

Supplementary Information

Plasma Levels of Organochlorine Pesticides in Historically Exposed Vector Control Workers from Rio de Janeiro, Brazil

**Ana Paula Neves,^{*,a} Heldis B. de Oliveira,^b Tatyane P. dos Santos,^b Leandro V. B. de Carvalho,^b
Eline S. Gonçalves,^c Ariane L. Larentis,^{b,d} Sergio R. Alves^b and Ana Cristina S. Rosa^b**

*^aEscola de Saúde Pública Sergio Arouca, Fundação Oswaldo Cruz, 21040-360 Rio de Janeiro-RJ,
Brazil*

*^bCentro de Estudos da Saúde do Trabalhador e Ecologia Humana (CESTEH), Escola Nacional de
Saúde Pública Sergio Arouca (ENSP), Fundação Oswaldo Cruz (FIOCRUZ), 21040-360 Rio de
Janeiro-RJ, Brazil*

*^cPrograma de Pós-Graduação em Geociências (Geoquímica), Instituto de Química, Universidade
Federal Fluminense (UFF), 24020-007 Niterói-RJ, Brazil*

*^dPrograma de Pós-Graduação em Educação Profissional em Saúde, Escola Politécnica de Saúde
Joaquim Venâncio, Fundação Oswaldo Cruz (FIOCRUZ), 21040-360 Rio de Janeiro-RJ, Brazil*

*e-mail: anapaulaneves@hotmail.com; ana.pneves@aluno.fiocruz.br

ORCID: <https://orcid.org/0000-0003-0942-8225>

Table S1. Selective reaction monitoring transitions of the 26 quantified analytes of OCP

Organochlorine	Retention time / min	Precursor ion (<i>m/z</i>)	Product ion (<i>m/z</i>)	Collision energy / eV
alpha-HCH	17.32	182.8	146.7	12
		218.8	146.6	20
		218.8	183	8
Hexachlorobenzene	17.46	283.8	213.8	30
		283.8	248.8	18
		285.8	250.8	18
Pentachloroanisole	17.62	264.8	236.9	10
		266.8	238.9	10
		279.9	236.8	22
beta-HCH	18.06	180.9	145	14
		218.7	146.6	18
		218.7	183	8
gamma-HCH	18.36	180.9	109	26
		180.9	145	14
		218.7	183	8
delta-HCH	19.26	182.8	146.7	14
		218.8	146.5	20
		218.8	182.9	8
Heptachlor	20.97	100.1	65.1	10
		236.9	119	25
		271.9	237	15
Aldrin	22.40	263	193	30
		263	227.9	15
		293	186.1	35
Heptachlor epoxide	24.10	262.9	192.9	30
		352.8	262.9	16
		354.7	264.9	12
gamma-Chlordane	25.18	271.7	236.8	12
		372.7	263.7	20
		374.7	265.9	22
<i>o,p'</i> -DDE	25.37	246	176.1	28
		317.8	246	20
		317.8	248	18

		194.7	125	22
alpha-Edosulfan	25.77	194.7	159.4	8
		240.6	205.9	14
alpha-Chlordane	25.80	372.8	265.8	20
		374.7	265.8	20
		376.6	268	20
<i>trans</i> -Nonachlor	25.97	236.8	142.9	24
		262.8	192.9	28
		408.7	300	18
<i>p,p'</i> -DDE	26.98	246	176.1	28
		317.8	246	20
		317.8	248	18
Dieldrin	27.10	262.8	190.9	30
		262.8	192.9	30
		262.8	227.8	16
<i>o,p'</i> -DDD	27.27	235	165.1	20
		235	199	14
		236.8	165	20
Endrin	28.10	245	173	22
		262.8	192.9	30
		280.8	245.3	8
beta-Endosulfan	28.69	158.9	123	12
		194.7	159	8
		240.6	205.8	12
<i>p,p'</i> -DDD	29.08	235	165.1	20
		235	199	14
		236.8	165	20
<i>o,p'</i> -DDT	29.18	235	165.1	22
		235	199.5	10
		236.8	165	22
Endosulfan sulfate	30.65	238.7	203.9	12
		271.7	234.9	12
		271.7	236.8	12
<i>p,p'</i> -DDT	31.10	235	165	22
		235	199.5	10
		236.8	165	22
Methoxychlor	34.03	227.1	141.1	32
		227.1	169.1	22

		227.1	212.1	12
		111	74.9	12
Dicofol	34.10	139	111	12
		250.9	139	12
		236.8	142.9	26
Mirex	35.97	272	236.8	14
		273.8	238.8	14

HCH: hexachlorocyclohexane; DDE: dichlorodiphenyldichloroethylene; DDT: dichlorodiphenyltrichloro-ethane; DDD: dichlorodiphenyldichloroethane.

Table S2. Method validation parameters: calibration slope, intercept, R², limit of detection (LOD), limit of quantification (LOQ), recovery at low/mid/high levels and mean (with SD/CV), repeatability (intraday CV), intermediate precision (interday CV) values, homoscedasticity and matrix effect evaluation

