Consolidated analysis of soil contaminants

Four-fold increase in the sample throughput with GC-Orbitrap

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Keywords: Analytical environmental testing, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), persistent organic pollutants (POPs), QuEChERS, targeted quantification, screening, unknowns, gas chromatography, high resolution mass spectrometry, full scan (FS), sensitivity, Orbitrap Exploris GC, electron ionization (EI), chemical ionization (CI), Chromeleon, Compound Discoverer

Goal

The purpose of this study was to assess the quantitative performance and advantages of PAHs and PCBs using the Thermo Scientific™ Orbitrap Exploris™ GC in addition to screening of unknown soil contaminants.

Introduction

Polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) are toxic organic compounds that can contaminate soils, air, sediments, and water as a result of natural and anthropogenic processes. PCBs and PAHs are resistant to environmental degradation and can be transported over long distances. Moreover, due to their lipophilicity these chemicals can undergo biomagnification and accumulation in the food chain and can pose significant health risks to humans. Their toxicity even at very low concentrations means that their presence in the environment needs to be monitored so that the risk of uptake of these compounds into to the food chain and subsequently into human populations is minimized.

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More recently it has become apparent that oxidized and substituted derivatives of PAHs (such as oxy and methyl PAHs) have similar or increased toxicities compared to non-substituted versions; therefore, governments have already began monitoring them in soil and particulate matter.[1, 2] Nitrogen, sulfur, and oxygen-containing polyaromatic heterocycles (NSO-PAHs) are another class of compounds that have gained interest due to their ubiquitous presence in the environment and lack of data on their toxicities.[2, 3]

PCBs and PAHs (and derivatives) are typically analyzed by gas chromatography (GC) coupled to mass spectrometry (MS). The challenges for the analysis of PAHs and PCBs are the requirement for complicated and costly sample preparation such as Sohxlet extraction. Often long chromatographic separations (>40 min per sample) are required, which overall will result in low sample throughput and high cost of analysis.

To comprehensively characterize an environmental sample, multiple methods are employed for both the sample preparation and GC-MS analysis of these compounds. Having multiple chromatographic methods for the same sample increases the requirement for both labor and instrumentation. Multiple methods and chemists to review the process and report the data add to the time and cost of analysis.

In this application note a consolidated approach for the rapid and cost-effective analysis of sixteen EPA PAHs, seven marker PCBs, three oxyPAHs, ten methylPAHs, and nine NSO-PAHs in soil samples using a sensitive HRMS instrument was employed. For this, a modified QuEChERS sample extraction and clean up was investigated. Chromatographic separation of target compounds was optimized for a <20 min/sample method and detection was achieved using the Orbitrap Exploris GC system.

The evaluation of system robustness and method suitability for PAH and PCB GC-MS analysis was outside of the scope of this application but is discussed in a supporting technical note (TN10728).

Experimental

Sample preparation
Calibration standards containing 45 native PCB, PAHs, methyl PAHs, oxyPAHs, PANHs, PASHs, and PAOHs at twelve concentration levels (Appendix 1 – Table 1), and 14 (^{13}C-labeled) internal standards (Appendix 2 – Table 2), were acquired from Fisher Scientific, AccuStandards, and Wellington Laboratories Inc. (Ontario, Canada).

For the calculation of MDLs and LOQs QuEChERS soil extract was spiked at 0.5, 1.0, 1.5, 2.5, and 5.0 pg/µL. Soil was freeze dried, homogenized, and sieved prior to a modified QuEChERS extraction and clean up procedure. A summary of the QuEChERS methodology can be seen in a recent application note (AN10720).

GC-MS analysis
An Orbitrap Exploris GC instrument equipped with the ExtractaBrite™ electron ionization source was used for this analysis. This configuration allows vent-free column changes and ionization source maintenance in under 2 minutes representing a 98% time saving versus traditional venting approaches, which take up to 4 hours. This is achieved using state of the art NeverVent technology, which increases laboratory productivity through the minimization of instrument downtime.

Liquid injections of the sample extracts were performed using a Thermo Scientific™ TriPlus™ RSH series autosampler and chromatographic separation was achieved by a Thermo Scientific™ TraceGOLD™ TG-5 SilMS 30 m × 0.25 mm i.d. × 0.25 µm film (P/N 26096-1420) capillary column. Additional details of instrument parameters are displayed in Tables 1 and 2. Full details of all consumables used can be found in the Thermo Scientific™ AppsLab™ library.

Table 1. GC conditions. Full list of consumables and instrument can be found in the AppsLab library.

