 ± 13	125 ± 4	112 ± 20	2.8	9.4
Fenthion oxon sulfoxide	110 ± 4	98 ± 5	109 ± 6	0.13	0.43
Fenthion sulfone	85 ± 20	109 ± 15	120 ± 6	4.2	14
Fenthion sulfoxide	89 ± 5	93 ± 20	106 ± 16	0.41	1.4
Fluroxypyr	BLOD	103 ± 18	102 ± 14	29	95
Imidacloprid	124 ± 20	103 ± 12	81 ± 18	0.87	2.9
Irgarol	89 ± 7	121 ± 16	87 ± 21	0.85	2.8
Isoproturon	91 ± 24	98 ± 16	90 ± 3	0.15	0.50
Linuron	122 ± 3	108 ± 8	114 ± 8	0.58	1.9
Malaoxon	90 ± 19	117 ± 16	123 ± 14	0.15	0.50
Malathion	83 ± 5	82 ± 12	82 ± 12	3.4	12
MCPA	118 ± 6	101 ± 20	82 ± 7	5.5	19
Mecoprop	92 ± 17	109 ± 4	81 ± 13	1.1	3.6
Methiocarb	110 ± 16	123 ± 11	108 ± 12	0.41	1.4
Metolachlor	112 ± 3	108 ± 7	114 ± 4	0.086	0.32
Molinate	93 ± 16	82 ± 17	122 ± 8	1.1	3.6

Oxadiazon	100 ± 4	82 ± 19	88 ± 19	1.3	4.5
Pendimethalin	BLOD	94 ± 4	93 ± 7	17	55
Propanil	122 ± 15	112 ± 10	112 ± 17	0.90	3.0
Quinoxyfen	109 ± 12	86 ± 3	92 ± 7	1.1	3.6
Simazine	113 ± 12	96 ± 20	104 ± 13	0.31	1.1
Terbuthylazine	122 ± 13	117 ± 6	115 ± 9	0.14	0.48
Terbutryn	92 ± 11	106 ± 4	120 ± 4	0.19	0.66
Thiacloprid	97 ± 3	110 ± 18	80 ± 14	0.059	0.21
Thiamethoxam	119 ± 22	120 ± 20	89 ± 1	1.8	6.0
Thifensulfuron methyl	83 ± 1	118 ± 12	80 ± 19	0.022	0.06
Triallate	114 ± 20	110 ± 14	118 ± 4	3.8	13

BLOD: Below limit of detection

Table S4. Concentrations (ng/L) of the individual pesticides and cumulative pesticide concentrations (TOTAL) measured in the water samples collected in the Llobregat River.

PESTICIDES	**Pt 1**	**Pt 2**	**Pt 3**	**Pt 4**	**Pt 5**	**Pt 6**	**Pt 7**	**Pt 8**	**Pt 9**	**Pt 10**	**Pt 11**
2,4-D	n.d.	n.d.	n.d.	n.d.	n.d.	200	n.d.	n.d.	130	n.d.	n.d.
Alachlor	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	18	n.d.	n.d.	24	n.d.
Atrazine	n.d.	13	<6.7	n.d.	n.d.	<6.7	17	n.d.	n.d.	21	<6.7
Azinphos ethyl	n.d.	10	n.d.	n.d.	n.d.	n.d.	69	n.d.	n.d.	110	n.d.
Bromoxynil	n.d.	74	<22	1500	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chlorfenvinphos	n.d.	4.8	n.d.	n.d.	4.8	<2.9	48	n.d.	n.d.	67	<2.9
Chlortoluron	n.d.	67	n.d.	n.d.	30	n.d.	18	n.d.	n.d.	27	n.d.
Cyanazine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	29	n.d.
Diazinon	20	2.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	71	18
Dichlorvos	n.d.	<20	<20	n.d.	<20	n.d.	n.d.	<20	n.d.	130	n.d.
Diflufenican	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	130	n.d.	n.d.	150	n.d.
Diuron	500	24	250	250	260	91	42	120	61	63	240
Fenthion oxon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	37	n.d.	n.d.	n.d.	n.d.
Fenthion sulfoxide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	32	n.d.	n.d.	n.d.	n.d.
Imidacloprid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<10	n.d.	n.d.	190	<10
Irgarol	n.d.	n.d.	n.d.	<6.6	<6.6	n.d.	33	<6.6	n.d.	41	n.d.
Isoproturon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	24	<7.1	n.d.	25	n.d.
Linuron	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	520	n.d.	132	480	n.d.
Malaoxon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	24	n.d.	n.d.	24	n.d.
Malathion	n.d.	n.d.	n.d.	<17	n.d.	n.d.	25	n.d.	n.d.	32	n.d.
Methiocarb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	50	n.d.	n.d.	130	n.d.
Metolachlor	5.1	n.d.	n.d.	n.d.	n.d.	n.d.	25	n.d.	n.d.	28	n.d.
Molinate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	33	n.d.	n.d.	27	n.d.
Propanil	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	19	n.d.	n.d.	n.d.	n.d.
Simazine	16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20	n.d.
Terbuthylazine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	24	n.d.	3.5	30	n.d.
Terbutryn	120	8.9	63	63	71	160	45	130	24	55	n.d.
Thiacloprid	<0.79	n.d.	n.d.	n.d.	n.d.	n.d.	16	n.d.	n.d.	31	n.d.
TOTAL	661	205	313	1813	366	451	1249	250	351	1805	258

