

GC/Q-TOF workflows for comprehensive pesticide analysis

Authors

Christoph Moschet¹,
Tarun Anumol², Philip L. Wylie²,
and Thomas M. Young¹

¹ Department of Civil and
Environmental Engineering,
University of California,
One Shields Avenue, Davis,
California 95616, USA

² Agilent Technologies, Inc.
2850 Centerville Rd.,
Wilmington, DE 19808, USA

Abstract

High-resolution GC/Q-TOF mass spectrometry optimizes simultaneous qualitative and quantitative screening, providing benefits in throughput and characterization of environmental samples.

This Application Note presents three complementary GC/Q-TOF workflows for the comprehensive analysis of pesticides and related compounds in environmental samples:

- Target quantification
- Suspect screening using high-resolution accurate mass GC/Q-TOF data
- Nontarget screening using spectral deconvolution and library searching

An Agilent 7200 GC/Q-TOF was used to analyze 51 water samples taken from the Sacramento/San Joaquin River delta in California before, during, and after two rain events. After filtering, contaminants in the water extracts were isolated by solid phase extraction and concentrated by solvent evaporation. The filters were extracted to recover contaminants bound to particulates. A quantitative analysis method was validated for 21 target pesticides analyzed by the GC/Q-TOF in negative chemical ionization mode. Sixteen of these target pesticides were found in at least two of the water extracts. Samples were then re-analyzed using electron ionization (EI). These data files were processed using Agilent MassHunter Qualitative Analysis Software using the Find by Formula (FBF) workflow. Samples were screened for approximately 750 pesticides and related compounds contained in the Agilent Pesticide Personal Compound Database and Library (PCDL) for GC/Q-TOF. Accurate mass data provide high selectivity while retention time locking helped to reduce false positive results. Forty-one additional suspects were identified through this technique, with most being confirmed by the analysis of standards. Of these 41, 24 were also found by LC/Q-TOF, and 17 compounds were uniquely detected by GC-EI-Q-TOF.

Nontarget screening used the Agilent MassHunter Unknowns Analysis Software. This software first deconvolutes the spectra in the chromatogram, and searches the deconvoluted components against a mass spectral library of choice: NIST14 and the Agilent GC/Q-TOF Pesticides PCDL. Five pesticides and one transformation product (TP) not found by the first two GC-Q/TOF approaches were tentatively identified in Unknowns Analysis. In addition, several halogenated and nonhalogenated organophosphorus flame retardants, several phenolic antioxidants, and various organohalogen compounds were tentatively identified.

Introduction

To assess exposure and risk, it is necessary to monitor micropollutants in waste, surface, ground, and drinking water. Traditionally, this has been done by GC/MS in scan or selected ion monitoring (SIM) mode. However, for complex environmental samples, a single quadrupole instrument is not sufficiently selective. A GC triple quadrupole MS operating in Multiple Reaction Monitoring (MRM) mode offers much better selectivity, but this technique is optimal for targeted compounds only. Compounds not on the target list will be missed no matter what their concentration. This restricted approach can lead to inaccuracies in exposure and risk assessment. An ideal scheme would quantify target compounds for which standards are available. It would also look for a broad range of other contaminants that can be detected and quantified once standards become available.

This Application Note describes three GC/Q-TOF workflows that have been used to identify nonpolar and semipolar micropollutants (for example, pesticides, and so forth) in surface waters. The first approach (target method) is to quantify

compounds for which standards are available. In this case, the Q-TOF was operated in negative chemical ionization mode (NCI), as most of the 21 target compounds were halogenated, thereby providing optimal sensitivity in NCI mode. The second approach (suspect screening) uses EI data with Agilent MassHunter Qualitative analysis tools and the Agilent GC/Q-TOF Pesticides Personal Compound Database and Library (PCDL). The Find by Formula^a workflow extracts chromatograms for the most significant ions for each compound at its known retention time. The number of ions extracted along with the retention time and mass windows are user-settable, as are the requirements for compound identification. This approach allows users to presumptively identify compounds without the need for analytical reference standards.

^a In the most recent version of Agilent MassHunter Qualitative Analysis Software (B.08.00 Workflows), this process is called Find by Fragments.

The third approach (nontarget screening) uses Agilent MassHunter Unknowns Analysis. This software deconvolutes spectra over the whole chromatogram, and finds individual components with cleaned spectra—that is, spectra where interferences have been identified and removed. Each of the components is searched against a large mass spectral library. This work queried the NIST14 unit mass spectral library with spectra for more than 240,000 compounds, and the Agilent GC/Q-TOF Pesticides PCDL. Figure 1 shows the overall workflow used.

This combined target and suspect pesticide screening GC/Q-TOF workflow was applied to 51 surface water samples collected from the Cache Slough in the Sacramento-San Joaquin River Delta in Northern California. To get an idea of other compounds that could be found in the extracts, six of the samples were analyzed using Unknowns Analysis.