Compound	Slope (a)	Linear coefficient	R	R ²	Standard deviation at 0.2 ng mL ⁻¹ or 2.0 ng mL ⁻¹ levels	LOD / (ng mL ⁻¹)	LOQ / (ng mL ⁻¹)	Recovery / %						CV Day 1	CV Day 2	CV Interday	CV Analyst 1	CV Analyst 2	Homoscedasticity	Matrix effect (0.2 ng mL ⁻¹)		
								0,5 ng mL ⁻¹	5 ng mL ⁻¹	015 ng mL ⁻¹	Mean	SD	CV	1.3	8.3	4.8	0.9	6.0		F test (tabulated 9,3)	T test (tabulated 2,3)	Matrix effect
<i>o,p'</i> -DDD	164424.4	−105963	0.9847	0.9696	3116	0.06	0.19	90	100	102	102.1	7	7	2.1	8.8	5.4	3.9	6.0	heteroscedastic	0.8	1.5	no
<i>o,p'</i> -DDE	133466.4	−104848	0.9824	0.9651	2688	0.07	0.2	93	96	117	102.4	13	13	3.8	1.0	2.4	3.9	2.6	heteroscedastic	0.8	1.3	no
<i>o,p'</i> -DDT	206666.9	−144347	0.9658	0.9328	1310	0.02	0.06	100	105	103	104.5	3	3	1.8	11.8	6.8	5.3	8.5	heteroscedastic	0.7	1.3	no
<i>p,p'</i> -DDD	212081.7	6675	0.9360	0.8761	1906	0.03	0.09	119	91	104	101.1	14	14	0.6	2.9	1.7	1.4	8.1	heteroscedastic	0.2	1.5	no
<i>p,p'</i> -DDE	111655.3	−10067	0.9778	0.9562	2285	0.07	0.21	107	92	104	98.8	8	8	4.0	6.2	5.1	3.8	4.2	homoscedastic	1.0	1.6	no
<i>p,p'</i> -DDT	205722.4	−225929	0.9657	0.9326	2976	0.05	0.15	92	106	99	102.2	7	7	6.0	6.7	6.3	1.6	0.2	heteroscedastic	0.1	1.4	no
alpha-Chlordane ^a	11662.61	−14012	0.9787	0.9579	777	0.24	0.72	–	93	105	97.2	8	8	0.4	3.9	2.1	2.7	2.7	heteroscedastic	1.0	1.5	no
gamma-Chlordane ^a	10049.2	−16508	0.9634	0.9281	1335	0.47	1.42	–	85	100	92.6	11	12	3.9	9.4	6.7	5.0	5.3	homoscedastic	1.0	1.4	no
alfa-Endosulfan ^a	5767.7	−9127	0.9631	0.9276	601	0.37	1.12	–	99	96	105.0	2	2	7.0	10.2	8.6	3.4	3.5	heteroscedastic	1.0	1.6	no
beta-Endosulfan ^a	5994.429	−7198	0.9946	0.9893	339	0.2	0.62	86	92	104	101.4	9	10	6.1	2.0	4.0	0.7	6.9	heteroscedastic	0.1	1.5	no
Endosulfan sulfate	29623.88	−31105	0.9620	0.9255	2990	0.09	0.27	–	102	104	102.1	1	1	11.3	0.1	5.7	14.9	5.8	homoscedastic	0.5	1.5	no
alfa-HCH	92536.19	−70175	0.9832	0.9667	1859	0.07	0.2	–	88	122	94.3	24	22	1.2	1.1	1.1	0.5	11.3	heteroscedastic	0.0	1.6	no
beta-HCH	58035.03	−39474	0.9865	0.9733	307	0.02	0.05	–	91	111	97.3	14	14	0.1	11.8	6.0	2.3	6.0	heteroscedastic	0.4	1.6	no
delta-HCH	30644.79	−19539	0.9808	0.9620	527	0.06	0.17	81	116	95	97.4	18	18	4.2	0.3	2.2	3.2	5.9	heteroscedastic	0.6	1.6	no
gamma-HCH	39580.85	−19643	0.9875	0.9752	838	0.07	0.21	82	106	99	95.9	12	13	3.3	0.6	1.9	0.2	4.4	heteroscedastic	0.0	1.4	no
Dicofol	89022.35	−93846	0.9921	0.9843	903	0.03	0.1	85	110	97	94.2	12	13	1.2	6.9	4.0	0.5	2.4	heteroscedastic	0.3	1.5	no

Dieldrin ^a	7141.434	−14131	0.9881	0.9763	310	0.16	0.48	–	86	102	103.0	11	12	5.1	10.3	7.7	2.0	5.0	homoscedastic	0.5	1.5	no
Aldrin ^a	4576.407	−8718	0.9855	0.9712	342	0.27	0.82	104	109	94	98.9	8	7	3.3	1.6	2.5	11.3	0.3	homoscedastic	0.0	1.4	no
Endrin ^a	8257.716	−17180	0.9808	0.9619	556	0.24	0.73	99	104	104	95.6	3	3	4.7	1.1	2.9	4.7	3.5	homoscedastic	0.9	1.3	no
Heptachlor	32598.17	−27788	0.9784	0.9572	527	0.05	0.16	83	99	106	96.1	12	12	0.1	1.5	0.8	4.2	4.5	homoscedastic	0.9	1.5	no
Heptachlor epoxide ^a	8442.877	−14195	0.9809	0.9622	923	0.39	1.19	–	91	108	99.5	12	12	5.1	2.4	3.8	12.4	9.9	heteroscedastic	0.9	1.5	no
Hexachlorobenzene	278528.6	−48803	0.9830	0.9663	1258	0.02	0.05	85	92	103	93.5	9	10	0.5	1.7	1.1	5.2	3.3	homoscedastic	0.7	1.6	no
Methoxychlor	99450.33	−96189	0.9649	0.9310	1576	0.05	0.16	99	102	96	99.0	3	3	0.1	0.1	0.1	6.4	0.6	heteroscedastic	0.1	1.4	no
Mirex	74864.07	−68552	0.9765	0.9535	1119	0.05	0.15	92	103	109	101.4	8	8	3.0	8.4	5.7	8.1	3.5	heteroscedastic	0.5	1.5	no
Pentachloroanisole	96295.83	−92861	0.9726	0.9460	1374	0.05	0.82	74	96	115	94.9	21	22	6.6	0.7	3.7	0.5	4.2	heteroscedastic	0.2	1.6	no
<i>trans</i> -Nonachlor ^a	5848.215	−7052	0.9826	0.9655	340	0.21	0.14	–	98	107	102.9	6	6	11.3	11.8	8.6	14.9	11.3	heteroscedastic	1.0	1.2	no
Maximum			0.9946	0.9893	2990	1,4186	0,4681	74	85	95	105.0	23.6	22.5	0.1	0.1	0.1	0.2	0.2		0.0		
Minimum			0.9360	0.8761	307	0.0452	0.0149	119	116	122	92.6	0.9	0.8	1.3	8.3	4.8	0.9	6.0		0.2		

^aCalculated from 2 ng mL^{−1} level. [#]*F* tabulated for df = 1 and 95% confidence is equal to 18.51. CV: coefficients of variations; SD: standard deviation; HCH: hexachlorocyclohexane; DDE: dichlorodiphenyldichloroethylene; DDT: dichlorodiphenyltrichloro-ethane; DDD: dichlorodiphenyltrichloro-ethane.

