

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

Ming Luo¹, Lu Wang¹, Zeying He¹, Yi Peng¹, Shan Zhou², Wenwen Wang² and Xiaowei Liu^{1*}

¹Agro-Environmental Protection Institute, Ministry of Agriculture, Tianjin 300191, P.R. China

²Agilent Technologies (China) Company, Ltd., Beijing 100102, China

2015 PTS
PM-23



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 Ions MS feature integrated in Masshunter software was employed to rapidly screen, identify and confirm many pesticides and some other contaminants in soil matrices.

Experimental

Sample Preparation

1. Weigh 10 g soil sample into tube with 20 mL acetonitrile, and then shake for 1 hour at 180 rpm/min by oscillator.
2. Take the supernatant into another tube and add 5g Sodium chloride.
3. Add another 20 mL acetonitrile into soil sample tube, repeat step 1 and 2, then combine the supernatant to the centrifuge tube.
4. Centrifuge the supernatant tube for 5 min at 4000 rpm. 10mL upper layer was taken and evaporated to dryness. Redissolve the residue in 2.5 mL of solvent (EAC:ACE=49:1).

Instrument Conditions

GC system: Agilent 7890B;
Column: HP-5ms UI (30 m × 0.25 mm × 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: 1 μL;
Mass system: Agilent 7200
GC/TOF;
MS Acquisition: Full Scan 45-550
m/z; 5Hz
Ion source: EI;
Ion source polarity: Positive ion;
Ionization voltage: 70 eV;
Ion source temperature: 280°C;
Interface temperature: 280°C;
Solvent delay: 3 min