TRACE 1310 GC parameters	
Injection volume (µL)	1.0
Liner	Single gooseneck with glass wool LinerGOLD™ (P/N 453A1925-UI)
Inlet (°C)	300
Inlet module and mode	SSL, Splitless
Splitless time (min)	1.0
Split flow (mL/min)	50.0
Septum purge flow (mL/min)	5.0
Carrier gas, flow rate (mL/min)	He, 1.2
Oven temperature program	
Temperature 1 (°C)	40
Hold time (min)	1.0
Temperature 2 (°C)	285
Rate (°C/min)	28
Hold time (min)	0
Temperature 3 (°C)	305
Rate (°C/min)	3
Hold time (min)	0
Temperature 4 (°C)	350
Rate (°C/min)	30
Hold time (min)	5
Total GC run time (min)	20

Table 2. Mass spectrometer conditions

Orbitrap Exploris GC EI GC-MS parameters	
Transfer line (°C)	320
Ion source (ionization type)	ExtractaBrite (EI)
Ion source (°C)	350
Electron energy (eV)	70
Emission current (µA)	50
Acquisition mode	Full scan (FS)
Mass range (m/z)	50–550
Mass resolution	60,000 (FWHM @ m/z 200, scan speed 7.4 Hz):
Lock mass (m/z)	207.03235

Table 2 continued. Mass spectrometer conditions

Orbitrap Exploris GC CI GC-MS parameters	
Transfer line (°C)	320
Ion source (ionization type)	ExtractaBrite (PCI)
Reagent gas type	10% ammonia in methane
Flow rate (mL/min)	0.6
Ion source (°C)	190
Electron energy (eV)	70
Emission current (µA)	100
Acquisition mode	Full scan (FS)
Mass range (m/z)	65–690
Mass resolution (FWHM @ m/z 200)	60,000 (scan speed 7.4 Hz)
Lock mass	None

Data processing

Data were acquired using full scan (FS) mode, processed, and reported using Thermo Scientific™ Chromeleon™ 7.3 chromatography data system (CDS). Additional screening of unknowns was performed using Compound Discover software. Thermo Scientific™ Compound Discoverer™ software, version 3.2, was also used for spectral deconvolution, NIST library searching, and compound identification using the EI and CI nodes.

Results and discussion

Chromatography, selectivity, and linearity were evaluated using solvent based standards. Assessment of sensitivity (as matrix detection limits and limits of quantitation), recovery, and selectivity were performed in soil using a modified QuEChERS extraction method, which is described in the experimental section.

Chromatography

All compounds were analyzed in <20 min and excellent separation of the critical pairs was obtained for the 16 EPA PAH standard (i) phenanthrene/anthracene, (ii) benzo(a) anthracene/chrysene, (iii) benzo(b)fluoranthene/benzo(k) fluoranthene (Figure 1, A-D). As expected, with fast multiresidue methods of this nature, some coelution did occur in which case the data was reported as a sum of the combined area (ex: included (i) 1-ethylnapthanalene/ 2-ethylnapthalene, (ii) 1,3-dimethylnapthalene/ 1,6-dimethylnapthalene). Due to the superior inertness of the TraceGOLD silphenylene GC columns, excellent peak shape was observed for all compounds including the strongly basic compound quinoline which had a European Pharmacopeia (EP) asymmetry value of 1.0[3].