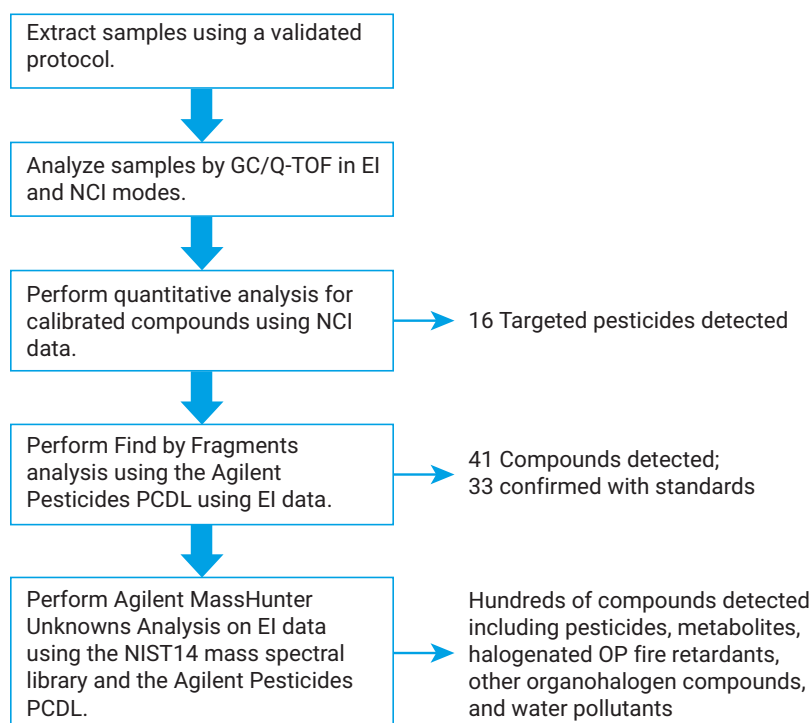


Figure 1. GC/Q-TOF workflow for 1) quantifying target pesticides, 2) screening for hundreds of pesticides using the Agilent Pesticides PCDL, and 3) screening for other compounds found in the NIST mass spectral library.

Samples were collected before, during, and after two rain events. An article entitled *LC- and GC-Q-TOF-MS as Complimentary Tools for a Comprehensive Micropollutant Analysis in Aquatic Systems*¹ describes, in detail, the quantitative target method and the qualitative suspect screening method. Because not all the compounds studied are amenable to GC/MS analysis, the research article also describes a complementary LC/Q-TOF workflow^{1,2} that provides a comprehensive chemical profile of the samples.

Experimental

Target compounds and standards

Twenty-one GC-amenable pesticides (Table 1) were included in the targeted GC/Q-TOF workflow. Most were pyrethroids, and most contained halogens, making them good candidates for analysis by NCI. One internal standard (4,4'-dibromooctafluorobiphenyl) and two surrogates (chlorpyrifos D10 and etofenprox D5) were used. For method validation and quality control, prespiked (before extraction), post spiked (before injection), and procedural blank (extracted from ultrapure water) samples were run in triplicate.

Table 1. Target pesticides with their validation results for extracts of water and the filters.

Compound	CASRN	MDL (ng/L)	Absolute recovery water extraction (%)	Absolute recovery filter extraction (%)	Accuracy (%)	Precision (n = 3) (%)
Bifenthrin	82657-04-3	0.2	73 %	82 %	106 %	1 %
Bioallethrin	28434-00-6	0.1	76 %	72 %	111 %	0 %
Chlorothalonil	1897-45-6	0.6	94 %	0 %	103 %	7 %
Chlorpyrifos	2921-88-2	0.1	80 %	62 %	108 %	0 %
Cyfluthrin ¹	68359-37-5	1.0	–	–	–	–
Cyhalothrin	91465-08-6	0.1	82 %	82 %	110 %	1 %
Cypermethrin	65731-84-2	1.0	85 %	62 %	120 %	1 %
Cyphenothrin	39515-40-7	0.5	48 %	81 %	113 %	2 %
Deltamethrin	52918-63-5	1.0	96 %	66 %	123 %	1 %
Esfenvalerate	66230-04-4	0.1	93 %	80 %	118 %	1 %
Fipronil	120068-37-3	0.5	92 %	77 %	105 %	3 %
Fipronil amide	–	0.1	98 %	82 %	116 %	0 %
Fipronil-desulfinyl	205650-65-3	0.2	77 %	96 %	87 %	1 %
Fipronil-desulfinyl amide	–	0.2	88 %	74 %	247 %	0 %
Fipronil-sulfide	120067-83-6	0.1	79 %	89 %	74 %	1 %
Fipronil-sulfone	120068-36-2	0.2	91 %	85 %	102 %	3 %
Novaluron	116714-46-6	0.05	48 %	91 %	96 %	3 %
Permethrin	52645-53-1	2.0	84 %	80 %	113 %	2 %
Phenothrin	26002-80-2	5.0	47 %	75 %	123 %	2 %
Prallethrin	23031-36-9	0.1	299 %	36 %	81 %	6 %
Tetramethrin	7696-12-0	5.0	80 %	205 %	106 %	1 %

¹ Not determined, as reference standard was acquired after the validation experiments.