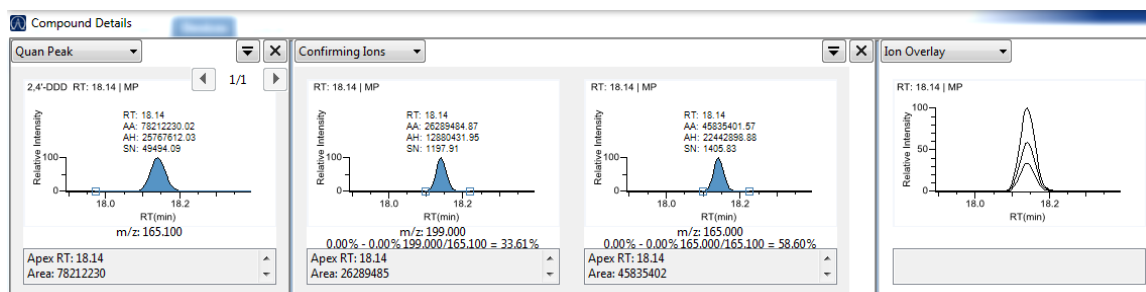


Figure S1. Total ion chromatography and full-scan mass spectrum of *o,p*-DDD.

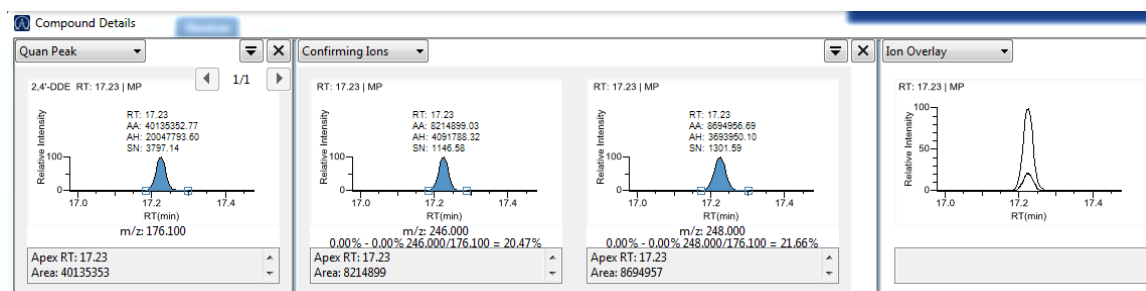


Figure S2. Total ion chromatography and full-scan mass spectrum of *o,p*-DDE.

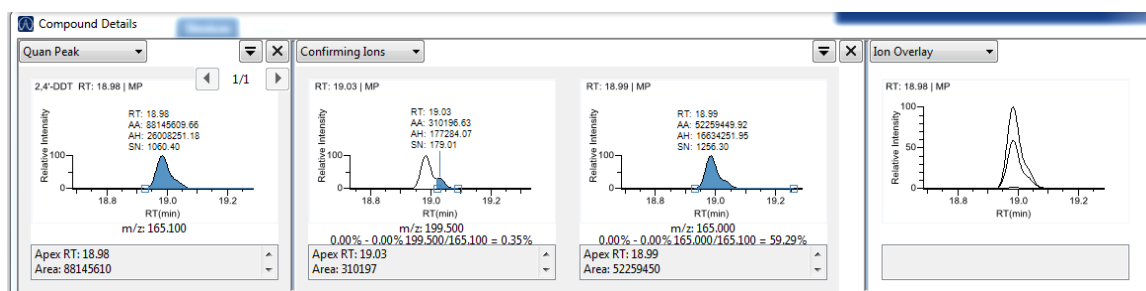


Figure S3. Total ion chromatography and full-scan mass spectrum of *o,p*-DDT.

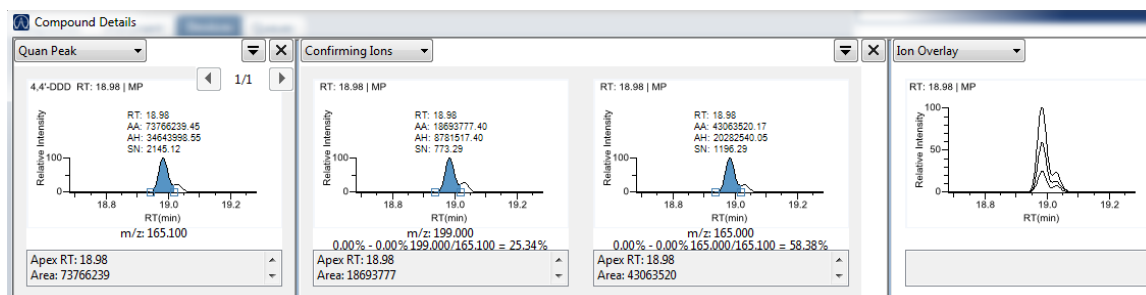


Figure S4. Total ion chromatography and full-scan mass spectrum of *p,p*-DDD.

