

Supplementary information

Atmospheric pressure soft ionization for gas chromatography with dielectric barrier discharge ionization-mass spectrometry (GC-DBDI-MS)

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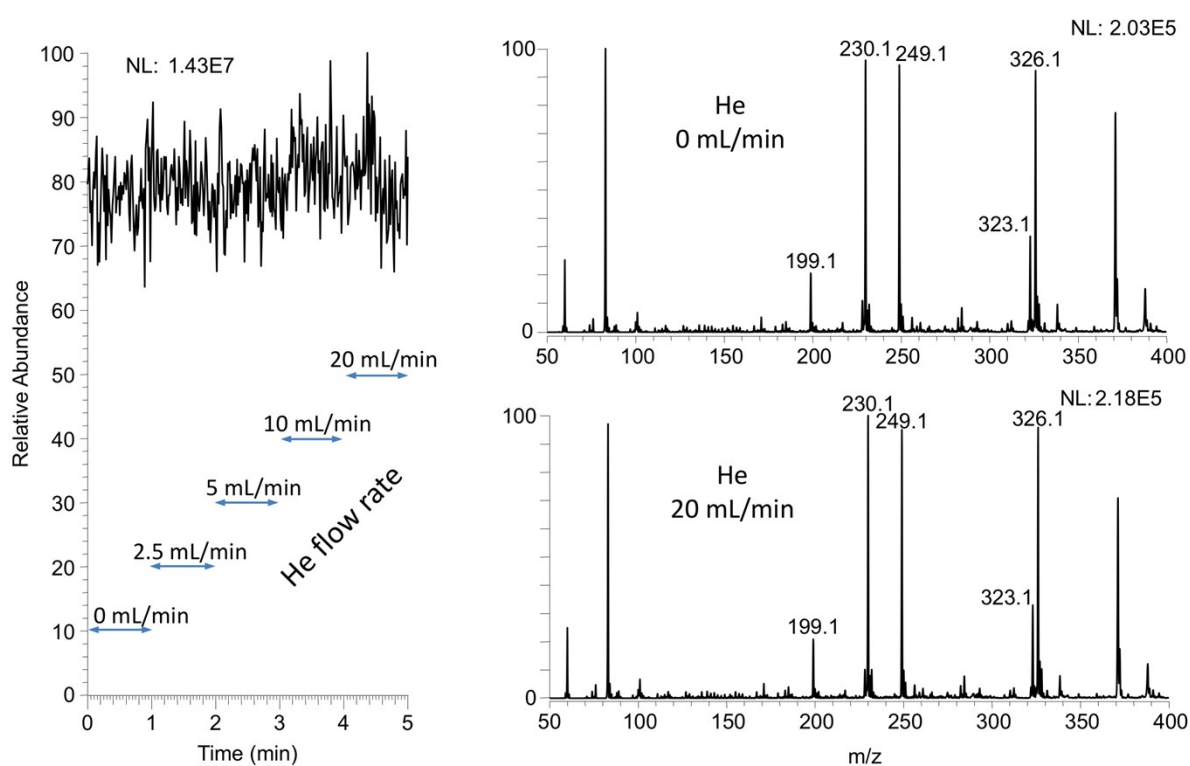


Fig. S1. Ionization efficiency for 9 organophosphate and 7 triazine pesticides at 10 µg/mL (compounds n. 1-9, 11-15, 17 and 22 from Table 1) with a variable concentration of He gas in the DBDI source.

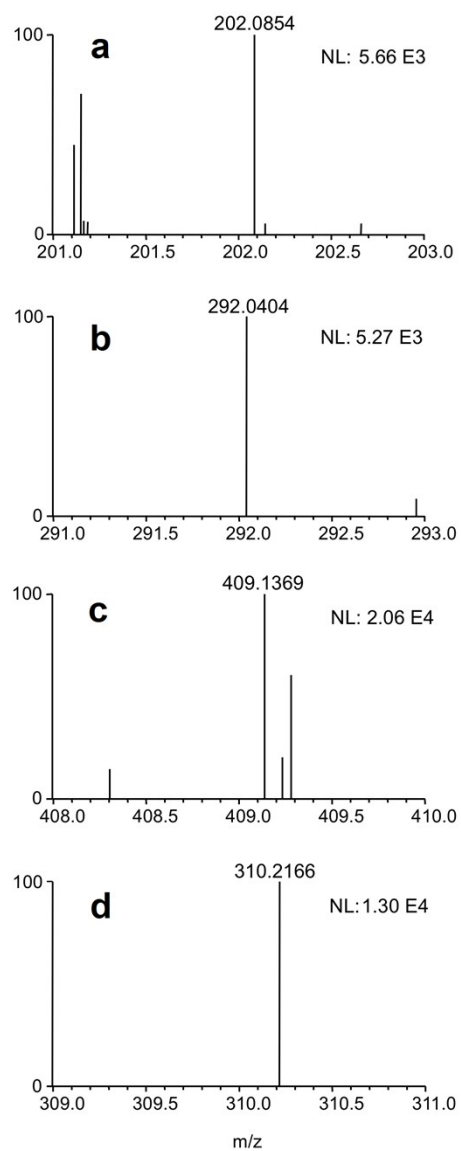


Fig. S2. Low concentration MS spectra in fullscan, acquired with a LTQ Orbitrap. a) simazine, b) parathion, c) trifloxystrobin and d) methadone.