Due to the diversity of sample matrices with various degrees of complexity, selectivity can be challenging in GC-MS analysis of soils. An example of sample complexity is shown in Figure 1, E-F as an overlay of the TIC EI full scan of a sonicated unspiked QuEChERS soil extract (top chromatogram) and of a FS XIC (bottom chromatogram) showing the incurred residues.
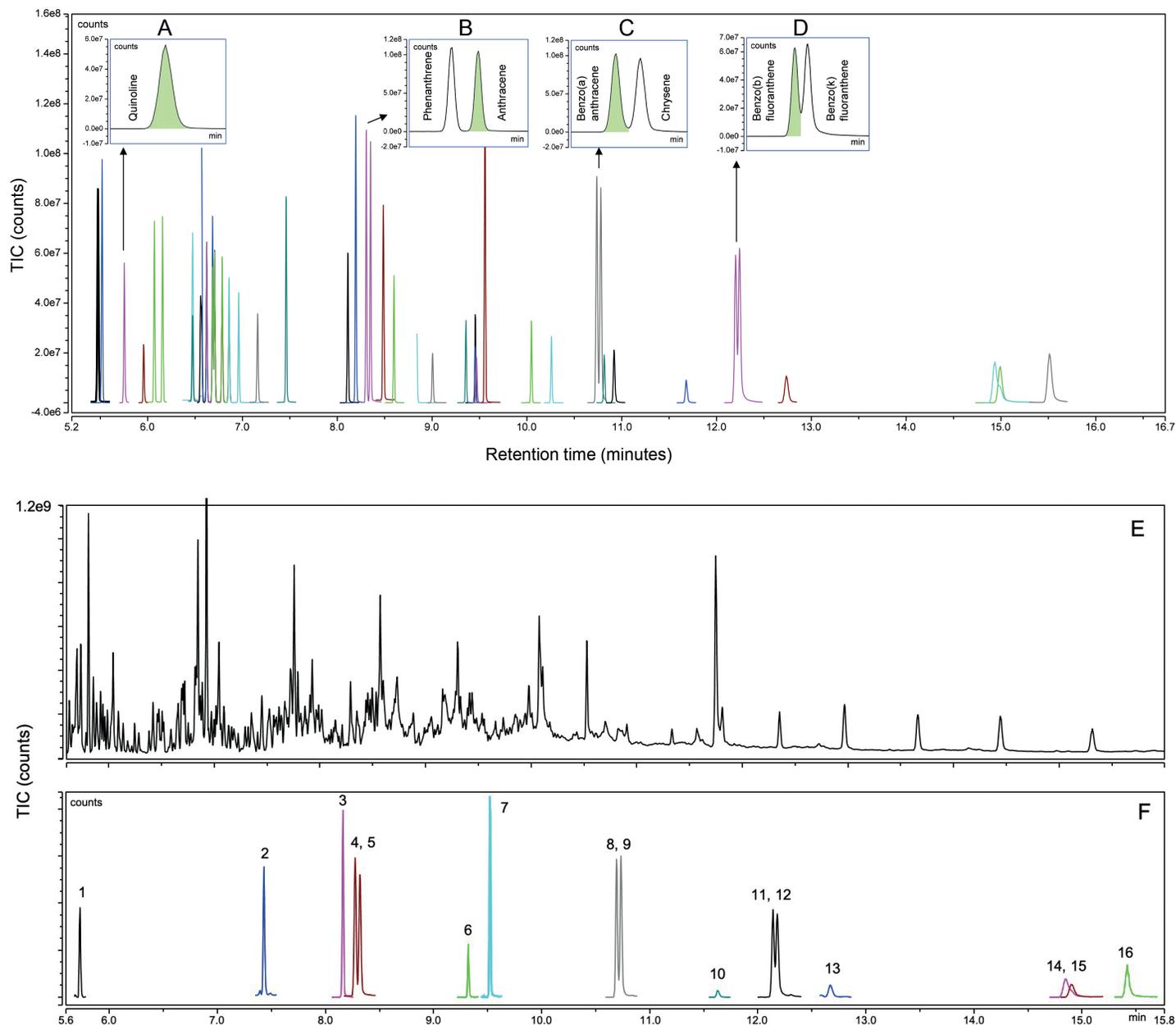

Figure 1. Example chromatograms showing overlaid native PAHs and PCBs FS XICs for a 50 pg/µL (50 pg on column (OC)) solvent standard in *n*-hexane with excellent chromatographic peak shapes for all compounds in <20 min. A) Peak shape for nitrogen containing polyaromatic heterocycle quinoline with peak asymmetry of 1.0; (B) Resolution of critical components phenanthrene and anthracene with EP resolution of 1.5; (C) Resolution of critical components benzo(a)anthracene and chrysene with chromatographic resolution of 1.3; (D) Resolution of critical components benzo(b)fluoranthene and benzo(k)fluoranthene with EP resolution of 1.0. (E) QuEChERS soil extract unspiked, FS, *m/z*=50–550; (F) QuEChERS soil extract unspiked, native incurred residue XICs; Compounds: 1= Quinoline, 2=Fluorene, 3=Dibenzothiophene, 4, 5=Phenanthrene/Anthracene 6=Fluoranthene, 7=Pyrene, 8, 9=Benzo[a]anthracene,Chrysene, 10=5,12-Napthacenequinone, 11, 12=Benzo[b/k]fluoranthene, 13=Benzo[a]pyrene, 14=Indeno[1,2,3-cd]pyrene, 15=Dibenzo[a,h]anthracene, 16=Benzo[ghi]perylene. C[13]-labeled internal standards were not displayed to show native peak shapes clearly.

Sensitivity: determination of method detection limits (MDLs)

To practically assess the MDLs, n=18 replicate injections of the lowest serially diluted matrix-matched standard (0.5, 1.0, 2.5 pg/uL) with a peak area % RSD of <15% were used. The MDL was then calculated by considering the injected amount, peak area % RSD, and t-score of 2.567, corresponding to 17 (n-1) degrees of freedom at the 99% confidence interval (Figure 2). The MDL values calculated ranged from 118 to 475 fg on column (corresponding to 0.1–0.5 µg/kg in sample).

