Analysis of pesticides and other contaminants in soil samples by gas chromatography coupled with quadrupole time-of-flight mass spectrometry

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## Introduction

Pesticides, PAHs, PCBs and other contaminants coming from the human activity are transported and heavily presented in soil. The simultaneous screening, identification and quantification of these co-occurring contaminants, which are highly dynamic and require complex analytical instrumentation, are of great importance. In this research, an analytical method for the routine determination of pesticides and some other organic contaminants in soil by gas chromatography coupled with quadrupole time-of-flight mass spectrometry (GC–QTOF) was developed. Simple shaking extraction by oscillator was applied for the sample preparation to keep all the chemicals present in original samples. GC-QTOF provides high sensitivity and selectivity by operating at TOF scan mode, and a remarkable number of compounds can be simultaneously analyzed in a single run. The accurate mass provides very selective information for compound identification. In addition, an accurate mass PCDL library of more than 800 pesticides and environmental contaminants containing information about their fragment ions and retention time was used for compound identification and confirmation. The All lons MS feature integrated in Masshunter software was employed to rapidly screen, identify and confirm many pesticides and some other contaminants in soil matrices.

## **Results and Discussion**

#### **PCDL : Personal Compound Database & Library**

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									20- 57.03 10- 7.8 0- 40 6 m/z	316 5 0 80	206.02931       105.04433     160.03635       9.52     13.98       7.30     6.92       1     1       100     120       100     120       100     120       100     120       100     120       100     120       100     120       100     120       100     120       100     120       120     140       120     140       120     140       120     140       120     140       130     200       220     240       260     280       300     320       340     1
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i	ngle Search Results: 993 hits	_				BT			20- 10- 40 6 m/z	3316 55 50 80	206.02931     105.04433     160.03635     13.98     318.10583       7.30     9.52     9.52     6.92       1.0.0     100.120     140.160     180.200     220.240     260.280     300.320     340
iı	ngle Search Results: 993 hits Compound Name	Formula	Mass	Anion	Cation	RT (min)	CAS	ChemSpider	20- 10- 57.03 7.8 40 6 m/z	1316 55 0 80	105.04433     160.03635     13.98     318.10583       7.30     9.52     9.52     9.52       1.1.1     11.1     11.1     11.1       100     120     140     160     180     200     220     240     260     280     300     320     340       100     120     140     160     180     200     220     240     260     280     300     320     340
i	ngle Search Results: 993 hits Compound Name	Formula C11H9Cl2	Mass 257.00103	Anion	Cation	RT (min) 11.325	CAS 101-27-9	ChemSpider 7270	20- 57.03 10- 7.8 0- 40 6 m/z 4-Chloro-2-but	1316 15 10 80 10PA	105.04433 160.03635 13.98 318.10583   7.30 9.52 13.98 16.92   1.1 1.1 1.1 1.1   100 120 140 160   100 120 140 160   Name Num
i	ngle Search Results: 993 hits Compound Name Barban BDMC-1(4-bromo-3,5-dimethylphenyl-N-methylcar	Formula C11H9Cl2 C10H12B	Mass 257.00103 257.00514	Anion	Cation	RT (min) 11.325 8.199	CAS 101-27-9 672-99-1	ChemSpider 7270	20- 10- 7.8 0- 40 6 m/z 4-Chloro-2-but	1316 15 0 80	105.04433 160.03635 13.98 318.10583   7.30 9.52 13.98 16.92   1.100 120 140 160 180 200 220 240 260 280 300 320 340
i	ngle Search Results: 993 hits Compound Name Barban BDMC-1(4-bromo-3,5-dimethylphenyl-N-methylcar Beflubutamid	Formula C11H9C12 C10H12B C18H17F	Mass 257.00103 257.00514 355.11954	Anion	Cation	RT (min) 11.325 8.199 10.338	CAS 101-27-9 672-99-1 113614-0	ChemSpider 7270 4953638	20- 57.03 10- 7.8 0- 40 6 m/z 40 6 m/z 40 6 2-[4-Fluoro-3-0	1316 50 80	105.04433 160.03635 13.98 318.10583 6.92 7.30 9.52 13.98 4 6.92 1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.