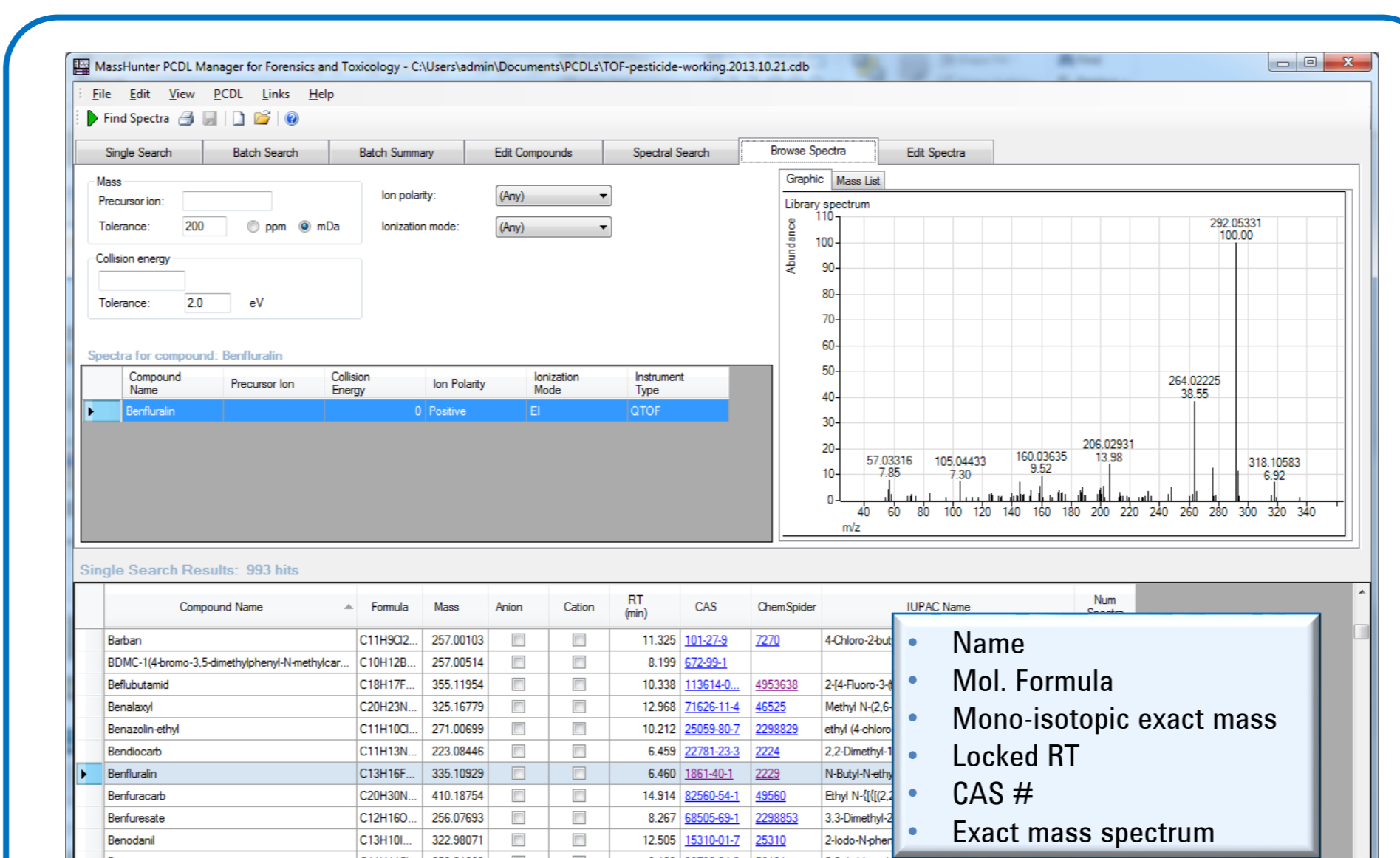
Data Acquisition and Analysis

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 Ions" 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).



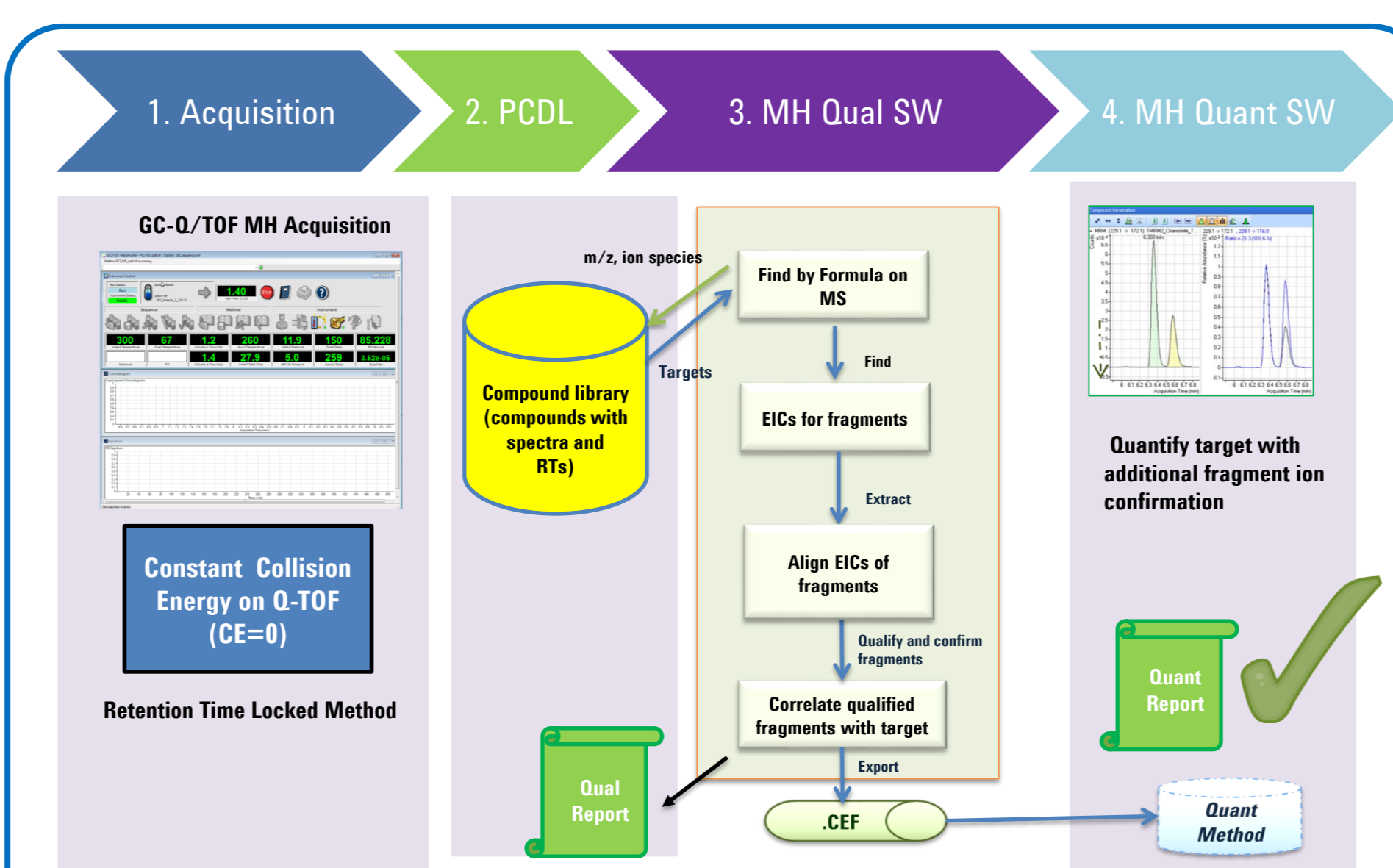
Results and Discussion

PCDL: Personal Compound Database & Library



- 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 Ions" Screening Workflow



- "All Ions" Screening Workflow
- Lock GC Retain Times in PCDL
- Analyze Samples by GC/Q-TOF in EI TOF mode
- Load data file into Masshunter Qualitative Analysis Software
- Under Find by Formula, choose PCDL to use "All Ions" 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 Ions" 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 μg/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.