Sample preparation

Fifty-one 1-L samples were collected at a depth of approximately 30 cm from the Sacramento-San Joaquin River Delta in Northern California before, during, and after two different rain events. All the samples were cooled during transport, and stored at 4 °C in the dark until extraction. Water samples (1 L) were passed through a GF/F filter, and the filtrate was spiked with the two surrogates before being passed through a polymeric solid phase extraction (SPE) cartridge. After drying for one hour, the cartridges were eluted with 10 mL of ethyl acetate. To account for losses due to sorption of pyrethroids to the glass wall, the 1-L containers were rinsed with dichloromethane (3 × 4 mL). The combined extracts were reduced to 0.2 mL. The GF/F filters were extracted by sonicating them with 1:1 hexane/acetone (2 × 20 mL), and the combined filter extracts were reduced to 0.2 mL. All samples were spiked with 10 ng of 4,4'-dibromooctafluorobiphenyl. A 10-point calibration curve between 0.1 and 250 ng/mL (in ethyl acetate) was generated using the same ISTD and surrogate concentrations.

Sample analysis

Samples were analyzed on an Agilent 7890B GC coupled to an Agilent 7200B Q-TOF MS, once by NCI with methane reagent gas, and once by EI. Table 2 lists the instrument conditions.

Table 2. Instrumentation and conditions for analysis.

GC-NCI-MS Method	
Injection volume	2.5 µL
Injection mode	Splitless
Purge flow to split vent	33 mL/min at 0.75 minutes
Inlet temperature	280 °C
GC Settings	
Column	Agilent HP-5MS (30 m × 0.25mm, 025 µm)
Initial oven temperature	100 °C, hold 1 minute
Ramp 1	15 °C/min to 200 °C
Ramp 2	3.8 °C/min to 290 °C
Ramp 3	10 °C/min to 300 °C, hold 4 minutes
He Flow	1.35 mL/min, constant flow
Transfer line temperature	300 °C
MS Settings	
N ₂ Collision gas	1.5 mL/min
Reagent gas (methane)	40 %
Source temperature	200 °C
Emission current filament	90 µA
Electron energy	70 eV
Acquisition range	35–1,000 <i>m/z</i>
Acquisition speed	3 spectra/sec
Mass calibration	Automated mass calibration after every second sample
GC-EI-MS Method	
Injection volume	2.5 µL
Injection mode	Splitless
Purge flow to split vent	33 mL/min at 0.75 minutes
Inlet temperature	280 °C
GC Settings	
Column	Agilent HP-5MS (30 m × 0.25mm, 025 µm)
Initial oven temperature	60 °C, hold 1 minute
Ramp 1	40 °C/min to 120 °C
Ramp 2	5 °C/min to 310 °C
Optimized He flow for RT locking	0.776 mL/min, constant flow
Transfer line temperature	280 °C
MS Settings	
N ₂ Collision gas	1.5 mL/min
Source temperature	300 °C
Emission current filament	35 µA
Electron energy	70 eV
Scan range	35–1,000 <i>m/z</i>
Scan speed	4 spectra/sec
Mass calibration	Automated mass calibration after every second sample

Results and Discussion

Target method data processing and analysis

Target pesticides in all sample extracts were quantified using Agilent MassHunter Quantitative Analysis Software (B.07.00) applied to the NCI data. The main NCI fragment was used as the quantifier, and two additional fragments were used as qualifiers.

Validation results for the 21 GC-NCI-Q-TOF target compounds showed that 17 had absolute recoveries >70 % in the water extracts, while 15 of the filter extracts had recoveries >70 %. Nineteen had accuracies between 70 and 130 %; all 21 had precisions <10 %. Eighteen had MDLs <1 ng/L (Table 1). All of the compounds with recoveries less than 70 % (phenothrin, cyphenothrin, and prallethrin) were synthetic pyrethroids that contained no halogens, so they would be expected to have lower responses in the NCI mode.

Suspect screening using GC/Q-TOF with the Pesticides PCDL

The water extracts were rerun in EI mode to perform a suspect screening for additional pesticides and related compounds. The Find By Formula (FBF) workflow within MassHunter Qualitative Analysis Software (B.07.00) was applied to screen for the 750 compounds^b in the Agilent Pesticides PCDL for the GC/Q-TOF. The PCDL contains curated exact mass spectra for all the compounds, along with locked retention times, for the EI GC/MS method shown in Table 2. Locked retention times are available for one 20-minute method and one 40-minute method using two 15-m columns configured for backflushing³. A third available method uses a backflushing configuration with a 5-m column followed by a 15-m column with locked retention times for a 20-minute run.

The GC retention times were first adjusted to be close to the PCDL values by adjusting the column flow rate. Then, retention time locking was performed by making five runs: one at the nominal flow rate, and four more at $\pm 10\%$ and $\pm 20\%$ of the nominal flow rate. MassHunter Acquisition Software automatically creates a calibration curve relating the column flow rate to the retention time of the locking standard. Chlorpyrifos, a pesticide that elutes near the middle of the chromatogram, was used as the locking standard. Using the calibration curve, it does a final adjustment of the flow rate to bring the RTs for all compounds within 0.2 minutes of their PCDL values.