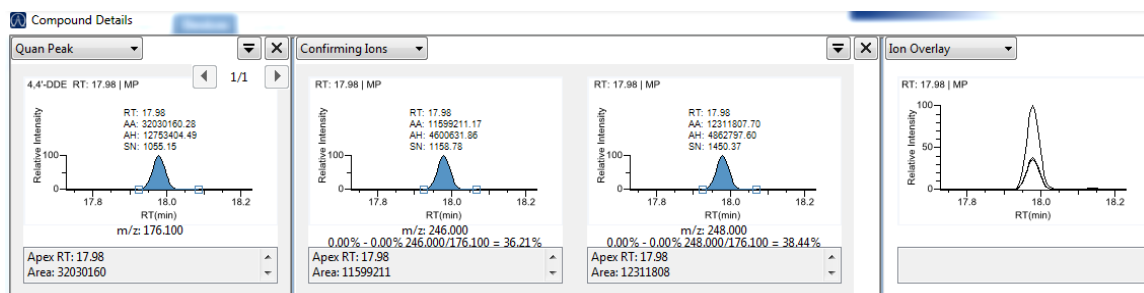


Figure S5. Total ion chromatography and full-scan mass spectrum of p,p-DDE

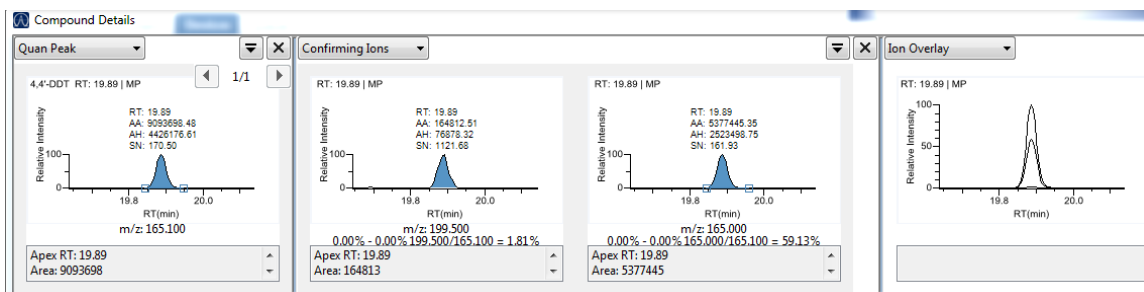


Figure S6. Total ion chromatography and full-scan mass spectrum of p,p-DDT.

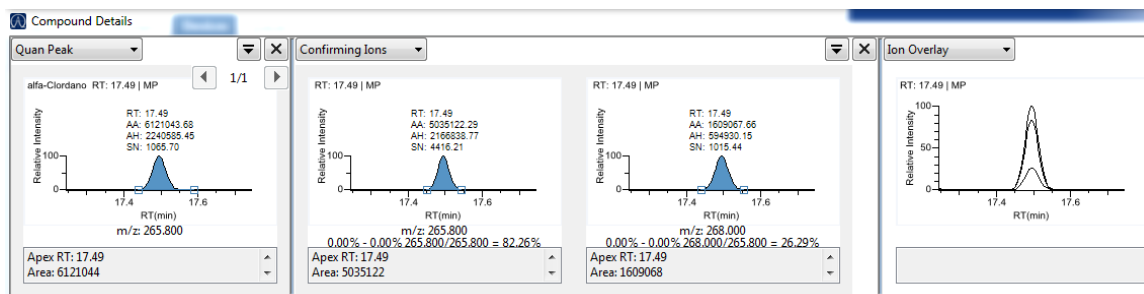


Figure S7. Total ion chromatography and full-scan mass spectrum of alpha-chlordane.

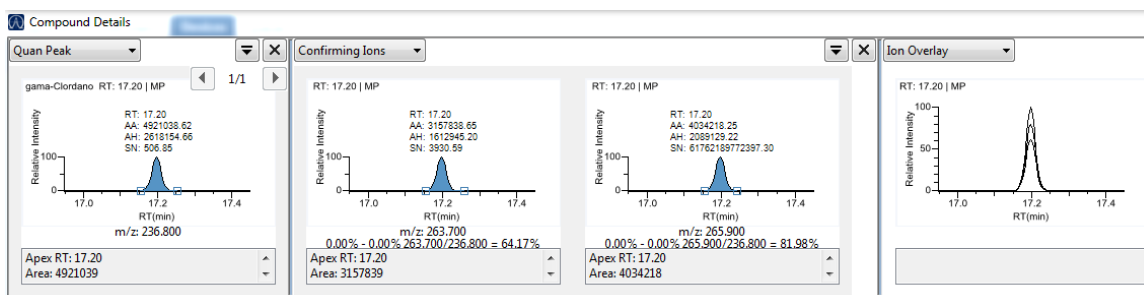


Figure S8. Total ion chromatography and full-scan mass spectrum of gamma-chlordane.

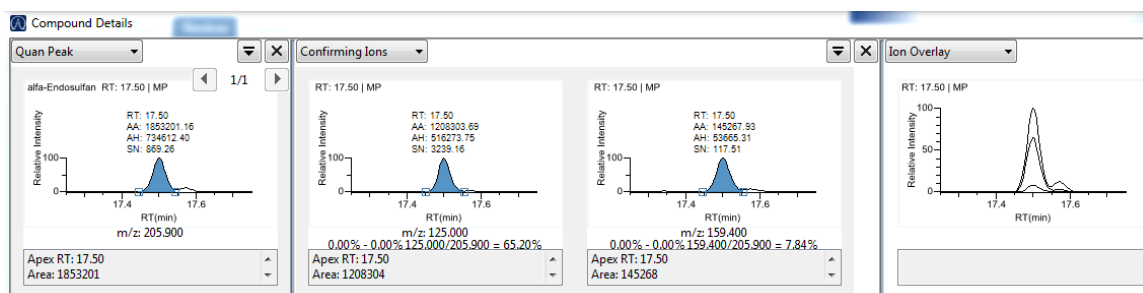


Figure S9. Total ion chromatography and full-scan mass spectrum of alpha-endosulfan.

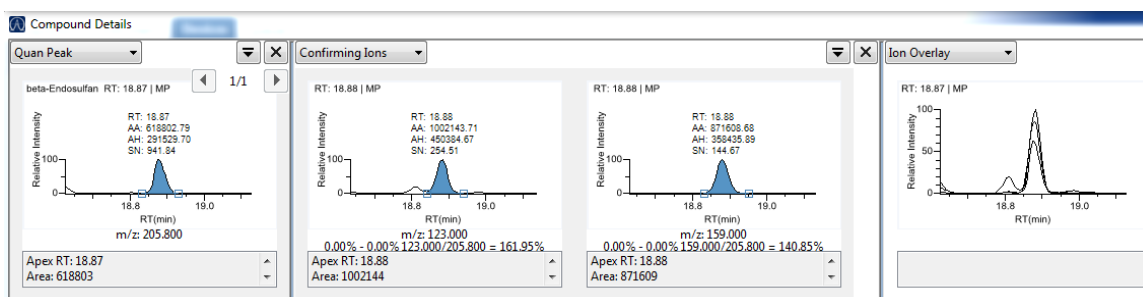


Figure S10. Total ion chromatography and full-scan mass spectrum of beta-endosulfan.