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:11	Ingle Search Results: 993 hits Compound Name Barban BDMC-1(4-bromo-3,5-dimethylphenyl-N-methylcar Beflubutamid Benalaxyl Benazolin-ethyl	Formula C11H9Cl2 C10H12B C18H17F C20H23N C11H10Cl	Mass 257.00103 257.00514 355.11954 325.16779 271.00699	Anion	Cation	RT (min) 11.325 8.199 10.338 12.968 10.212	CAS 101-27-9 672-99-1 113614-0 71626-11-4 25059-80-7	ChemSpider 7270 4953638 46525 2298829	20- 57.03 10- 7.8 40 6 m/z 40 6 m/z 2-[4-Fluoro-3-ft Methyl N-(2,6- ethyl (4-chloro	1316 15 10 80	105.04433 100.03635 13.98 13.98 13.98 13.98 13.98 10.120 10.12
ii	Igle Search Results: 993 hits Compound Name Barban BDMC-1(4-bromo-3,5-dimethylphenyl-N-methylcar Beflubutamid Benalaxyl Benazolin-ethyl Benalocarb	Formula C11H9Cl2 C10H12B C18H17F C20H23N C11H10Cl C11H10Cl C11H13N	Mass 257.00103 257.00514 355.11954 325.16779 271.00699 223.08446	Anion	Cation	RT (min) 11.325 8.199 10.338 12.968 10.212 6.459	CAS 101-27-9 672-99-1 113614-0 71626-11-4 25059-80-7 22781-23-3	ChemSpider 7270 4953638 46525 2298829 2224	20- 10- 57.03 10- 7.8 40 6 m/z 40 6 m/z 2-[4-Fluoro-3-6 Methyl N-(2,6- ethyl (4-chloro 2,2-Dimethyl-1	1316 15 10 80 10PA	105.04433 160.03635 13.98 318.10583   7.30 9.52 13.98 318.10583   9.52 13.98 10.10 6.92   100 120 140 160 180 200 220 240 260 280 300 320 340
in	Igle Search Results: 993 hits Compound Name Barban BDMC-1(4-bromo-3,5-dimethylphenyl-N-methylcar Beflubutamid Benalaxyl Benalaxyl Benacoln-ethyl Bendiocarb Benfluralin	Formula C11H9CI2 C10H12B C18H17F C20H23N C11H10CI C11H13N C13H16F	Mass 257.00103 257.00514 355.11954 325.16779 271.00699 223.08446 335.10929	Anion	Cation	RT (min) 11.325 8.199 10.338 12.968 10.212 6.459 6.460	CAS 101-27-9 672-99-1 113614-0 71626-11-4 25059-80-7 22781-23-3 1861-40-1	ChemSpider 7270 4953638 46525 2298829 2224 2229	20- 57.03 10- 7.8 40 6 m/z 40 6 m/z 40 6 m/z 2-[4-Fluoro-3-ft Methyl N-{2,6- ethyl (4-chloro 2Dimethyl-11 N-Butyl-N-ethyl	1316 15 10 80 10 10 10 10 10 10 10 10 10 10 10 10 10	105.04433 160.03635 13.98 318.10583   7.30 9.52 13.98 318.10583   7.30 9.52 13.98 10.100   100 120 140 160 180 200 220 240 260 280 300 320 340
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511	Ingle Search Results: 993 hits Compound Name Barban BDMC-1(4-bromo-3,5-dimethylphenyl-N-methylcar Beflubutamid Benalaxyl Benazolin-ethyl Bendiocarb Benfluralin Berfluracarb Berfluracarb Berfuresate	Formula C11H9Cl2 C10H12B C18H17F C20H23N C11H10Cl C11H13N C13H16F C20H30N C12H160	Mass 257.00103 257.00514 355.11954 325.16779 271.00699 223.08446 335.10929 410.18754 256.07693		Cation	RT (min) 11.325 8.199 10.338 12.968 10.212 6.459 6.460 14.914 8.267	CAS 101-27-9 572-99-1 113614-0 71626-11-4 25059-80-7 22781-23-3 1861-40-1 82560-54-1 68505-69-1	ChemSpider 7270 4953638 46525 2298829 2224 2229 49560 229853	20- 57.03 10- 7.8 40 6 m/z 40 7 40	1316 15 10 10 10 10 10 10 10 10 10 10 10 10 10	Name Mol. Formula Mono-isotopic exact mass Locked RT CAS #
ŝin	Ingle Search Results: 993 hits Compound Name Barban BDMC-1(4-bromo-3,5-dimethylphenyl-N-methylcar Beflubutamid Benalaxyl Benazolin-ethyl Benalocarb Benfluralin Berfuracarb Berfuracarb Berfuresate Bendanil	Formula C11H9Cl2 C10H12B C18H17F C20H23N C11H10Cl C11H13N C13H16F C20H30N C12H160 C12H160 C13H10I	Mass 257.00103 257.00514 355.11954 325.16779 271.00699 223.08446 335.10929 410.18754 256.07693 322.98071	Anion	Cation	RT (min) 11.325 8.199 10.338 12.968 10.212 6.459 6.460 14.914 8.267 12.505	CAS 101-27-9 572-99-1 113614-0 71626-11-4 25059-80-7 22781-23-3 1861-40-1 82560-54-1 68505-69-1 15310-01-7	ChemSpider 7270 4953638 46525 2298829 2224 2229 49560 2298853 2298853 2298853	20- 57.03 10- 7.8 0- 40 6 m/z 40 6 m/z 40 6 m/z 40 6 m/z 40 6 m/z 40 6 m/z 40 6 m/z 2-[4-Fluoro-3-t] Methyl N-(2.6- ethyl (4-chloro 2.2-Dimethyl-1 N-Butyl-N-ethyl Ethyl N-{[[(2,2] 3.3-Dimethyl-2 2-[odo-N-pher		Name Mol. Formula Mono-isotopic exact mass Locked RT CAS # Exact mass spectrum

