Poster Reprint

ASMS 2025
Poster number ThP 083

New Pollutant Screening of Environmental Samples Using High-Resolution GC/Q-TOF and Accurate Mass Spectral Library of Emerging Environmental Pollutants

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Introduction

This paper conducts qualitative and semi - quantitative analysis of complex GC/Q-TOF sample data by using high-resolution, accurate-mass gas chromatography/quadrupole time-of-flight mass spectrometry (GC/Q-TOF), an accurate mass spectral library of environmental pollutants specifically created for emerging pollutant screening, and analytical software with a screening process platform. Actual environmental water samples are used to verify the sensitivity, accuracy, and spiked recovery rate of the solution. All results confirm that this solution is simple, stable, and effective, providing technical support for emerging pollutant screening.

Experimental

Sample Preparation

The pretreatment of environmental water samples entails the extraction of organic substances via an optimized liquid-liquid extraction solvent. This procedure can be performed either manually or automatically using the PAL3 RTC automated processing platform. Following this, data acquisition is carried out using the Agilent 7250 GC/Q-TOF instrument platform.

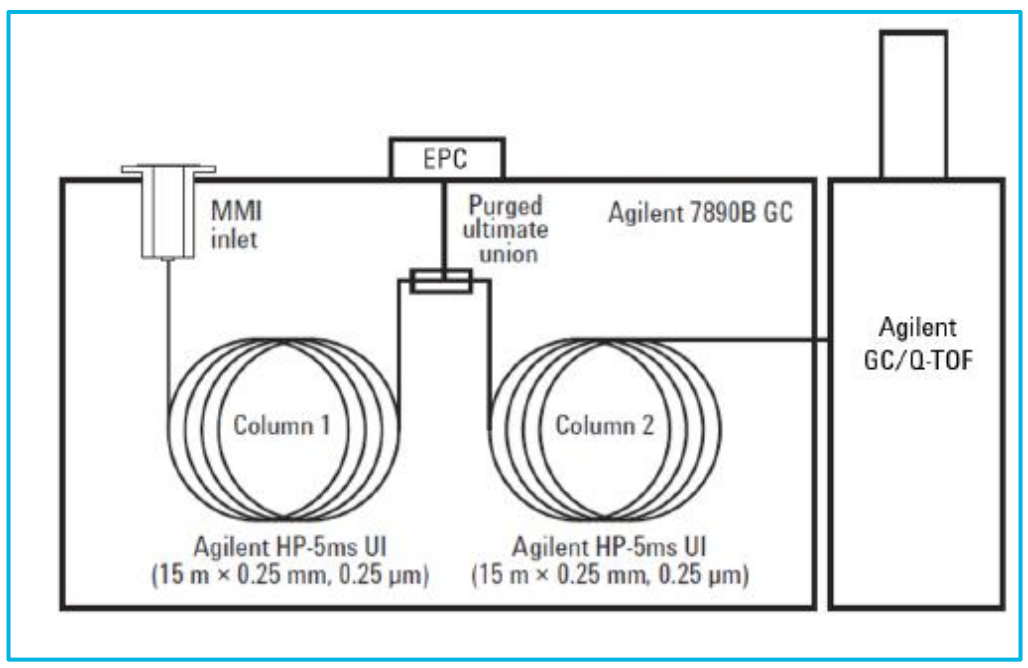


Figure 1. 7250 GC/Q-TOF system and hardware setup

Experimental

Instrument Analysis

The samples were analyzed by Agilent 8890 GC and 7250 high resolution accurate mass GC/Q-TOF system, It was configurated with a mid-column backflush setup (Figure 1). A 55.5 - min retention time locked GC oven temperature program is utilized which is listed in Table 1. The key mass spectrometry parameters of the GC/Q-TOF are as follows: It operates in the Electron Ionization (EI) mode with an energy of 70 electron volts, conducts detection in the time-of-flight scan mode within a mass-to-charge ratio range of 50 - 1000. The spectral acquisition rate is 5 Hz, and both the interface temperature and the source temperature are set at 280 °C. Data analysis is performed with the assistance of MassHunter data analysis software. The high-resolution accurate mass spectral library employed in the screening process is independently created by the laboratory.

Table 1. GC-Q/TOF Operational Conditions.