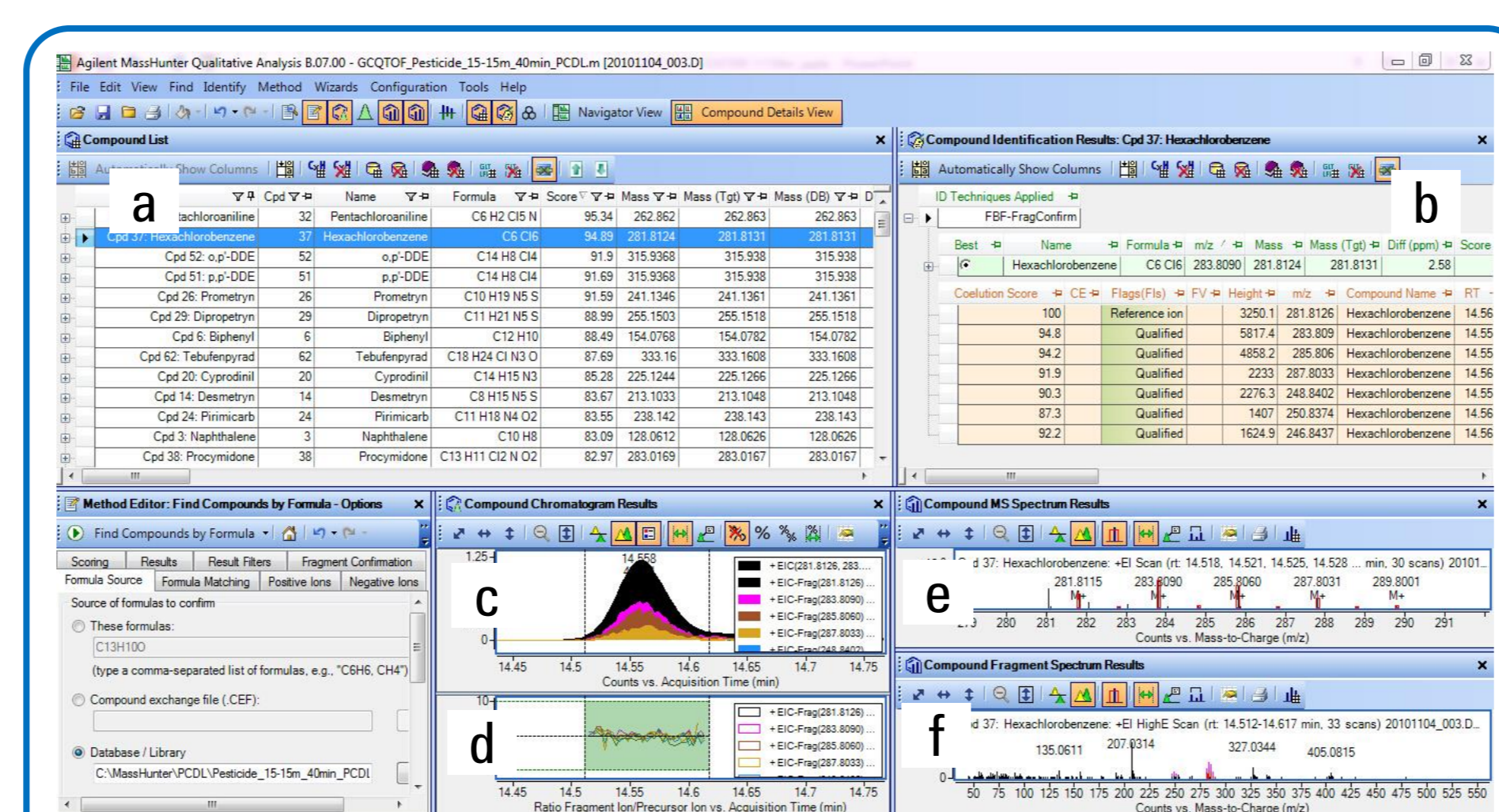


Fig. 1 "All Ions" tool results overview for pesticides spiked into soil extract (10 μg/kg). a) Compound list showing hits, b) Compound identification results for hexachlorobenzene, c) Extracted ion chromatograms for the most significant hexachlorobenzene ions, d) Coelution plot, e) Molecular ion isotope ratio plot, f) TIC averaged across the chromatographic peak.