#### **Results and Discussion**

#### **Linear Correlation, Recovery and Precision**

190 pesticides and 16 PAHs were spiked in soil for analysis. The results showed that most of the compounds had good linear response (R<sup>2</sup>>0.99) at a concentration of 10µg/L to 200µg/L. By using the spiked level of  $100\mu$ g/kg to calculate recovery and precision (n=5), the results showed that 91.7% of the recoveries were between  $70\% \sim 120\%$  and 93.2% of the relative standard deviations were less than 15%. Some results were listed in table 1. The overlap of Quantifier with Qualifiers for various compounds in soil extract at a concentration of 10  $\mu$ g/kg were showed in Fig.2.

## **Experimental**

## Sample Preparation



- Exact mass spectra for more than 800 pesticides and environmental contaminants
- Two sets of retention times for pre-tested retention time locked screening methods
- Automated & unique RT locking process allows to easily replicate the locked retention times in the library
- Retention times help verify hits as another measure of confirmation in addition to exact mass spectra
- MassHunter PCDL manager software allows to easily manage libraries

#### "All lons" Screening Workflow



Table 1. Linear Correlation, recoveries and relative standard deviation (RSDs) of part pesticides and PAHs for soil sample

Compounds	RT/(min)	Quantifier Ion	Qualifier Ion-1	Qualifier Ion-2	R <sup>2</sup>	Rec(%)	RSD(%)
Fluorene	12.1	166.0777	165.0699	164.0621	0.992	89.3	6.8
Cycloate	13.0	154.1226	83.0855	55.0542	0.996	75.8	12.2
Benfluralin	14.0	292.0528	264.0227	206.0298	0.996	72.5	0.4
Phorate	14.2	75.0263	121.0413	230.9732	0.995	63.3	0.2
Propazine	15.5	214.0854	172.0384	229.1089	0.995	92.4	3.2
Terbuthylazine	15.8	214.0854	173.0463	138.0774	0.997	88.8	3
Propetamphos	15.9	138.0137	109.9824	193.9797	0.995	80.6	1
Diazinon	16.4	137.0709	179.1179	152.0944	0.998	82.8	1.2
Pentachloroaniline	17.3	264.8595	262.8624	266.8565	0.998	83.7	5.2
Desmetryn	17.6	213.1043	198.0808	171.0573	0.998	83.1	1.8
Ametryn	18.4	227.1199	212.0964	170.0495	0.997	86.3	2.4
Prometryn	18.6	184.0651	241.1356	226.1121	0.997	89.2	3.3
Terbutryn	19.1	185.0730	170.0495	226.1121	0.995	86.2	0.1
Ethofumesate	19.3	161.0597	207.1016	137.0597	0.998	92.5	3.4
Aldrin	19.5	262.8564	264.8535	292.9267	0.997	87.9	4.4
Dipropetryn	19.6	255.1512	240.1277	222.1713	0.998	88.9	2.5
Triadimefon	20.1	208.0267	128.001	181.0163	0.999	83.6	4.7
Tetraconazole	20.3	336.0521	338.0492	170.9763	0.998	69.4	4.6
Procymidone	21.8	96.0570	283.0161	285.0132	0.999	94.6	1.8
Chlordane-trans	21.9	372.8254	374.8225	376.8195	0.999	93.5	4.6
Pyrene	22.2	202.0777	201.0699	200.0621	0.996	103.2	9
Endosulfan I	22.4	236.8408	192.9373	159.9841	0.998	86.5	2.9
Chlorfenson	22.8	174.9615	110.9996	301.9566	0.998	93.4	4.3
Napropamide	22.9	72.0808	128.107	271.1567	0.996	83	1.1
Dieldrin	23.3	79.0542	262.8564	344.8983	0.997	90.9	1.5
Methoprotryne	23.9	256.1227	212.0964	226.1121	0.997	76.9	4.1
Endosulfan II	24.5	236.8408	192.9373	159.9841	0.995	85.2	2.8
Chrysene	28.0	228.0934	226.0777	200.0621	0.995	111.2	6.3
Tebufenpyrad	28.6	171.0320	318.1368	333.1602	0.998	88.6	1.9