GC and MS Conditions	Value
Column (2 ea.)	HP-5MS UI, 15 m, 0.25 mm ID,0.25 µm film
Inlet	MMI,4-mm UI liner with wool
Injection	1µL by automatically in splitless mode 5µL by manually in solvent vent mode
Injection temperature	280 °C
Inlet flow (column 1)	~ 1.0 mL/min
PUU flow (column 2)	column 1 flow + 0.2 mL/min
Oven program	60 °C for 1 min 40°C/min to 120°C,0 min 5°C/min to 310°C,15 min
Backflushing conditions	5 min (Post-run),310 °C(Oven) 45psi (Aux EPC),2 psi (Inlet)
Transfer line temperature	280°C
Ion source	EI, 70 eV
Ion source temperature	280°C
Quadrupole temperature	150 °C
Spectral Acquisition	50-1000 m/z, 5 spectra/sec

Data Analysis

- The data processing used Agilent Masshunter data analysis software, including Suremass.
- The target screening of new pollutants was based on an independently created by the laboratory GC/Q-TOF PCDL library[1].

Results and Discussion

Results of Compound Screening and Semi-Quantification

Analysis by GC/Q-TOF provided high-efficiency screening of new pollutants. An accurate mass pesticides library (Figure 2) was employed to perform targeted screening using a tool to search by principle ions of each compound with the identified hits verified via mass accuracy, S/N, library match factor, RT match and coelution score. After rapid and efficient screening, Agilent's MassHunter quantitative software can be used to conduct semi - quantitative analysis on the positive results of the samples(Figure 3), meeting the qualitative and quantitative analysis needs of different operators.