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 ($R^2 > 0.99$) at a concentration of 10 μg/L to 200 μg/L. By using the spiked level of 100 μg/kg to calculate recovery and precision (n=5), the results showed that 91.7% of the recoveries were between 70%~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 μg/kg were showed in Fig.2.

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

Compounds	RT/(min)	Quantifier Ion-1	Qualifier Ion-1	Qualifier Ion-2	R ²	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
Terbutylazine	15.8	214.0854	172.0384	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
Desmethyln	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
Procydimone	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
Chlorfensone	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
Methoprotryn	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

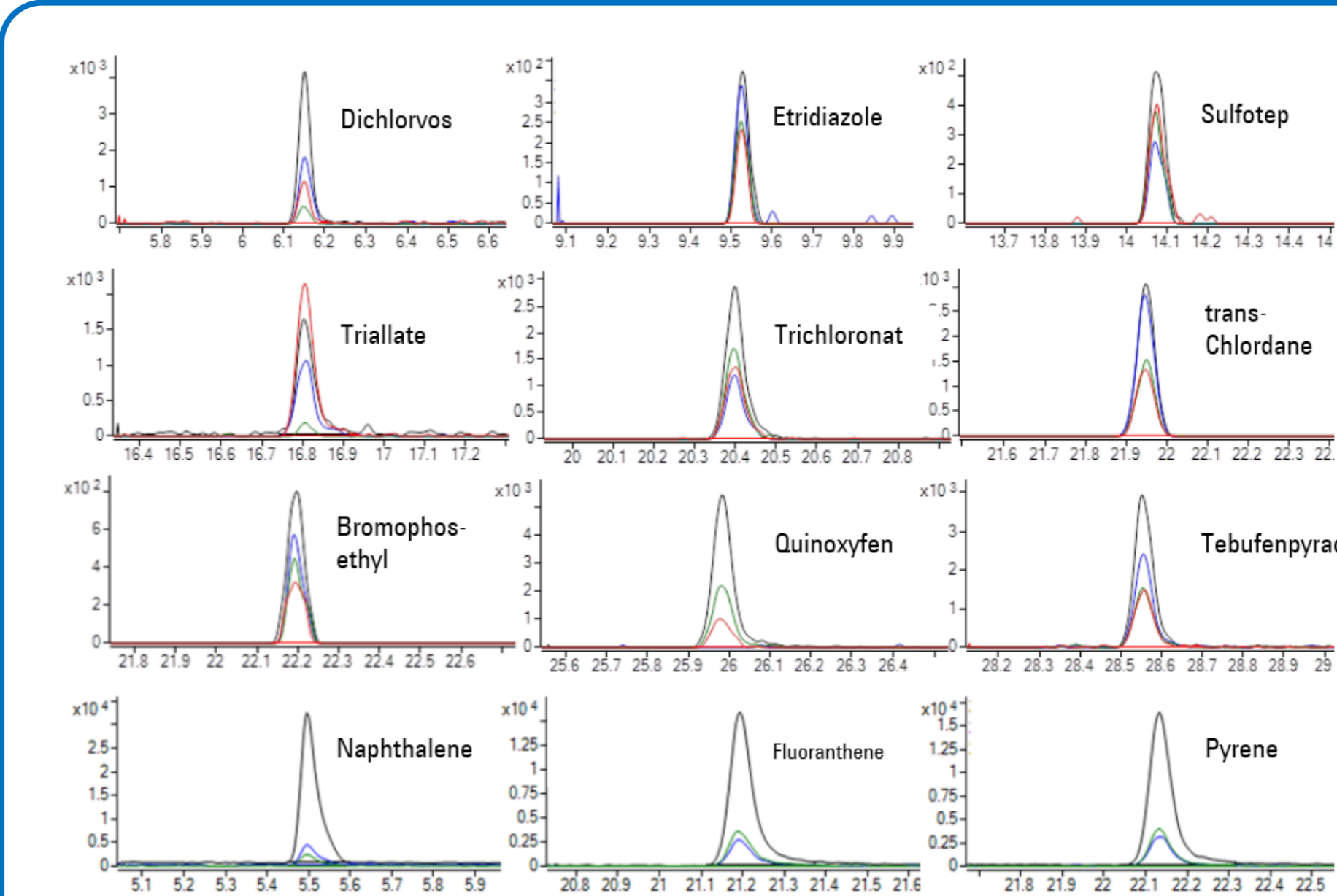


Fig. 2 Overlap of Quantifier with Qualifiers for various compounds in soil extract at a concentration of 10 μg/kg

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 samples.

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
Isoprotiholane	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]fluoranthene	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[ghi]perylene	38.7-563.3

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.