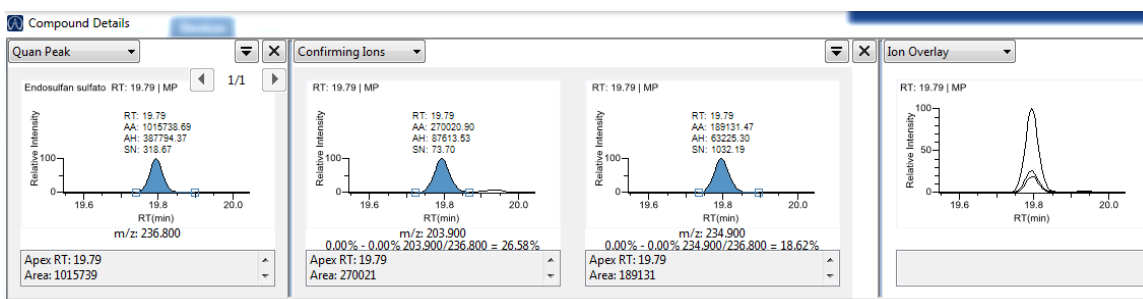


Figure S11. Total ion chromatography and full-scan mass spectrum of endosulfan sulfate.

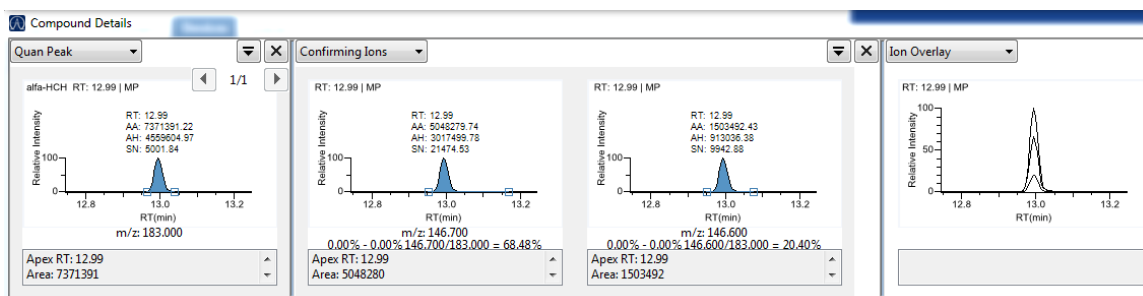


Figure S12. Total ion chromatography and full-scan mass spectrum of alpha-HCH.

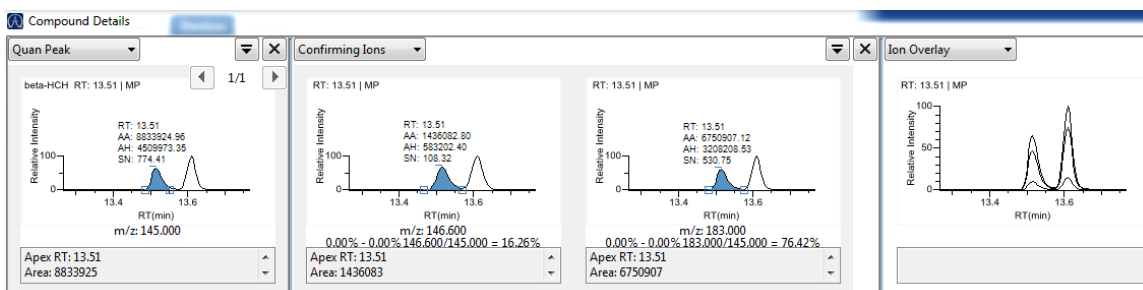


Figure S13. Total ion chromatography and full-scan mass spectrum of beta-HCH.

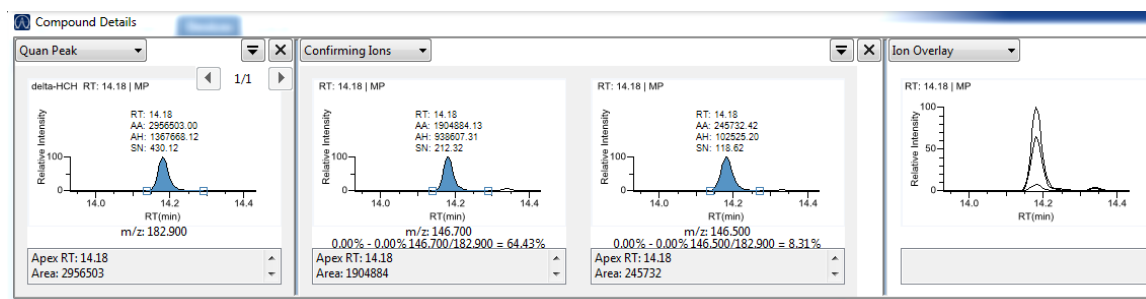


Figure S14. Total ion chromatography and full-scan mass spectrum of delta-HCH.

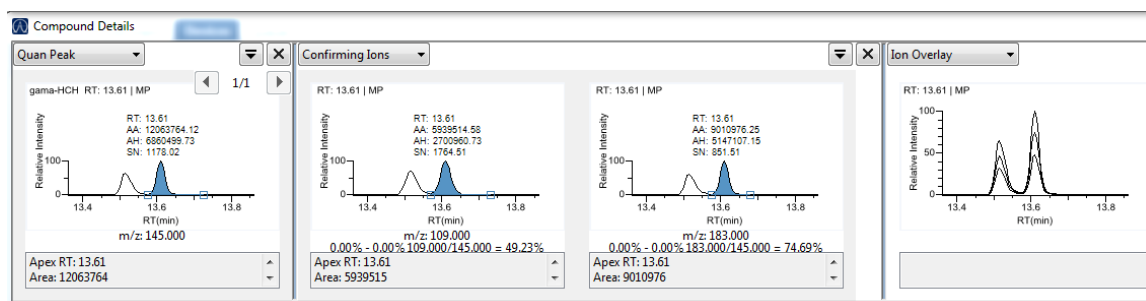


Figure S15. Total ion chromatography and full-scan mass spectrum of gamma-HCH.