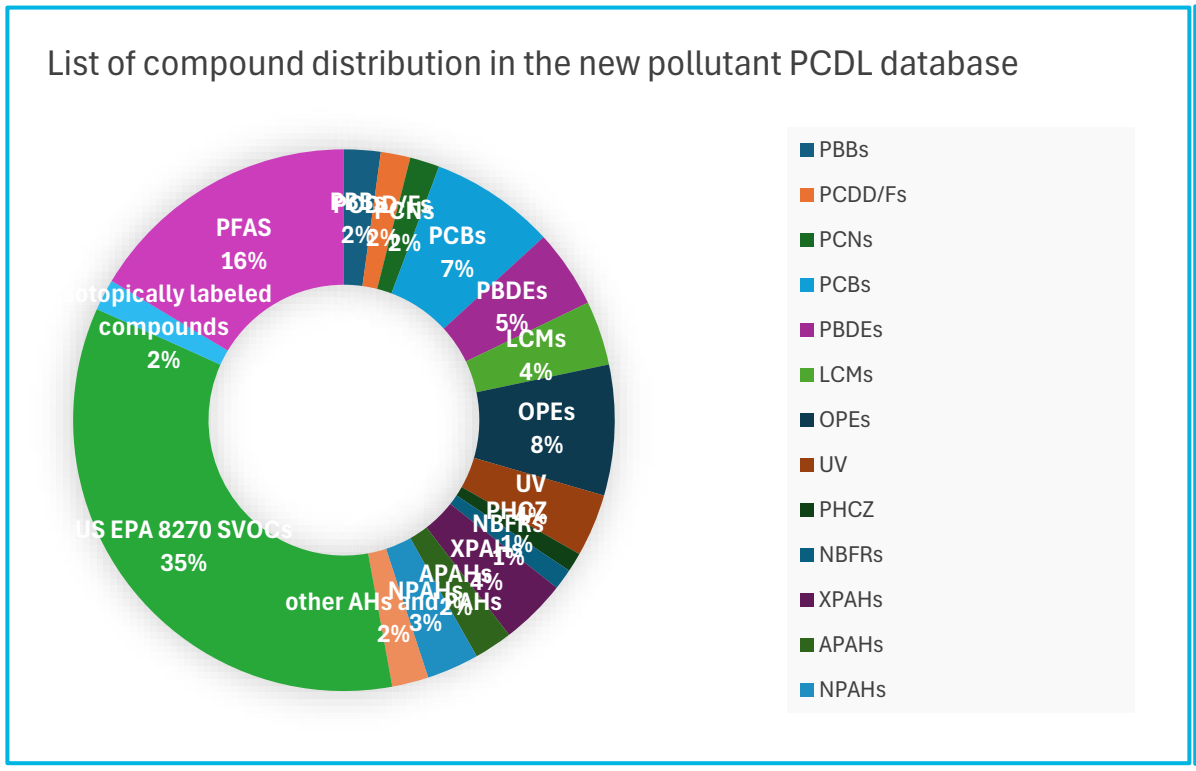


Figure 2. List of compound distribution in the new pollutant PCDL

Name	Formula	Mass	Retention Time	Retention Index	CAS	Description
Chlordane-cis (α-Chlordan)	C10H6Cl8	405.79777	22.555	2140	5103-71-9	顺-氯丹(α)
Butachlor (Machete)	C17H26ClNO2	311.16521	22.703	2149	23184-66-9	丁草胺
Nonachlor-trans	C10H5Cl9	439.7588	22.743	2151	39765-80-5	反式-九氯
Fenamiphos	C13H22NO3PS	303.1058	22.978	2164	22224-92-6	苯线磷
Prothiofos	C11H15Cl2O2PS2	343.96281	23.191	2176	34643-46-4	丙硫磷
Isoprothiolane	C12H18O4S2	290.06465	23.249	2179	50512-35-1	稻瘟灵
Profenofos	C11H15BrClO3PS	371.93514	23.306	2183	41198-08-7	丙溴磷
Barban	C11H9Cl2NO2	257.00103	23.391	2188	101-27-9	燕麦灵/氯炔草灵
Dieldrin	C12H8Cl6O	377.87063	23.391	2188	60-57-1	狄氏剂
3,3',4-Trichlorobiphenyl_35#	C12H7Cl3	255.96133	19.7009	1983	37680-69-6	PCB-35; 多氯联苯
p,p'-DDE	C14H8Cl4	315.93801	23.418	2189	72-55-9	4,4'-滴滴伊
Pretilachlor	C17H26ClNO2	311.16521	23.447	2191	51218-49-6	丙草胺
o,p'-DDD	C14H10Cl4	317.95366	23.719	2206	53-19-0	2,4'-滴滴滴
3-Amino-9-ethylcarbazole	C14H14N2	210.1157	23.822	2212	132-32-1	3-氨基-N-乙基咔唑
Nitrofen	C12H7Cl2NO3	282.9803	24.168	2233	1836-75-5	除草醚
Endrin	C12H8Cl6O	377.87063	24.168	2233	72-20-8	异狄氏剂
Benzenamine, N,N-dimethyl-4-(phenylazo)-	C14H15N3	225.1266	24.199	2235	60-11-7	对二甲氨基偶氮苯
Aramite(I)	C15H23ClO4S	334.10056	23.838	2213	140-57-8	杀螨特
Aramite(II)	C15H23ClO4S	334.10056	24.215	2236	140-57-8	杀螨特
β-Endosulfan	C9H6Cl6O3S	403.81688	24.523	2254	33213-65-9	β-硫丹
Chlorobenzilate	C16H14Cl2O3	324.0320	24.618	2260	510-15-6	乙基杀螨醇/乙酯杀螨醇
2,4',5-Trichlorobiphenyl_31#	C12H7Cl3	255.96133	17.7249	1880	16606-02-3	PCB-31; 多氯联苯

Figure 3. Overview of the New Contaminants PCDL Database

Sample Screening

Targeted screening was set up to automatically extract six ions per new pollutants from the PCDL, and to require at least two of these to produce EICs with a coelution score ≥75 and an S/N ≥ 3. If a compound passing these requirements had an RT within ±0.1 minutes, it was considered identified. this workflow is very simple and efficient. The complex data collected by GC/Q-TOF can be directly imported into the Masshunter screening process software to achieve automatic spectral library retrieval, generation of screening reports, and generation of semi - quantitative reports. In this paper, actual water samples were collected from two different areas, namely rivers near farmland and ordinary surface water. Using this screening process, trace amounts of new pollutant compounds were detected in both cases (Figure 5).

Method Sensitivity and Stability Validation

To verify the reliability of the method, experiments for verifying sensitivity, stability, and spiked recovery of actual samples were designed. In terms of sensitivity and stability, this scheme can achieve five consecutive repeated injections at trace concentrations of 0.1 μg/L and 0.5 μg/L, with the data stability reaching RSD% < 10%. Regarding the spiked recovery of actual samples, for the automated pretreatment scheme, solvent standards were used to prepare reference substances, and the calculated recovery rates of samples spiked at a concentration of 5 μg/L were in the range of 84.4% - 151.7%. For the manual scheme, matrix - spiked reference substances were used to calculate the recovery rates of 5 μg/L spiked samples, which were in the range of 91.6% - 137% (Figure 4).