n.d.: not detected

<LOQ: below limit of quantification

Total concentration calculated considering only values >LOQ.

Table S5. Concentrations (ng/L) of the individual pesticides and cumulative pesticide concentrations (TOTAL) measured in the water samples collected in the Ter River.

PESTICIDES	Pt 1	Pt 2	Pt 3	Pt 4	Pt 5a	Pt 5b	Pt 6	Pt 7	Pt 8	Pt 9	Pt 10
Bentazone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	110	n.d.	n.d.	n.d.
Diazinon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.3	4.6	n.d.	n.d.
Diuron	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	14	n.d.	n.d.	n.d.	n.d.
Irgarol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5.4	n.d.
MCPA	n.d.	n.d.	18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Metolachlor	n.d.	n.d.	15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	24	n.d.
Terbutryn	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.1	5.3	n.d.
TOTAL	n.d.	n.d.	33	n.d.	n.d.	n.d.	14	112	8.7	34	n.d.

n.d.: not detected

Total concentration calculated considering only values >LOQ.

GW 100 ng/L

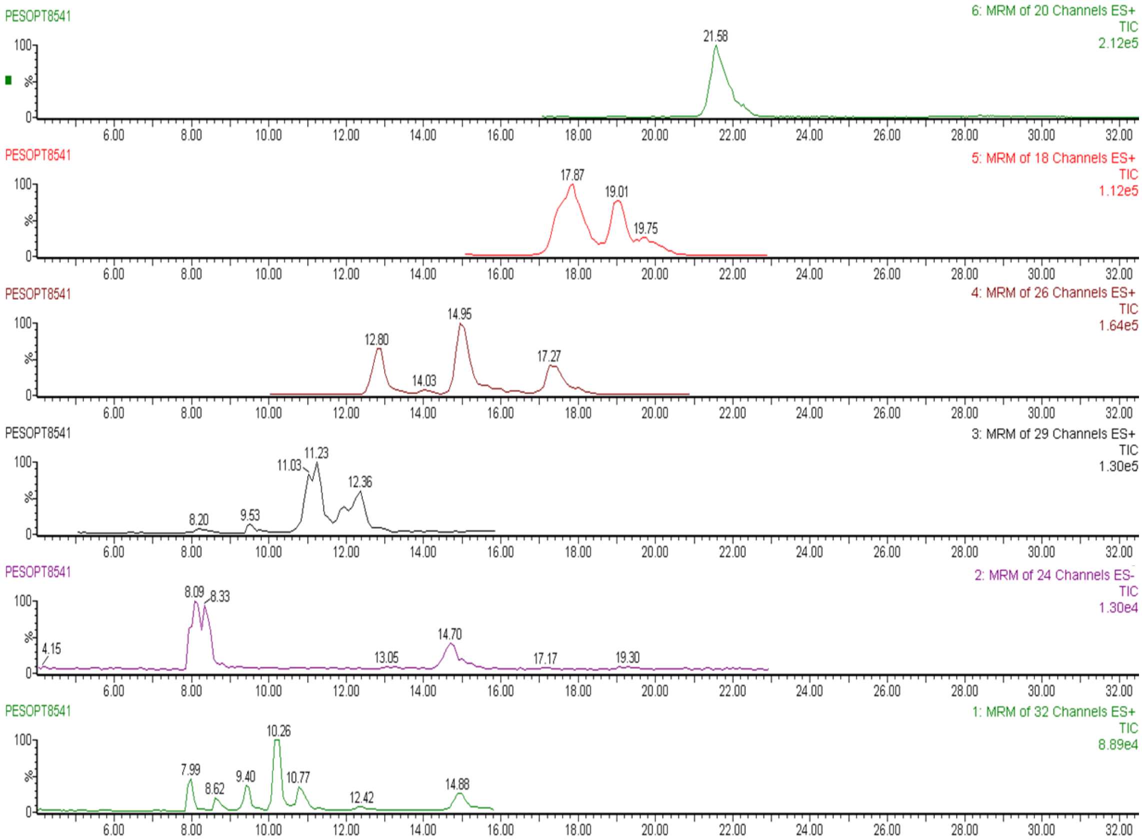

Figure S1. Total Ion Current (TIC) chromatograms obtained from the analysis of a fortified groundwater sample (100 ng/L) showing the acquisition of the 146 SRM transitions set for determination of the 51 target pesticides and their 45 SIL analogs in six different acquisition windows along the analytical run.