#### **Instrument Conditions**

GC system: Agilent 7890B; Column: HP-5ms UI (30 m $\times$ 0.25 mm $\times$ 0.25 µm); Oven temperature: 60 °C hold 1 min , at 40 °C /min to 120 °C, at 5 °C /min to 310 °C; Injection mode: Splitless, purge on after 1.5 min Injection port temperature: 280 °C; Carrier gas: Helium; Flow rate: 1.0mL/min; Injection volume: 1µL; Mass system : Agilent 7200 GCQTOF; MS Acquisition: Full Scan 45-550 m/z; 5Hz lon source: El; Ion source polarity: Positive ion; Ionization voltage: 70 eV; Ion source temperature: 280°C;

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"All lons" Screening Workflow

- Lock GC Retain Times in PCDL
- Analyze Samples by GC/Q-TOF in EI TOF mode
- Load data file into Masshuter Qualitiative Analysis Software
- Under Find by Formula, choose PCDL to use "All lons" setpoints
- Software compares RT & peak shape for each EIC; Assigns coelution score to each EIC
- Software extracts most significant extract mass ions for each compound in PCDL
- Choose 1.) No. of exact mass ions to extract , 2) No. of "qualified" ions required for identification, 3) Minimum coelution score (and a few more setpoints)
- Peak RT compared to locked RT in PCDL
- Automatic Creation of Quant Method
- Identification information summarized

# "All lons" Screening Result

As a validation study, 190 pesticides were spiked into soil matrices at certain levels. Most of the pesticides were found in the lowest level of  $10\mu g/L$  and their presence was verified by at least two additional fragment ions and their retention time. The screening result view (Fig.1) of the software allows users to easily scroll through all identified compounds, with the details of each compound also available for review purpose. Identified compounds can be verified by mass error of qualified ions, ratio of fragment ions, overlaid EICs and coelution plot, which adds confidence in identification.

Agilent MassHunter Qualitative Analysis B.07.00 - GCQTOF_Pesticide_15-15m_40min_PCDL.m [20101104_003.D]		
File Edit View Find Identify Method Wizards Configuration Tools Help		
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G Compound List	Compound Identification Results: Cpd 37: Hexachlorobenzene	×



## Analysis of real samples

The method was applied for the analysis of 10 soil samples collected from rice field along the roads located in Liaozhong city in Liaoning Province. Table 2 showed the detected pesticides and polycyclic aromatic hydrocarbons in real samples.

Table 2. Detected pesticides and polycyclic aromatic hydrocarbons in real sampl	les.
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Pesticides	Concentration Range ( µg/kg )	PAHs	Concentration Range ( µg/kg )
Atrazine-desethyl	1.2-11.5	Naphthalene	0.6-1.5
Atrazine	1.3-523.5	Acenaphthylene	1.6-10.2
Acetochlor	1.4-1561.5	Acenaphthene	5.2-8.2
β-666	2.0	Fluorene	8.3-16.9
Chlorpyrifos	0.5-12.3	Phenanthrene	20.4-184.3
Phorate Sulfone	1.8-5.7	Anthracene	10.5-27.3
Butachlor	2.1-21.3	Fluoranthene	16.9-243.1
lsoprothiolane	3.4-456.7	Pyrene	13.5-226.5
p,p'-DDD	0.3-1.3	Benz[a]anthracene	17.4-209.2
Triazophos	23.8-110.7	Chrysene	22.7-282.0
Tebuconazole	5.6	Benzo[b]fluorathene	21.6-366.9
Diphenyl	1.5-2.7	Benzo[k]fluoranthene	21.2-388.3
Hexachlorobenzene	5.6-13.5	Benzo[a]pyrene	20.9-435.7
Pentachloroaniline	2.3	Dibenz[a,h] anthracene	5.3-183.8
Thiobencarb	1.8	Indeno[1,2,3-cd]pyrene	11.8-428.2
Propazine	2.3-8.2	Benzo[g,h,i]perylene	38.7-563.3



#### **Data Acquisition and Analysis**

Interface temperature: 280°C;

The data were acquired with the MassHunter Acquisition Software B.07.02. Data analysis for the pesticides and environmental contaminants screening was performed with the "All lons" tool in MassHunter Qualitative Analysis Software (B.07.00) and the GC/QTOF pesticides and environmental contaminants PCDL. Quantitation was performed with the MassHunter Quantitative Analysis Software (B.07.01).