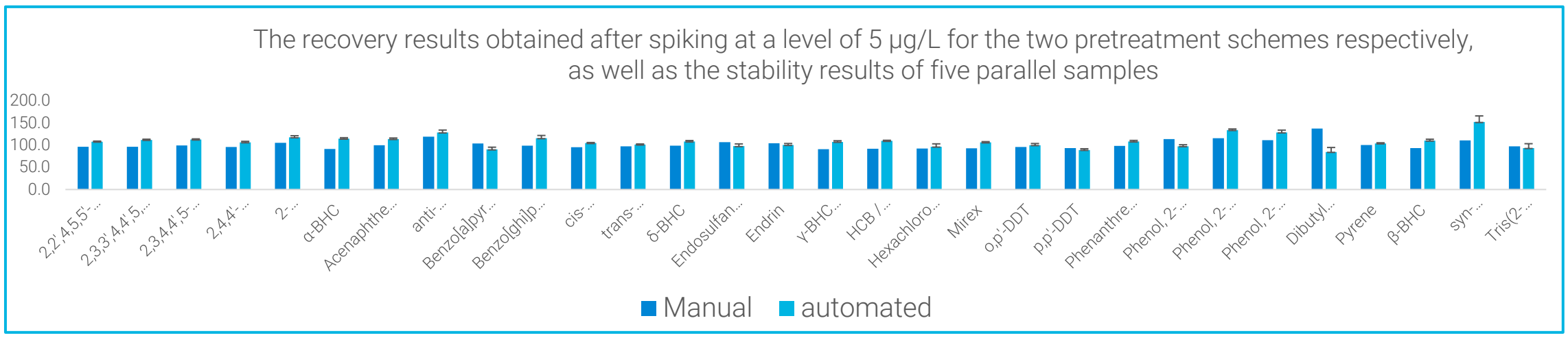
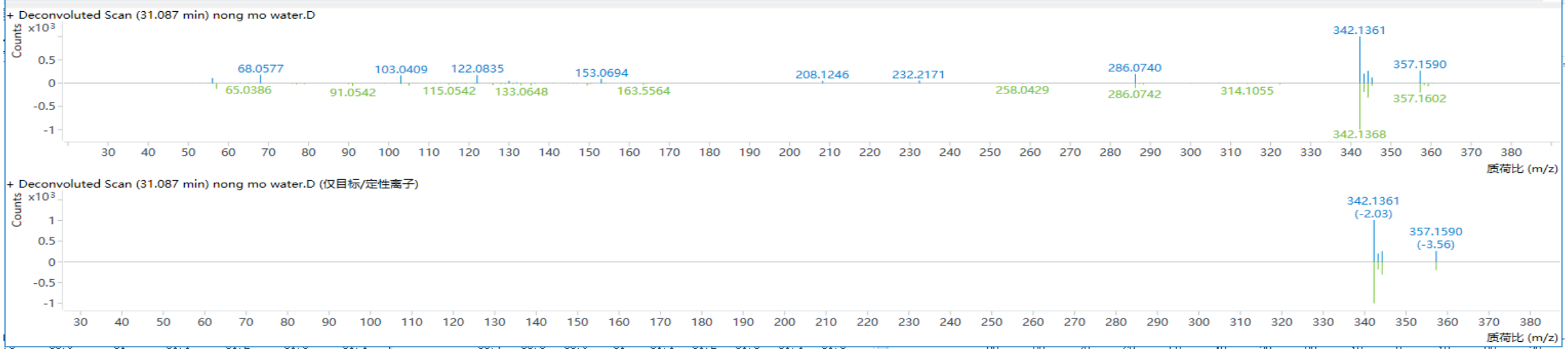


Figure 4. The recovery results obtained after spiking at a level of 5 μg/L for the two pretreatment schemes respectively

Results and Discussion

Figure 5. Based on the PCDL quantitative screening process, pollutants such as PCBs (Polychlorinated Biphenyls), PAHs (Polycyclic Aromatic Hydrocarbons), organophosphates, UV absorbers, and plasticizers were detected in a certain surface water.