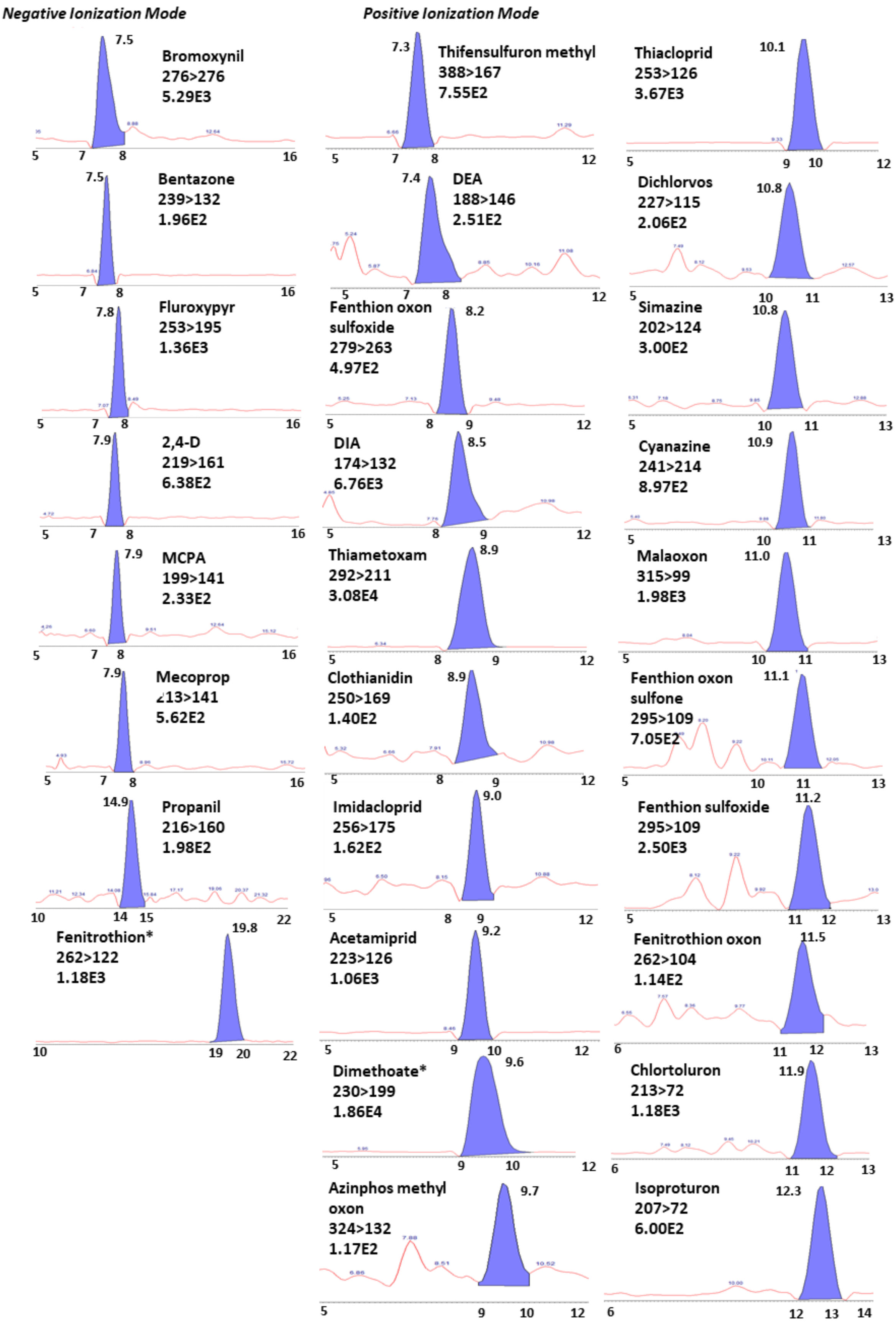

Figure S2. Extracted ion chromatograms (XIC) of the target pesticides after on-line SPE-LC-MS/MS analysis of a surface water sample fortified at a concentration of 100 ng/L (or 500 ng/L in the case of those compounds marked with *).