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2 77 (	Cpdマ中	Name 🛛 🖓	Formula ⊽+¤ S	core⊽⊽≠	Mass 🖓 🕂 I	Mass (Tgt) 🖓 🗗	Mass (DB) 🛛 🖶			ID Techniqu	ues Applied 👎					h	
tachloroaniline	32	Pentachloroaniline	C6 H2 CI5 N	95.34	262.862	262.863	262.863		•	FE	BF-FragConfirm					IJ	
Cpd 37: Hexachlorobenzene		Hexachlorobenzene	C6 CI6	94.89	281.8124	281.8131	281.8131	- 10		Rest +	Name	-P Formula -P	m/z / -¤	Mass - M	ass (Tot) -	Diff (nom) -	Score
Cpd 52: o,p'-DDE	52	o,p'-DDE	C14 H8 CI4	91.9	315.9368	315.938	315.938			10	Hexachlorobenze	ane C6 CI6	283 8090	281 8124	281 8131	2.58	
Cpd 51: p,p'-DDE	51	p.p'-DDE	C14 H8 CI4	91.69	315.9368	315.938	315.938				Thexademonoperize	00000	200.0000	201.0124	201.0101	2.00	
Cpd 26: Prometryn	26	Prometryn	C10 H19 N5 S	91.59	241.1346	241.1361	241.1361			Coelutio	on Score 🕂 CE 🕈	Flags(Fls) +	FV - Heig	ght+₽ m/z	+ Compou	Ind Name 🕂	RT -
Cpd 29: Dipropetryn	29	Dipropetryn	C11 H21 N5 S	88.99	255.1503	255.1518	255.1518				100	Reference ion	32	250.1 281.81	26 Hexach	lorobenzene	14.56
Cpd 6: Biphenyl	6	Biphenyl	C12 H10	88.49	154.0768	154.0782	154.0782				94.8	Qualified	58	317.4 283.8	09 Hexach	lorobenzene	14.55
Cpd 62: Tebufenpyrad	62	Tebufenpyrad	C18 H24 CI N3 O	87.69	333.16	333.1608	333.1608				94.2	Qualified	48	358.2 285.8	06 Hexach	lorobenzene	14.55
Cpd 20: Cyprodinil	20	Cyprodinil	C14 H15 N3	85.28	225.1244	225.1266	225.1266				91.9	Qualified		2233 287.80	33 Hexach	lorobenzene	14.56
Cpd 14: Desmetryn	14	Desmetryn	C8 H15 N5 S	83.67	213.1033	213.1048	213.1048	-	-	-	90.3	Qualified	22	276.3 248.84	02 Hexach	lorobenzene	14.55
Cpd 24: Pirimicarb	24	Pirimicarb	C11 H18 N4 O2	83.55	238.142	238.143	238.143			7	87.3	Qualified		1407 250.83	74 Hexach	lorobenzene	14.56
Cpd 3: Naphthalene	3	Naphthalene	C10 H8	83.09	128.0612	128.0626	128.0626	-	L.	-	92.2	Qualified	16	524.9 246.84	37 Hexach	lorobenzene	14.56
Cpd 38: Procymidone	38	Procymidone	C13 H11 CI2 N O2	82.97	283.0169	283.0167	283.0167										
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Fig. 1 "All lons" tool results overview for pesticides spiked into soil extract (10 µg/kg). a) Compound list showing hits, b) Compound identification results for hexachlorobenzene, c) Extracted ion chromatograms for the most significant hexachlorobenzene ions,

d) Coelution plot, e)Molecular ion isotope ratio plot,

f) TIC averaged across the chromatographic peak.

## Conclusion

The research demonstrates the effective combination of high resolution mass spectrometry and an exact mass library to identify a large variety of pesticides and other contaminants in soil matrices. Both the exact mass measurement with high resolution as well as the high sensitivity of the GC/Q-TOF system were essential to obtain superior results.

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