The FBF data mining tool in MassHunter Qualitative Analysis Software (B.07.00) used the Pesticides PCDL with the setpoints shown in Table 3. In this case, five of the most specific ions for each compound were extracted from the chromatogram inside a ± 0.2 -minute window around the compound's locked retention time and within a specified mass extraction window. The software automatically chooses one EIC as a reference for the RT and peak shape. It then compares the RT and peak shape of the other four EICs to see if they fall within the method's qualification criteria. In this case, the reference ion and two more ions must be qualified for the compound to be listed as a hit. Figure 2 shows the five EICs for boscalid, a fungicide that was found in all 51 samples of river water.

Table 3. Parameters for suspect screening by GC/Q-TOF-MS.

Parameter	Value
Software	Agilent MassHunter Qualitative Analysis (B.07.00)
Workflow	Find Compounds by Formula
Values to match	Mass and retention time (retention time optional)
Library	Agilent GC/Q-TOF – Pesticide PCDL (including retention times). 750 compounds
Extraction algorithm	Agile 2
Match tolerance masses	± 20 ppm
Retention time tolerance	± 0.2 minutes
Allowed adducts	pos: - electron
Allowed charge state	1
Isotope model	Common organic molecules
Peak spacing tolerance	0.0025 m/z, plus 7 ppm
Scoring (weight)	Mass score: 100 Isotope abundance score: 60 Isotope spacing score: 50 Retention time score: 100
Find by formula score	>70 (out of 100)
Absolute height	>1,000 counts
Confirm with fragment ions	Molecular ion optional
Number of most specific ions from MS/MS library	5
RT Difference	± 0.1 minutes
S/N	Not applied
Coelution score	>85 (out of 100)
Minimum number of qualified fragments	2

^b A more recent version of the Pesticides PCDL for GC/Q-TOF contains entries for more than 850 compounds.

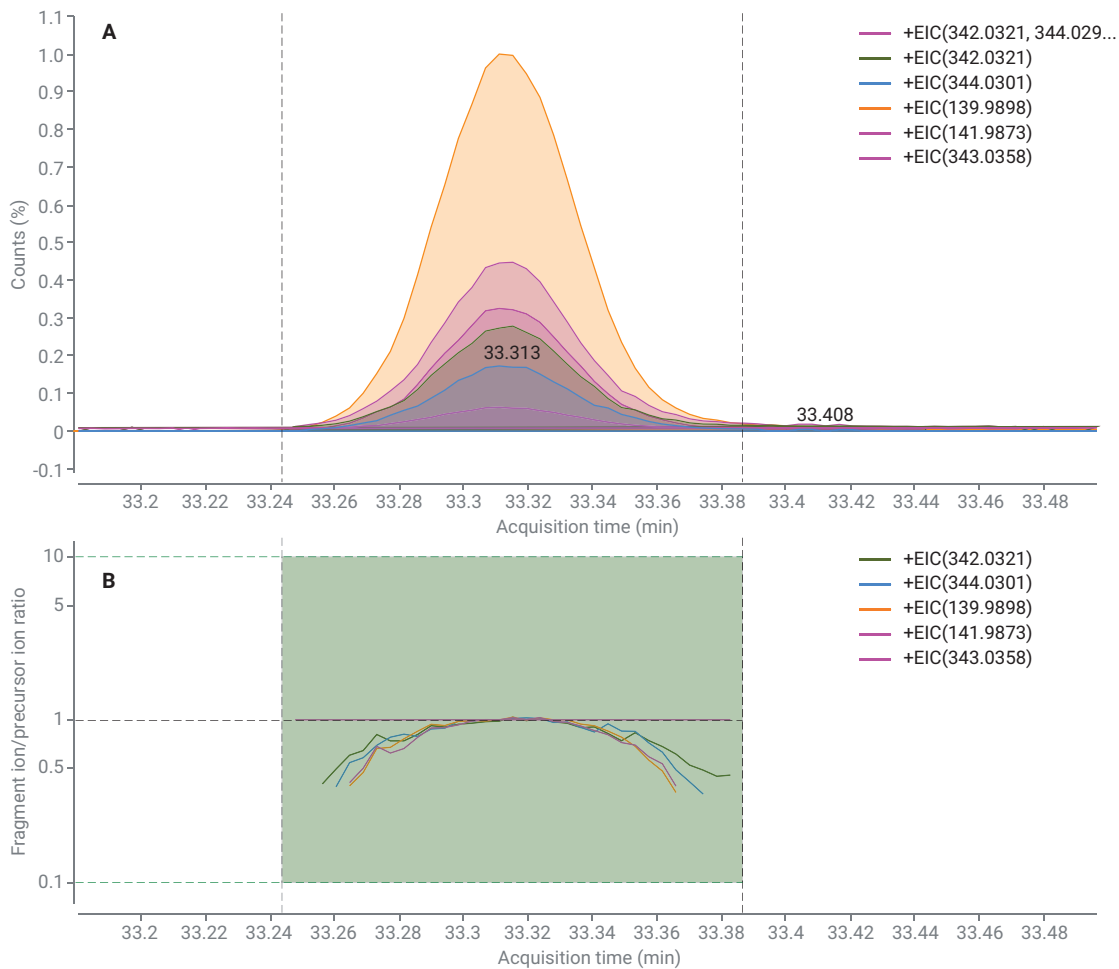


Figure 2. A) Extracted ion chromatograms for boscalid found in a sample of river water extract. The normalized coelution plot (B) shows how the peak shape of the four EICs match the shape of the reference ion. If their peak shapes were the same, the plot would be a horizontal straight line.