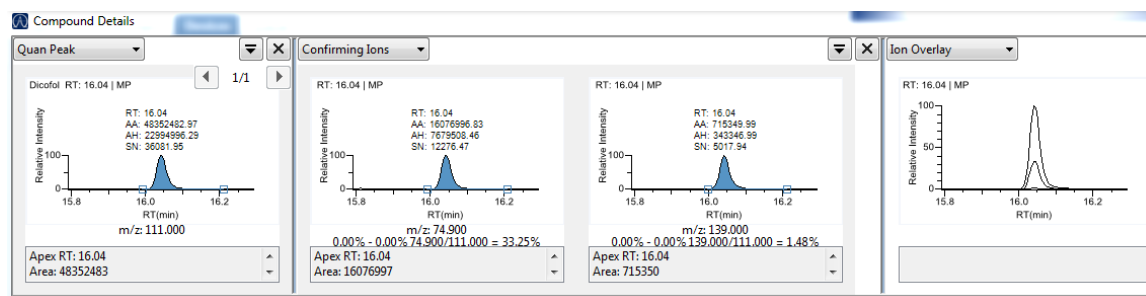


Figure S16. Total ion chromatography and full-scan mass spectrum of dicofol.

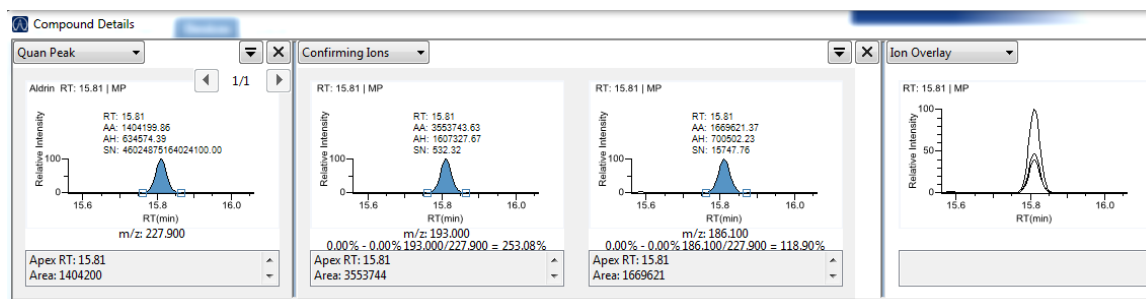


Figure S17. Total ion chromatography and full-scan mass spectrum of aldrin.

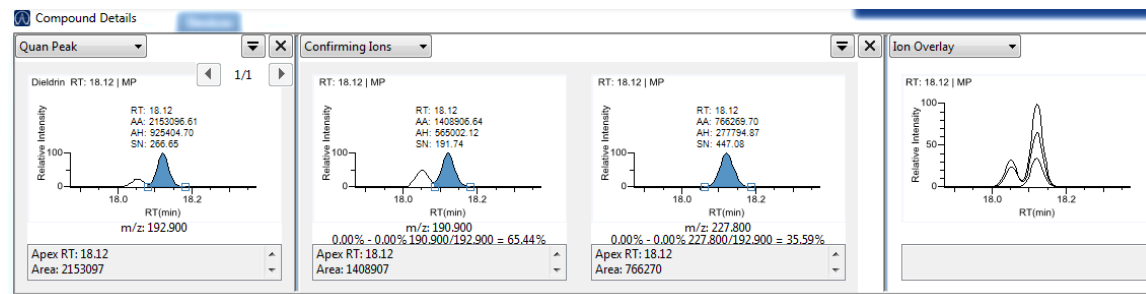


Figure S18. Total ion chromatography and full-scan mass spectrum of dieldrin.

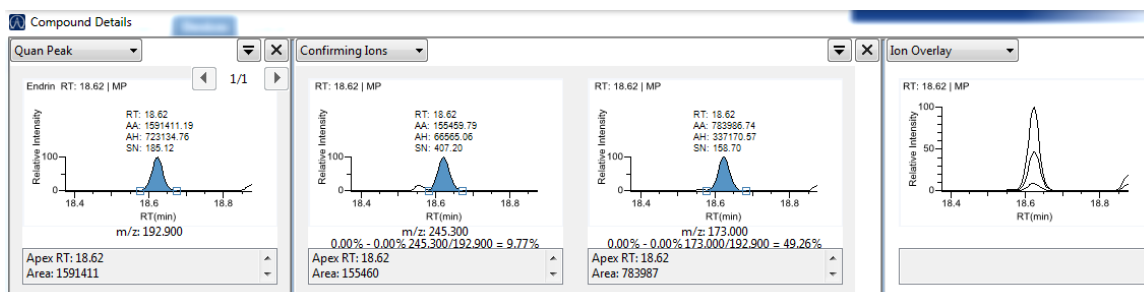


Figure S19. Total ion chromatography and full-scan mass spectrum of endrin.

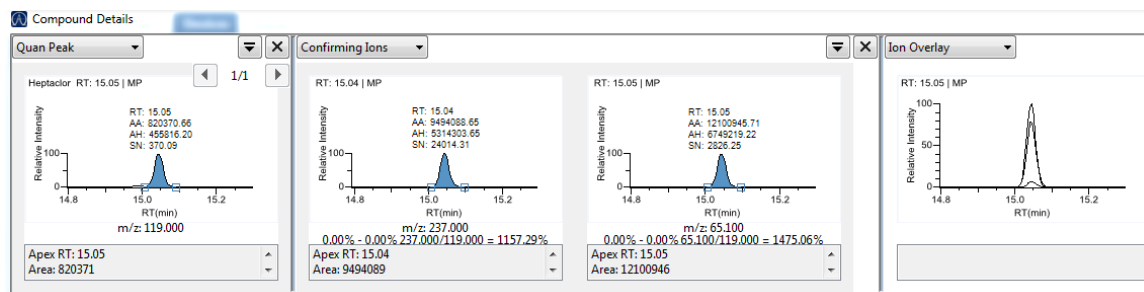


Figure S20. Total ion chromatography and full-scan mass spectrum of heptachlor.