状态	已更新	化合物名称	CAS#	离子式（分子式）	R.T.	R.T. 差	最终浓度	匹配分数	目标离子	质量精确度	确认的离子数	面积	峰高
✓	☐	p,p'-DDE	72-55-9	C14H8Cl4	23.412	0.012		81.4	245.9998	-2.6576	4	1117.8	350.5
✓	☐	1-Methylfluoranthene	25889-60-5	C17H12	23.884	0.037		99.7	215.0855	-3.4351	4	14807.7	2300.2
✓	☐	Retene	483-65-8	C18H18	23.991	0.019		99.4	219.1168	-1.6021	3	5639.0	1659.5
✓	☐	Pyrene, 1-methyl-	2381-21-7	C17H12	24.829	0.026		91.3	216.0934	-4.2160	4	9158.0	2704.4
✓	☐	DHP / Dihexyl phthalate (DHXP) (DnHP)	84-75-3	C20H30O4	26.206	0.066		80.5	149.0233	-3.9242	3	17458.5	5797.7
✓	☐	BBP / Benzyl butyl phthalate (Butylbenzylphthalate)	85-68-7	C19H20O4	26.206	0.011		95.9	149.0233	-3.9242	4	17602.0	5811.8
✓	☐	DEHA / Di(2-ethylhexyl) adipate	103-23-1	C22H42O4	26.960	0.003		98.8	129.0546	-3.0967	4	48002.4	16905.7
✓	☐	Piperonyl butoxide	51-03-6	C19H30O5	27.190	0.017		88.4	176.0832	-1.9740	3	3648.6	1260.3
✓	☐	Benz[a]anthracene	56-55-3	C18H12	27.805	0.030		98.0	228.0934	-3.5313	4	8008.5	2265.7
✓	☐	Chrysene	218-01-9	C18H12	27.971	0.021		98.6	228.0934	-3.4724	3	36101.8	8946.3
✓	☐	DEHP / Di(2-ethylhexyl) phthalate	117-81-7	C24H38O4	29.311	0.012		98.6	149.0233	-1.8854	4	2481251.5	838335.1
✓	☐	Bumetrizole (UV-326)	3896-11-5	C17H18ClN3O	29.335	0.011		98.9	300.0898	-2.9579	4	8907.5	2779.1
✓	☐	Phenol, 2-(5-chloro-2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)- (UV-327)	3864-99-1	C20H24ClN3O	31.087	0.009		98.2	342.1368	-2.0273	4	4604.8	1576.3
✓	☐	Benzo[b]fluoranthene	205-99-2	C20H12	32.530	0.022		99.2	252.0934	-3.2236	4	12919.1	2000.2
✓	☐	Tris(2,4-di-tert-butylphenyl) phosphate	95906-11-9	C42H63O4P	43.631	0.058		99.4	647.4224	-2.5643	4	51684.5	10966.3



Semi-Quantification Result

In response to the current requirement of sometimes needing to issue semi-quantitative analysis reports for screening analysis, this method also explored the results of automatically generating semi-quantitative analysis reports using software. By using the setting of inherited calibration reference standards available in the Masshunter software, all other compounds were treated as inherited targets of the three target substances (PAH) for semi-quantitative concentration calculation. Finally, combined with the customized screening semi-quantitative analysis report template of the software, the semi-quantitative results of samples can be presented in the form of a classic report (Figure 6).