Figure 3 shows more information provided by the FBF software including:

- The coelution scores (out of 100) for each fragment
- The difference between the measured and theoretical monoisotopic molecular ion mass
- The difference between the measured retention time and the value recorded in the PCDL for boscalid

In cases where there is a measurable molecular ion, the software compares the theoretical isotope spacing and

abundance to the measured values (Figure 4). The molecular ion is not necessary for compound identification, as the molecular ion is often not dominant in GC-EI-MS spectra (see the *Confirm with fragment ions* setting in Table 3)

The FBF approach identified 41 suspect compounds (Table 4) that were not on the target list shown in Table 1. Of these, 33 were unambiguously confirmed by analyzing a reference standard. For the additional eight compounds, no reference standard was available, and they remain tentatively identified.

The suspect screening approach using the FBF workflow allows one to presumptively identify any of the compounds contained in the PCDL without having an authentic standard. Multiple fragment ions as well as retention time matching requirements minimize the possibility of false positive identifications. This expands the scope of the analysis from the relatively few compounds that have standards to the many hundreds of compounds found in the PCDL. However, unambiguous confirmation and quantification of these tentatively identified compounds still requires an authentic standard.

Best	Name	Formula	Mass (Tgt)	Diff (ppm)	RT	RT (Tgt)	RT Diff	Notes		
A	Boscalid (Nicobifen)	C ₁₈ H ₁₂ Cl ₂ N ₂ O	342.0327	1.48	33.312	33.364	-0.052	Forensic and Toxicology drug; Pesticide; Herbicide; Veterinary drug		
Coelution Score	FragMassDiff(ppm)	Flags(FIs)	Height	Abundance(Lib)	mz(Lib)	m/z	ObsPkHeight(MS)	Compound Name	RT	RT Diff
99.61	7.5	Qualified	1188635.2	25.5	342.0321	342.0296	462191.6	Boscalid (Nicobifen)	33.315	0.003
99.57	3.7	Qualified	738186.8	17.1	344.0301	344.0289	284425.5	Boscalid (Nicobifen)	33.313	0.001
99.79	6.9	Qualified	4289525.9	100	139.9898	139.9888	1623222.8	Boscalid (Nicobifen)	33.314	0.002
99.64	9.2	Qualified	1392828.4	33.3	141.9873	141.986	518813.1	Boscalid (Nicobifen)	33.314	0.001
100	0.2	Reference ion	256859	5.1	343.0358	343.0357	119453.7	Boscalid (Nicobifen)	33.312	0

Figure 3. FBF results for boscalid showing: A) coelution scores, B) difference between the measured and theoretical monoisotopic molecular ion mass, and C) difference between the measured and database retention times.

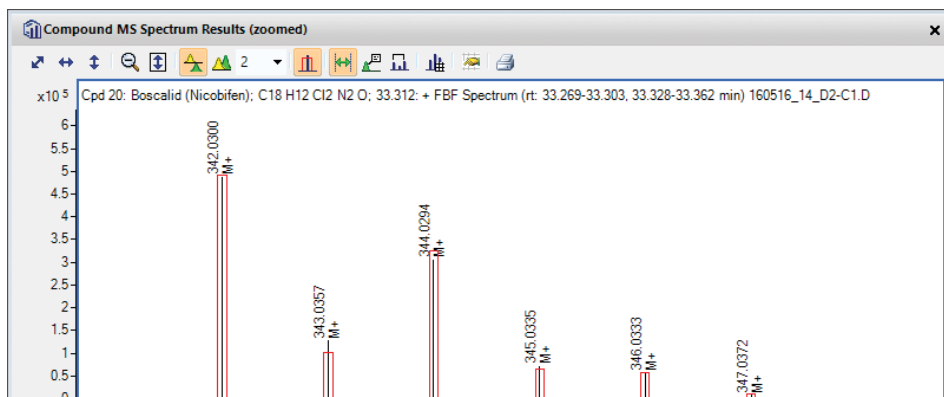


Figure 4. Theoretical (red rectangles) and measured molecular ion isotope pattern for boscalid found in a Cache Slough water extract.

Nontarget screening using MassHunter Unknowns Analysis software

Having screened the samples for all 750 pesticides in the PCDL, it may be desirable to determine whether there are any other compounds of interest in the extract. MassHunter Unknowns Analysis (UA) is designed to perform this nontarget screening. Unknowns Analysis deconvolutes the mass spectral data to isolate cleaned spectra from a complex mixture of overlapping spectra. These component spectra are then searched against a library, and a list of hits is generated. Since there is no large comprehensive accurate mass library available, the NIST unit mass library was used to generate the broadest possible list of hits. A new version of the pesticides PCDL (B.08.00), containing more than 850 compounds, was also used since it does contain exact mass spectra. Unknowns Analysis, using deconvolution, is a different data mining process than screening using the FBF workflow, and might identify some compounds missed by the FBF process. Table 5 shows the most important setpoints used for the Unknowns Analysis.