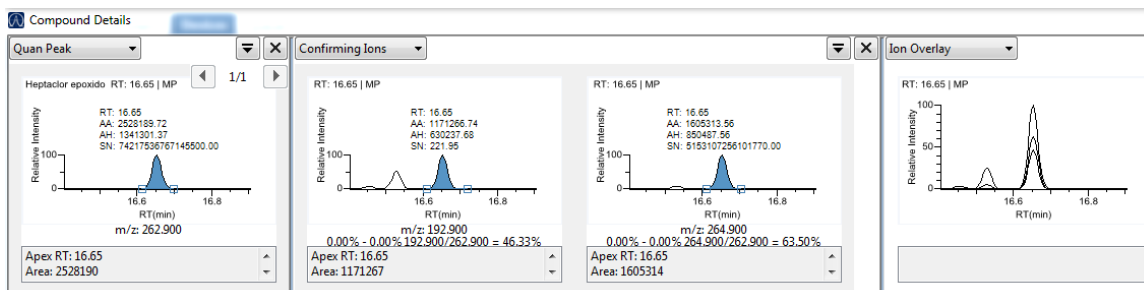


Figure S21. Total ion chromatography and full-scan mass spectrum of heptachlor epoxide.

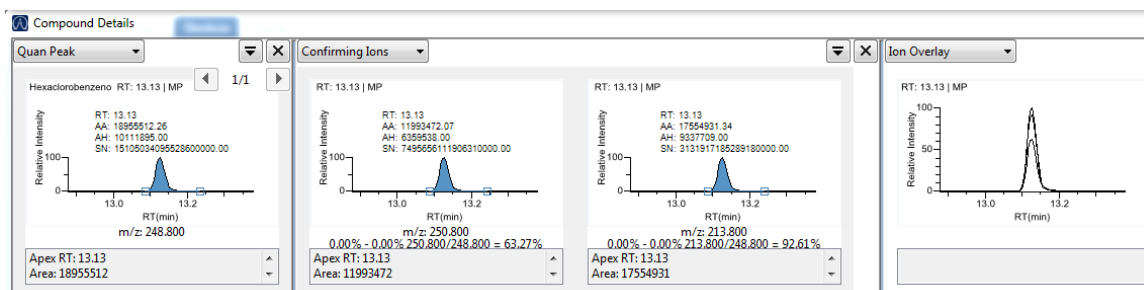


Figure S22. Total ion chromatography and full-scan mass spectrum of hexachlorobenzene.

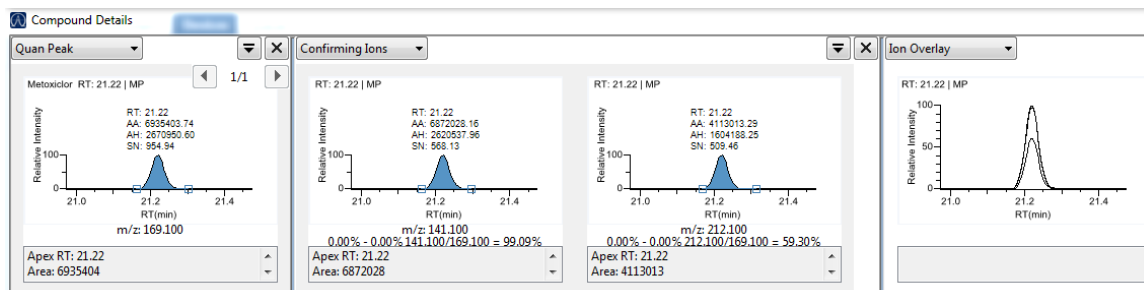


Figure S23. Total ion chromatography and full-scan mass spectrum of methoxychlor.

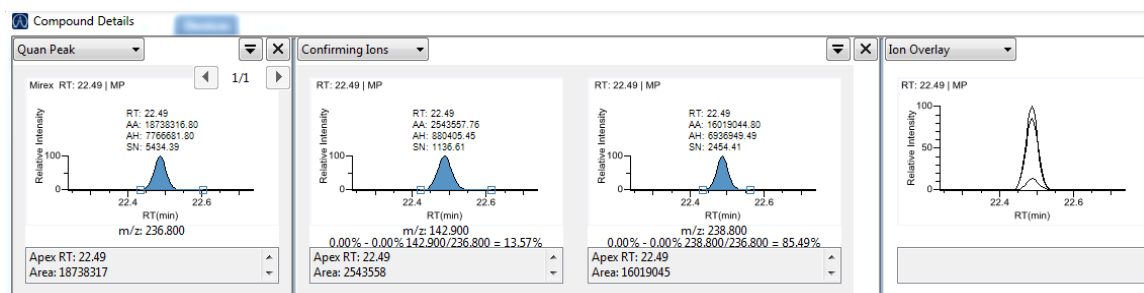


Figure S24. Total ion chromatography and full-scan mass spectrum of mirex.

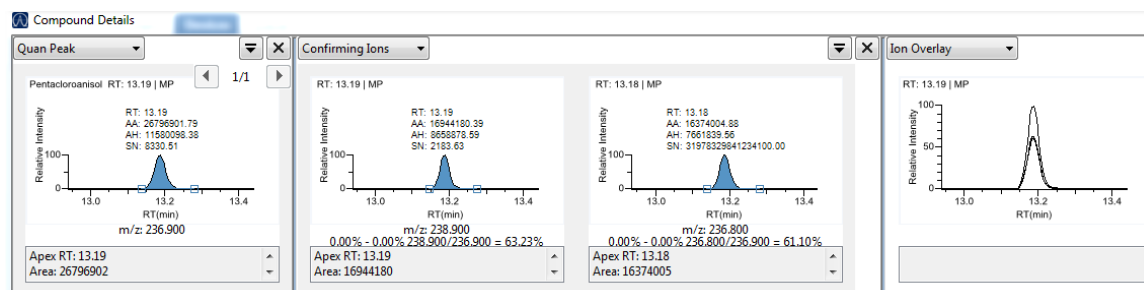


Figure S25. Total ion chromatography and full-scan mass spectrum of pentachloroanisole.