GC/Q-TOF筛查报告

Sample Name A sample Matrix sp5ppb **# of Hits** 31

Status	Compound	CAS#	Formula	RT/min	RT/min	Area	Height	Final Units Conc.	Lib Match Score	Mass Accuracy (PPM)	# of Verified Ions
+	Acenaphthene	83-32-9	C12H10	10.137	0.005	683541	258443	4.8633 ng/ml	99.8	153.0699	-1.69	4
+	Pyrene	129-00-0	C16H10	22.175	0.005	1252427	347907	8.2978 ng/ml	99.1	202.0777	-1.26	4
+	Benzo[a]pyrene	50-32-8	C20H12	33.817	0.003	680707	97954	72.2926 ng/ml	99.8	252.0934	-2.39	4
+	Hexachlorobutadiene	87-68-3	C4Cl6	5.820	0.005	26901	9622	0.1914 ng/ml	99.9	224.8408	-3.01	4
+	2-Chloronaphthalene_2#	91-58-7	C10H7Cl	8.198	0.001	738558	287299	5.2547 ng/ml	99.4	162.0231	-0.72	4
+	2-Chloronaphthalene	91-58-7	C10H7Cl	8.198	0.005	738015	287243	5.2508 ng/ml	99.2	162.0231	-0.72	4
+	α-BHC	319-84-6	C6H6Cl6	14.293	0.009	133340	44531	0.9487 ng/ml	99.9	182.9344	-1.45	4
+	HCB / Hexachlorobenzene	118-74-1	C6Cl6	14.559	0.001	446883	152238	3.1795 ng/ml	99.8	283.8096	0.26	4
+	β-BHC	319-85-7	C6H6Cl6	15.338	0.008	122828	40414	0.8739 ng/ml	99.9	182.9344	-0.82	4
+	TCEP / Tris(2-chloroethyl)phosphate	115-96-8	C6H12Cl3O4P	15.530	0.005	45448	13074	0.3234 ng/ml	97.5	248.9845	-0.61	4
+	γ-BHC (Lindane)	58-89-9	C6H6Cl6	15.560	0.001	132349	43927	0.9416 ng/ml	99.4	180.9373	-1.49	4
+	Phenanthrene	85-01-8	C14H10	15.896	0.000	1191643	383778	8.4783 ng/ml	99.3	178.0777	-0.57	4
+	δ-BHC	319-86-8	C6H6Cl6	16.501	0.007	87911	28479	0.5824 ng/ml	99.4	180.9373	-1.84	4
+	2,4,4'-Trichlorobiphenyl_28#	7012-37-5	C12H7Cl3	17.762	0.005	485843	156513	3.2189 ng/ml	99.9	255.9608	-0.78	4
+	Phosphoric acid, dibutyl phenyl ester	2528-36-1	C14H23O4P	17.838	0.002	111576	33001	0.7392 ng/ml	95.3	175.0155	-2.40	4
+	Chlordane-trans (γ-Chlordan)	5103-74-2	C10H6Cl8	22.002	0.000	164388	51719	1.0891 ng/ml	99.9	372.8254	-0.39	4
+	2,2',4,5,5'-Pentachlorobiphenyl_101#	37680-73-2	C12H5Cl5	22.354	0.001	301065	98409	1.9947 ng/ml	100.0	325.8799	-0.46	4
+	Chlordane-cis (α-Chlordan)	5103-71-9	C10H6Cl8	22.570	0.004	142741	46055	0.9457 ng/ml	99.9	372.8254	-0.73	4
+	Endrin	72-20-8	C12H8Cl6O	24.183	0.009	42793	12767	0.2835 ng/ml	99.9	262.8564	-2.75	4
+	2,3,4,4',5-Pentachlorobiphenyl_114#	74472-37-0	C12H5Cl5	25.034	0.005	351629	104173	2.3297 ng/ml	99.9	325.8799	-0.66	4
+	o,p'-DDT	789-02-6	C14H9Cl5	25.061	0.001	149773	46315	0.9923 ng/ml	98.8	235.0076	-2.10	4
+	Endosulfan sulfate	1031-07-8	C9H6Cl6O4S	26.095	0.013	18221	5345	0.1207 ng/ml	99.3	271.8096	-4.03	4
+	p,p'-DDT	50-29-3	C14H9Cl5	26.295	0.005	106953	34491	0.7086 ng/ml	97.4	235.0076	-1.63	4
+	Phenol, 2-(2H-1,2,3-benzotriazol-2-yl)-4,6-bis(1,1-dimethylethyl)-	3846-71-7	C20H25N3O	28.370	0.000	283203	77554	30.0768 ng/ml	99.1	308.1758	-0.92	4
+	Mirex	2385-85-5	C10Cl12	29.657	0.001	234855	70603	24.9421 ng/ml	99.9	271.8096	-1.05	4
+	2,3,3',4,4',5,5'-Heptachlorobiphenyl_189#	39635-31-9	C12H3Cl7	30.827	0.003	203719	50871	21.6354 ng/ml	99.9	393.8020	-0.73	4

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Figure 6. semi-quantitative screening analysis report can show the semi-quantitative results

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Conclusions

- Based on the currently collected list of new pollutants, a truly meaningful new pollutant PCDL high-resolution spectral library has been created.
- This work demonstrated a total workflow for targeted screening and semi-quantification in real water sample.
- The confidence in identification of new pollutants was enhanced by stable RT and excellent mass accuracy as a result of using an RTL backflush method and high-resolution accurate mass measurement.

References

[1]Wong, L., Black, G., Young, T., Nieto, S. Accurate Mass Library for PFAS Analysis in Environmental Samples and Workflow for Identification of Pollutants in Drinking Water Using GC/Q-TOF. *Agilent Technologies Application Note*, 5994-6966EN, 2023

DE-006381

Published in USA, May 15, 2025

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