To determine if there might be other pollutants of interest in the water extracts, Unknowns Analysis was applied to six of the 51 samples. Depending on the extract analyzed, the number of deconvoluted components ranged from approximately 1,500 to 4,500. Of these, between 90 and 325 had NIST library match factors >70, and approximately 60–120 had match factors >80. An efficient way to sort through all the hits was by scrolling down from one hit to the next while looking at the molecular structure. When a compound of interest was observed, the hit was scrutinized to see if the spectral match looked good and if the extracted ions appeared to coelute with good peak shape.

Table 4. Suspect compounds identified by the FBF algorithm.

Compound	Use	CAS No.
2,4,6-Tribromophenol ¹	Different uses	118-79-6
2,4-Dimethylphenol (2,4-xyleneol)	Different uses	105-67-9
2-Methylphenol	Different uses	95-48-7
4-Methylphenol	Different uses	106-44-5
Azoxystrobin	Fungicide	131860-33-8
Boscalid	Fungicide	188425-85-6
Bromacil	Herbicide	314-40-9
Carvone ¹	Insect repellent	99-49-0
Chlorthal-dimethyl (Dacthal or DCPA)	Herbicide	1861-32-1
Cyprodinil	Fungicide	121552-61-2
DEET	Insect repellent	134-62-3
Diazinon (Dimpylate)	Insecticide	333-41-5
Dichlobenil	Herbicide	1194-65-6
Dimethenamid (SAN 582H)	Herbicide	87674-68-8
Dimethoate	Insecticide	60-51-5
Diphenylamine ¹	Fungicide	122-39-4
Dithiopyr	Herbicide	97886-45-8
Diuron metabolite [3,4-Dichlorophenylisocyanate] ¹	Herbicide TP	–
Eugenol ¹	Insect attractant	97-53-0
Fluridone	Herbicide	59756-60-4
Hexazinone	Herbicide	51235-04-2
Iprodione (Glycophen)	Fungicide	36734-19-7
Malathion	Insecticide	121-75-5
Mepanipyrim ¹	Fungicide	110235-47-7
Metolachlor	Herbicide	51218-45-2
Napropamide	Herbicide	15299-99-7
Norflurazon	Herbicide	23576-24-1
Norflurazon-desmethyl	Herbicide TP	23576-24-1
Omethoate	Insecticide TP	1113-02-6
Oxadiazon	Herbicide	19666-30-9
Oxyfluorfen	Herbicide	42874-03-3
<i>p,p'</i> -DDE ¹	Insecticide TP	72-55-9
Pendimethalin	Herbicide	40487-42-1
Pentachlorophenol (PCP)	Different uses	87-86-5
Prodiamine	Herbicide	29091-21-2
Propiconazole	Fungicide	60207-90-1
Propyl cresol ¹	Different uses	–
Sulfentrazone	Herbicide	122836-35-5
Tebuthiuron	Herbicide	34014-18-1
Triclosan	Biocide	3380-34-5
Trifluralin	Herbicide	1582-09-8

¹ Tentatively identified (no reference standard comparison available)

The software calculates a component peak shape quality value (max = 100) and all but a few of the reported hits had a component shape quality >60. When using the Pesticides PCDL as the target library, retention times had to be close to the library value to report a hit, giving further confidence in the peak assignment.

Using the UA procedure, 25 pesticides, three pesticide transformation products (TPs), six organophosphates (three chlorinated flame retardants), and 13 other water pollutants (for example, phenolic antioxidant compounds) were found and tentatively identified in the six samples. Five pesticides and one TP were identified by UA that were not originally targeted by the GC/Q-TOF suspect screening procedure: 2,6-diisopropyl-naphthalene, 3,4-dichloroaniline, fenbuconazole, fluorpyram, fluxapyroxad, and simazine. The first two were not included in the earlier version of the Pesticides PCDL, and the latter four were targeted by LC/Q-TOF suspect screening.

Table 5. Key setpoints for the method used with Unknowns Analysis.

Tab/Parameter ¹	Setpoint
Peak detection	
Peak detection	Deconvolution
SNR Threshold	0
Area filters	Absolute area ≥1,000
Deconvolution	
RT Window size factor	25, 50, 100, 200
Left <i>m/z</i> delta	0.3 amu or 50 ppm
Right <i>m/z</i> delta	0.7 amu or 50 ppm
Use integer <i>m/z</i> values	Checked for unit mass, unchecked when using 50 ppm
Component shape	Use base peak shape checked
Sharpness threshold	75 %
Library search	
Libraries	NIST14.L and Pesticides PCDL (ver. B.08.00)
Adjust score	Checked
Remove duplicate hits	Unchecked
Use RT match	Unchecked for NIST, checked for PDCL
RT Penalty function	Gaussian (30 seconds)
RT Mismatch penalty	Multiplicative
Max RT penalty	20
Compound identification	
Max hit count	1
Min match factor	70 for NIST14.L, 20 for PCDL
Min <i>m/z</i>	30
Library search type	Spectral Search
Target match	Not applied
Blank subtraction	
Perform blank subtraction	Unchecked

¹ Parameters not listed used the default values

Figure 5 shows the Unknowns Analysis results for *tris*(2,3-dichloropropyl) phosphate, a flame retardant that was found in several samples. Because many organophosphates have been used as plasticizers or fire retardants, they are widely distributed in the environment, and can show up in procedural blanks.