Positive Ionization Mode

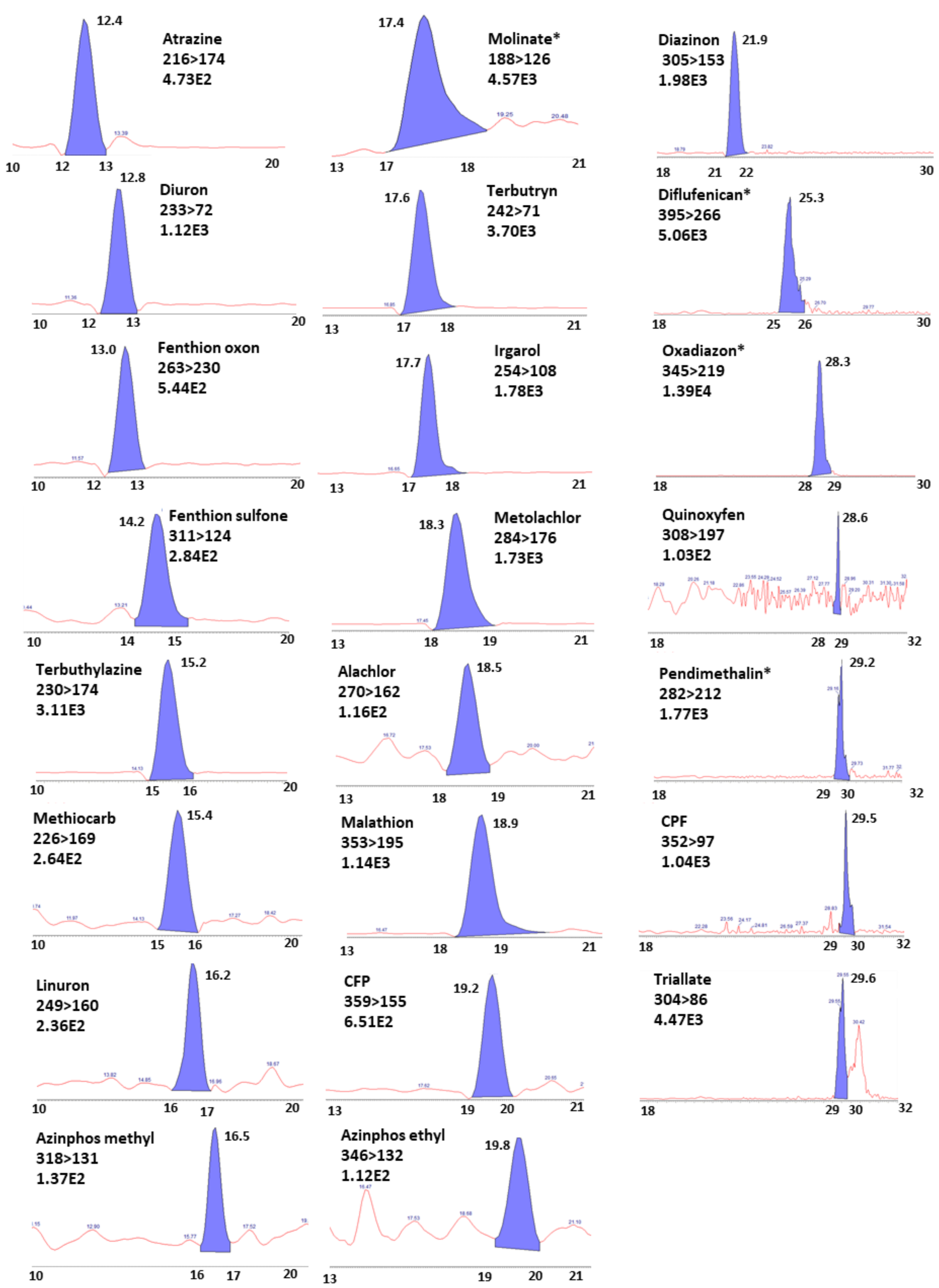

Figure S2. (continued).

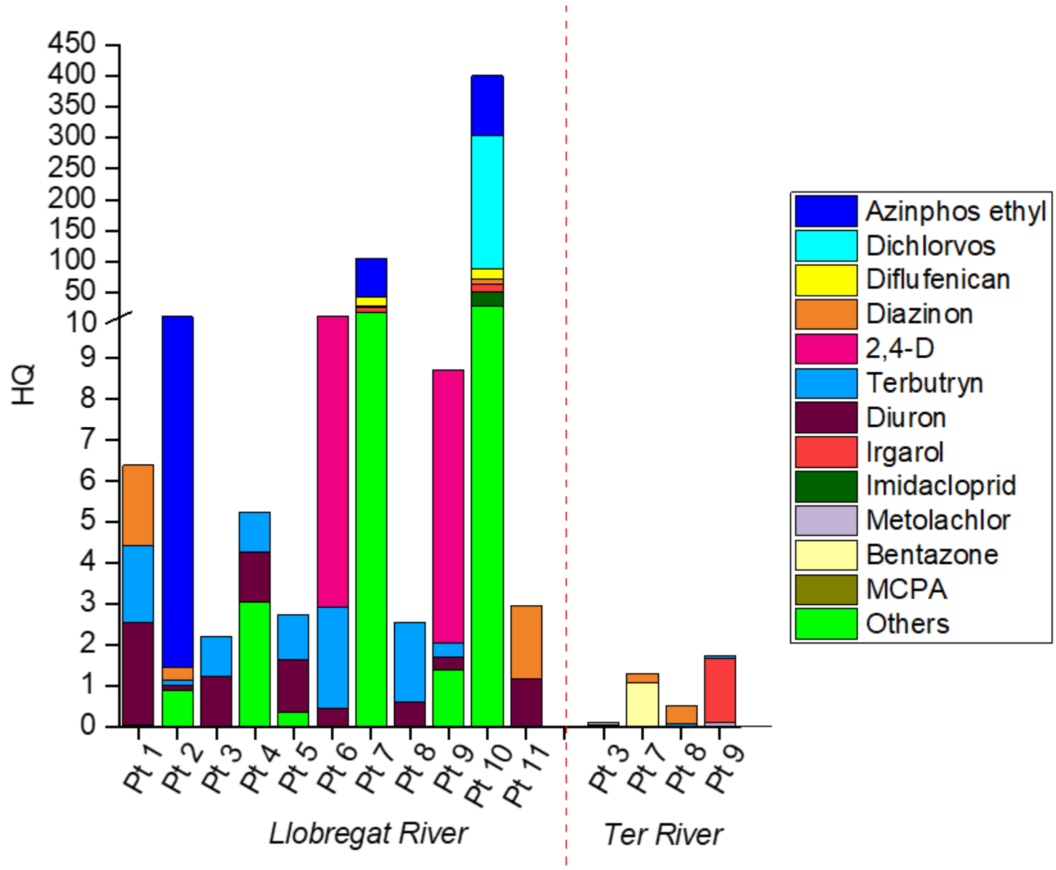

Figure S3. Hazard Quotients (HQ) in the samples analysed, based on the individual HQs of the pesticides measured in each sample. The HQs corresponding to those pesticides detected in the samples but not specified in the legend have been grouped as "*Others*".