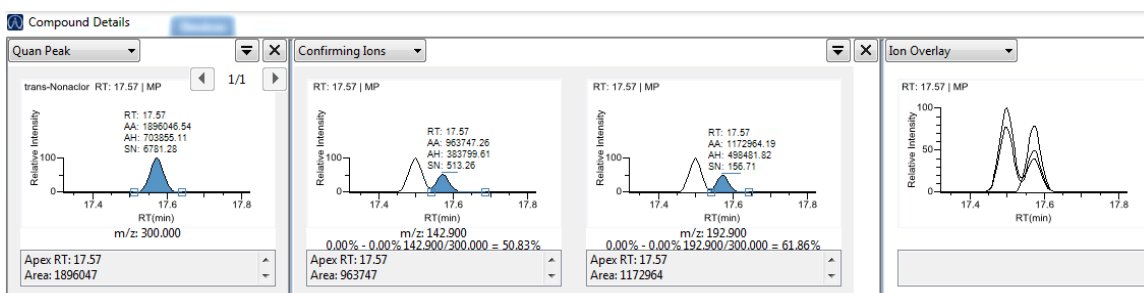


Figure S26. Total ion chromatography and full-scan mass spectrum of trans-nonachlor.

Table S3. Evaluation of homoscedasticity of analytes that gave results above the limit of detection

<i>p,p'</i> -DDE		<i>p,p'</i> -DDT		delta-HCH		Gamma-HCH	
Calculated	Replicas area	Calculated	Replicas area	Calculated	Replicas area	Calculated	Replicas area
0.19944	102726	0.2056	38183	0.2004	7772	0.19724	14096
0.19944	104807	0.2056	41192	0.2004	5794	0.19724	13923
0.19944	104212	0.2056	38299	0.2004	5178	0.19724	12889
0.5	73266	0.51	57335	0.5	10027	0.49	12297
0.5	70948	0.51	58888	0.5	10589	0.49	12324
0.5	74159	0.51	64370	0.5	10294	0.49	12926
1,000	123462	1.03	106658	1,000	15093	0.99	24666
1,000	135935	1.03	91732	1,000	15879	0.99	23666
1,000	131964	1.03	94214	1,000	15354	0.99	23886
1.99	228903	2.06	258912	2,000	37122	1.97	60339
1.99	242215	2.06	240817	2,000	35503	1.97	64365
1.99	228452	2.06	244026	2,000	35802	1.97	64089
4.99	182977	5.14	279623	5.01	53988	4.93	85081
4.99	186522	5.14	270536	5.01	55737	4.93	88996
4.99	178778	5.14	287159	5.01	64957	4.93	86489
7.12	733341	7.34	1074754	7.16	161127	7.04	210542
7.12	725597	7.34	1008767	7.16	151786	7.04	203400
7.12	756366	7.34	1069201	7.16	171560	7.04	203700
12.47	1395772	12.85	2111032	12.53	384386	12.33	455199
12.47	1367331	12.85	1976887	12.53	375027	12.33	452111
12.47	1364166	12.85	1944623	12.53	383041	12.33	435325
16.62	1689377	17.13	3741651	16.7	407515	16.44	600268
16.62	1724335	17.13	3394597	16.7	443245	16.44	542101
16.62	1712746	17.13	3903463	16.7	453894	16.44	600222
	variance		variance		variance		variance
0.2	1148797	0.2	2906164	0.2	1836796	0.2	425989
0.5	2746849	0.5	13659226	0.5	79026	0.5	126462
1	40604762	1	63966489	1	160257	1	276133
2	61138819	2	93219950	2	742160	2	5057892
5	15028027	5	69281499	5	34731060	5	3932456
7	256141920	7	1339564722	7	97852141	7	16318521
12	302974490	12	7787967000	12	25604017	12	114380236
15	317079474	15	67595701369	15	590174290	15	1126908774
	0.318		0.878		0.786		0.889
	homoscedastic		heteroscedastic		heteroscedastic		heteroscedastic
C _{tab}	0.5157						
C _{calc} < C _{tab}	homoscedastic						

HCH: hexachlorocyclohexane; DDE: dichlorodiphenyldichloroethylene; DDT: dichlorodiphenyltrichloro-ethane; DDD: dichlorodiphenyltrichloro-ethane.

Table S4. Example of p,p' -DDE for matrix effect evaluation

Concentration of point X ₁ / (µg L ⁻¹)	Area Y ₁	Y _{1est}	Y ₁ -Y _{1est}	(X ₁ - X _{1med}) ²	X ₁ ²	Homoscedasticity F test		Water		Evaluation	
						Snedecor		(b) Slope	2069678	s ² p	2.91075 × 10 ¹¹
0,5	703.742	728638	−655372	0.0625	0.25	S ² res water	2.86479 × 10 ¹¹	(a) interception	-306201	t _b	1.568559494
0,5	661.107	728638	−657690	0.0625	0.25	S ² res plasma	2.95671 × 10 ¹¹	S _{xx1}	0.375	t _a	0.326218378
0,5	821.065	728638	−654479	0.0625	0.25	GL _{(n1 + n2) - 4}	8	s ² res ₁	2.86479 × 10 ¹¹	GL _{(n1 + n2) - 4}	8
1	1.616.908	1763477	−1640015	0.0625	1	F _(1-a/2;GL)	9.3	n ₁	6	t _(1-a/2;GL)	2.306
1	1.843.743	1763477	−1627542	0.0625	1	F test	0.968913084	S _{x1²}	3.75		
1	1.829.780	1763477	−1631513	0.0625	1			X _{1med}	0.75		Result
										no matrix effect	
Plasma										no matrix effect	
Concentration at point X ₂ / (µg L ⁻¹)	area Y ₂	Y _{2est}	Y ₂ -Y _{2est}	(X ₂ - X _{2med}) ²	X ₂ ²	Plasma					
0,5	73266	72791	630951	0.0625	0.25			(b) Slope	115325.3333		
0,5	70948	72791	588316	0.0625	0.25			(a) Interception	15128.33333		
0,5	74159	72791	748274	0.0625	0.25			S _{xx2}	0.375		
1	123462	130453,66 67	1486454.33	0.0625	1			s ² res ₂	2.95671 × 10 ¹¹		
1	135935	130453,66 67	1713289.33	0.0625	1			n ₂	6		
1	131964	130453,66 67	1699326.33	0.0625	1			S _{x2²}	3.75		
								X _{2med}	0.75		