We found triphenyl phosphate, tributyl phosphate, *tris*(2-chloroethyl) phosphate, and *tris*(2,4-di-*tert*-butylphenyl) phosphate in at least one of two procedural blanks processed by UA.

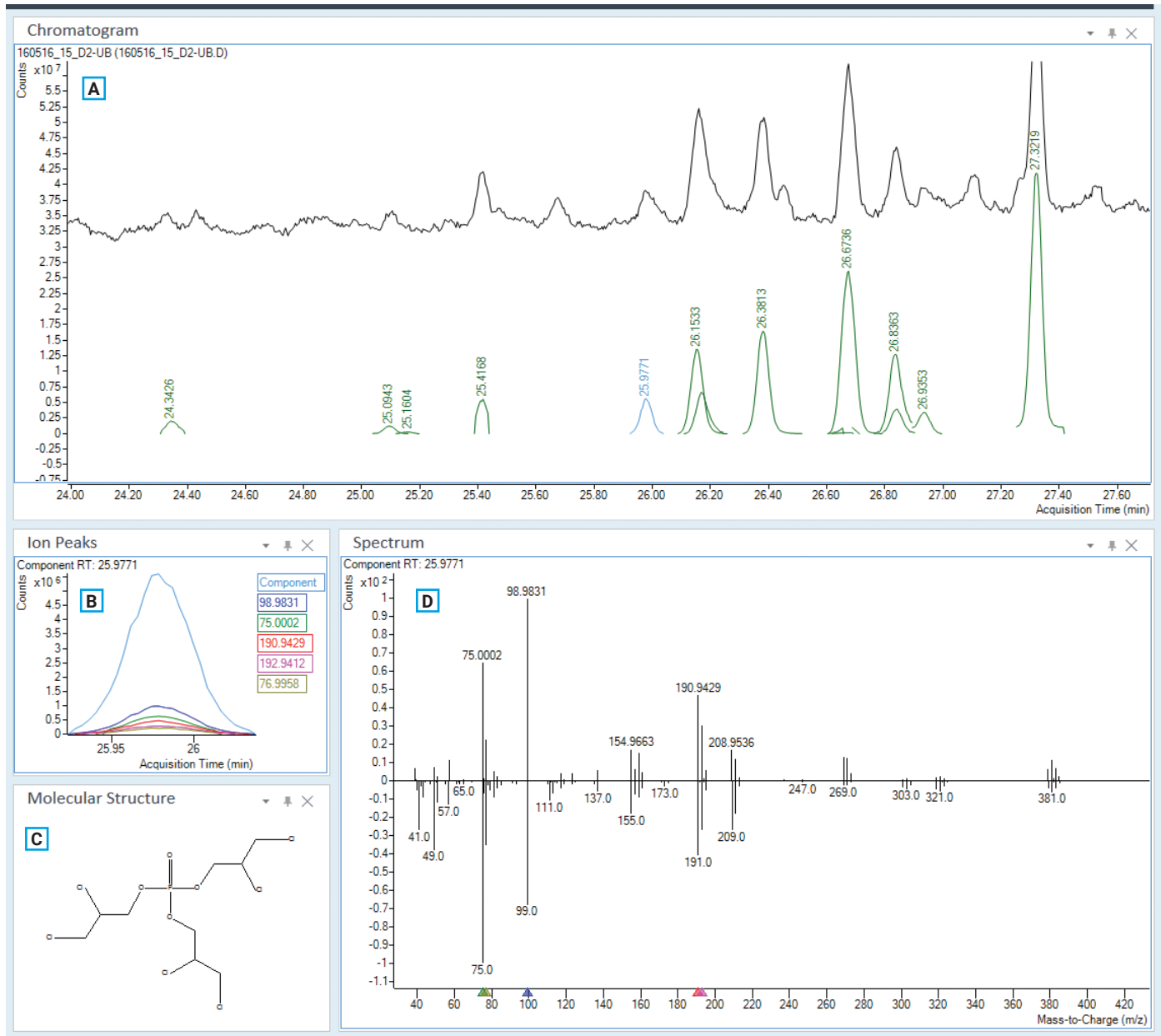


Figure 5. Agilent MassHunter Unknowns Analysis results for a Cache Slough water extract, showing the fire retardant *tris*(2,3-dichloropropyl) phosphate. A) TIC (black) and deconvoluted components [green (blue, peak for which results are displayed)]; B) plots of significant EICs overlaid with the component plot; C) molecular structure; D) component spectrum (top) positioned head-to-tail with the library spectrum. The compound had a NIST library match score of 84, and a component shape quality of 82.