	range pg/mL	n points	equation	R ²	LOD ^a	LOD ^b	LOQ ^b	MS ² transition
Prometon	1k-300k	6	y=0.0781x+0.0194	0.9981	1000	318	964	226 -> 184 (38)
Simazine	1k-300k	6	y=0.096x+0.0034	0.9924	1000	645	1954	202 -> 124 (36)
Atrazine	300-300k	7	y=0.0508x+0.0098	0.9901	300	738	2236	216 -> 174 (34)
Propazine	300-300k	7	y=0.1081x+0.0213	0.9889	300	783	2373	230 -> 188 (40)
Ametryn	300-300k	7	y=0.0474x+0.0240	0.9837	300	949	2875	228 -> 186 (40)
Prometryn	100-300k	8	y=0.1275x+0.0450	0.9913	100	690	2091	242 -> 200 (38)
Terbutryn	100-300k	8	y=0.1150x+0.0387	0.9858	100	885	2682	242 -> 186 (38)
Triethylthioph.	300-1M	8	y=0.0954x+0.0151	0.9972	300	647	1962	199 -> 171 (22)
Thionazin	300-1M	8	y=0.0998x+0.0105	0.9991	300	366	1109	249 -> 221 (28)
Sulfotep	100-300k	8	y=0.1315x-0.0162	0.9930	100	620	1879	323 -> 295 (24)
Phorate	100-1M	9	y=0.0910x+0.0002	0.9964	100	445	1350	261 -> 199 (22)
Parathion methyl	1k-300k	6	y=0.0134x-0.0015	0.9968	300	807	2444	264 -> 236 (30)
Parathion	100-1M	9	y=0.1411x-0.0075	0.9988	100	426	1290	292 -> 264 (26)
Famphur	100-1M	9	y=0.1265x-0.0053	0.9993	100	329	997	326 -> 299 (28)

Table S1. Linear regression parameters for the 14 pesticides investigated (in dichloromethane), measured using GC-DBDI and an LCQ DECA XP in tandem MS positive ionization mode. Metolachlor was used as internal standards, at a concentration of 10 ng/mL. LOD values were evaluated both experimentally and calculated from the linear regression (1/x weighted).

^adetermined by injecting standards at decreasing concentrations;

^bcalculated from the calibration curves;

	RSD% 1d, n=4									RSD% 3d, n=4								
	10 ng/mL			1 ng/mL			0.1 ng/mL			10 ng/mL			1 ng/mL			0.1 ng/mL		
	no	IS	IS	no	IS	IS	no	IS	IS	no	IS	IS	no	IS	IS	no	IS	IS
	IS	Atr.	Met.	IS	Atr.	Met.	IS	Atr.	Met.	IS	Atr.	Met.	IS	Atr.	Met.	IS	Atr.	Met.
Prometon	2	4	2	9	7	4	18	15	15	20	22	7	17	18	13	16	13	9
Simazine	2	1	2	6	7	12	11	11	14	4	2	15	5	6	10	12	10	12
Atrazine	0	3	2	3	2	4	8	5	6	2	3	16	4	1	6	14	8	15
Propazine	2	3	1	2	3	7	10	7	7	1	5	16	4	2	8	10	6	12
Ametryn	4	4	2	1	2	7	21	25	25	14	15	3	5	4	7	16	11	10
Prometryn	1	4	1	2	3	6	24	23	26	13	13	6	3	4	5	31	29	35
Terbutryn	1	3	1	4	3	4	6	3	6	11	12	6	3	3	3	4	4	9
Triethylthiophosphate	2	2	1	2	1	5	13	10	9	6	7	22	5	3	8	13	8	10
Sulfotep	3	3	1	3	2	4	20	16	19	3	3	15	2	4	3	25	18	26
Phorate	4	5	3	6	8	12	/	/	/	6	4	18	6	9	10	/	/	/
Dimethoate	6	8	5	9	11	15	/	/	/	22	24	10	12	15	15	/	/	/
Disulfoton	48	46	47	/	/	/	/	/	/	52	48	49	/	/	/	/	/	/
Parathion methyl	8	9	10	3	4	8	/	/	/	29	32	18	27	29	26	/	/	/
Parathion	8	8	10	2	4	8	/	/	/	34	37	23	20	22	19	/	/	/
Famphur	2	2	1	8	7	2	/	/	/	10	11	6	12	13	7	/	/	/
Pyrimethanil	3	3	4	2	2	5	5	7	9	6	2	15	2	2	6	41	33	41
Malathion	10	13	11	/	/	/	/	/	/	8	10	16	/	/	/	/	/	/
Cyprodinil	1	4	3	2	1	4	11	11	7	10	9	9	2	4	4	15	16	21
Flusilazole	2	3	0	7	6	5	7	10	11	20	23	9	18	20	15	27	26	21
Cyproconazole	5	7	5	5	3	3	7	4	6	22	26	12	23	24	20	16	17	10
Trifloxystrobin	2	1	2	7	5	1	3	1	3	5	3	14	6	4	4	9	5	12
Quinoxifen	1	3	2	5	3	2	21	17	19	7	9	8	4	5	4	23	16	20
Tebuconazole	3	5	3	8	7	7	27	24	27	19	23	11	19	20	16	52	52	49
Pyriproxyfen	4	7	6	5	5	8	12	10	13	6	6	14	1	4	6	21	20	16
Pyridaben	1	3	2	4	3	6	3	1	3	4	6	11	2	3	4	10	3	9
Difenoconazole	2	4	2	10	10	12	/	/	/	18	21	12	24	27	23	/	/	/
Azoxystrobin	6	8	6	13	13	11	/	/	/	13	12	28	16	13	16	/	/	/

Table S2. Intra-day RSD and inter-day RSD (3 days) for the considered pesticides (n=4, evaluated at 10, 1 and 0.1 ng/mL), measured using GC-DBDI and a LTQ Orbitrap. For each concentration, data for atrazine-d₅ and metolachlor as internal standards are shown, as well as the data without internal standard correction.