Among the other compounds detected using this approach, were an isomer of dichloronitrobenzene, *bis*(dichloromethyl) ether, cyanomelamine, dibenzazepine, and a trichloronaphthalene isomer. These compounds remain tentatively identified because no authentic standard was available for unambiguous confirmation.

Table 6 lists the compounds found using UA. The first 37 compounds listed in Table 6 were identified with increased confidence since their retention times matched the values in the PCDL. The remaining nine compounds were tentatively identified based only on their NIST library match score.

Table 6. Pesticides, TPs, and other water pollutants tentatively identified by UA.

Retention time confirmed w/ PCDL	Retention time confirmed w/ PCDL
2-Methylphenol ¹	Metolachlor ¹
4-Methylphenol ¹	Oxadiazon ¹
Trichloronaphthalene isomer	Oxyfluorfen ¹
2,6-Diisopropyl-naphthalene	Propiconazole ¹
3,4-Dichloroaniline (propanil TP)	Simazine
Azoxystrobin ¹	Sulfentrazone ¹
Boscalid ¹	Tributyl phosphate
Bromacil ¹	Trifluralin ¹
Chlorothalonil ²	<i>tris</i> (2-Butoxyethyl)phosphate
Chlorpyrifos ²	<i>tris</i> (2,4-Diterbutyl)phosphate
Cyprodinil ¹	<i>tris</i> (2,3-Dichloropropyl)phosphate
DEET ¹	<i>tris</i> (2-Chloroethyl)phosphate
Desmethylnorflurazon	<i>tris</i> (2-Chloroisopropyl)phosphate
Diazinon ¹	Compounds with NIST library search >80 but not confirmed with RT
Dimethenamid ¹	Benzothiazole
Dimethoate ¹	Dichloronitrobenzene isomer
Dithiopyr ¹	Benzenesulfonamide, N-butyl-
Diuron mnetabolite (3,4-dichlorophenylisocyanate) ¹	Benzonitrile
Fenbuconazole	<i>p</i> -Cresol
Fipronil ¹	Cyanomelamine
Fluorpyram	<i>bis</i> (dichloromethyl) ether
Fluridone ¹	Octodrylene
Fluxapyroxad	Dibenzazepine (iminostilbene)
Hexazinone ¹	

Key: Pesticides Transformation products Water pollutants Organophosphates

¹ Found by GC/Q-TOF suspect screening workflow

² Found by GC/Q-TOF target analysis

Conclusions

The Agilent GC/Q-TOF is an ideal tool for performing both target and nontarget analysis. River water extracts were analyzed in NCI mode for 21 targets (mostly pyrethroids) at sub-ng/L levels, and 16 of them were found in concentrations ranging from 0.6 to 33 ng/L. The Find by Formula approach paired with the Agilent Pesticides PCDL for GC/Q-TOF tentatively identified an additional 41 suspect compounds, most of which were confirmed by analyzing standards. Five of the most significant ions were extracted around the locked retention time for each compound in the database. Hits required that a reference ion and two additional ions meet the specified requirements for a hit (Table 3) and that the retention time matches the PCDL value. Six of the extracts were subjected to a nontarget screening using Agilent MassHunter Unknowns Analysis, which uses deconvolution to pick out cleaned spectra for hundreds

of individual components. These were then searched against the NIST14 mass spectral library and the Agilent Pesticides PCDL. Twenty-five pesticides, three pesticide TPs, six organophosphates, antioxidants, several halogenated compounds, and other pollutants were found. Most could be tentatively identified by matching their retention time to the PCDL.

With the GC-Q/TOF workflows (target, suspect, and nontarget), it was possible to identify nearly 80 semipolar to nonpolar water contaminants. Running the same samples by LC/Q-TOF identified approximately 100 polar to semipolar water contaminants^{1,2}. Although approximately 30 chemicals from the middle of the polarity range were detected on both instruments, this result shows that GC-Q/TOF and LC-Q/TOF are complementary, and it is necessary to rely on both platforms to obtain the full contaminant profile in environmental samples.

References

1. Moschet, C.; *et al.* LC- and GC-QTOF-MS as Complimentary Tools for a Comprehensive Micropollutant Analysis in Aquatic Systems. *Environ. Sci. Technol.* **2017**, *51*(3), 1553–1561.
2. Moshet, C.; Young, T. M.; Anumol, T. LC/Q-TOF Workflows for Comprehensive Micropollutant Analysis. *Agilent Technologies Application Note*, publication number 5991-8459EN, October 2, **2017**.
3. Chen, K.; Sanderson, J. Screening of Pesticides and Other Contaminants in Food Matrices Using a Novel Highresolution GC/Q-TOF with a Lowenergycapable EI Source. *Agilent Technologies Application Note*, publication number 5991-8170EN, June 16, **2017**.

www.agilent.com/chem

This information is subject to change without notice.

© Agilent Technologies, Inc. 2018
Printed in the USA, March 14, 2018
5991-9132EN