Sensitivity: determination of limit of quantitation (LOQ)

Method LOQs were calculated using serially diluted matrix-matched standards at 0.5, 1.0, 2.5, and 5.0 pg/µL. Eighteen (n=18) replicate injections of each of the diluted standards ranging between 0.5 pg/µL and 5.0 pg/µL were performed (0.5–5.0 µg/kg in sample) (Appendix 3 – Table 3).

The criteria used to assess individual LOQs were:

- Ion ratios within ±30% of the expected values calculated as an average across a calibration curve ranging from 0.1 to 500 pg/µL (corresponding to 0.1–500 µg/kg in sample, Figure 3)

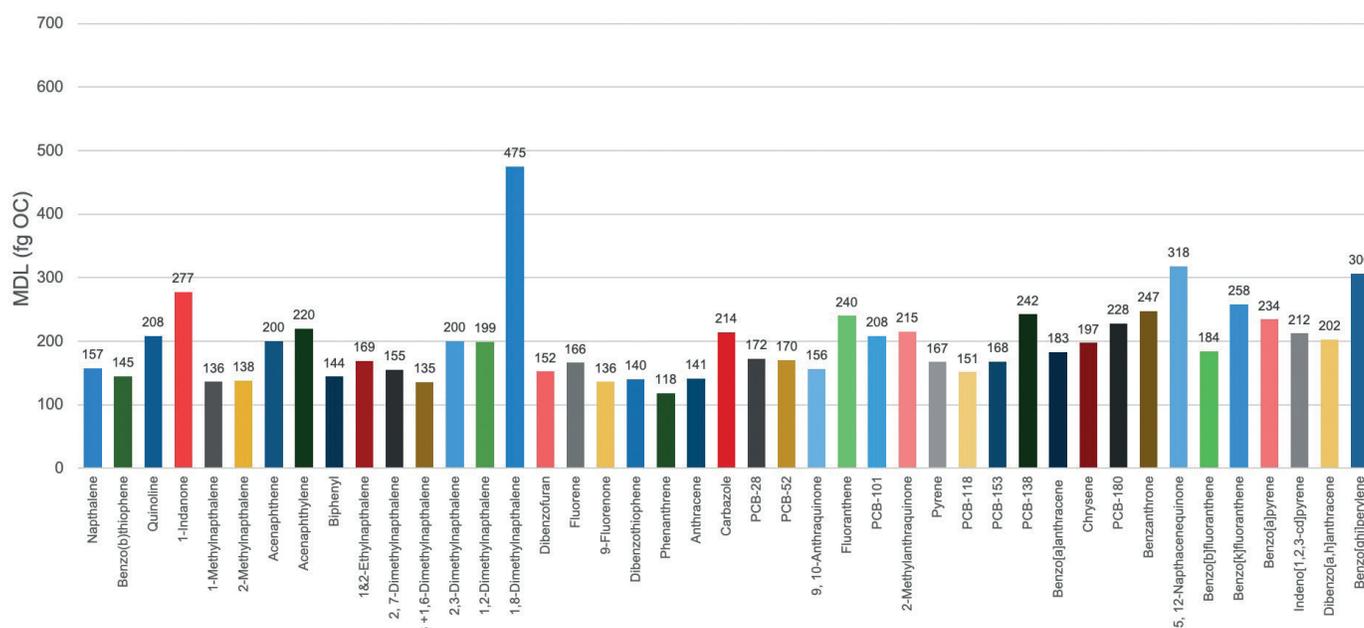- Peak area repeatability of <15% RSD

Figure 2. Graph showing individual MDLs (as detectable fg on column) for 45 native PCB, PAH, methyl PAH, oxyPAH, and NSO-PAHs calculated from n=18 replicate injections of the lowest serially diluted matrix-matched standards. *1,8-Dimethyl naphthalene 1.0 pg OC had a peak area % RSD >15% so the nearest standard 2.5 pg OC was used giving a higher MDL; however, by using a lower amount OC ~1.5 pg the true MDL value would be expected to be lower.
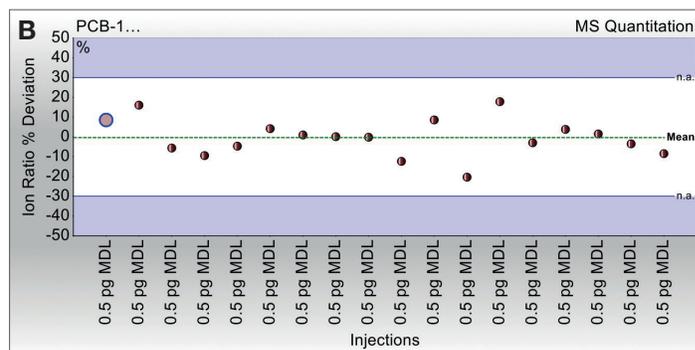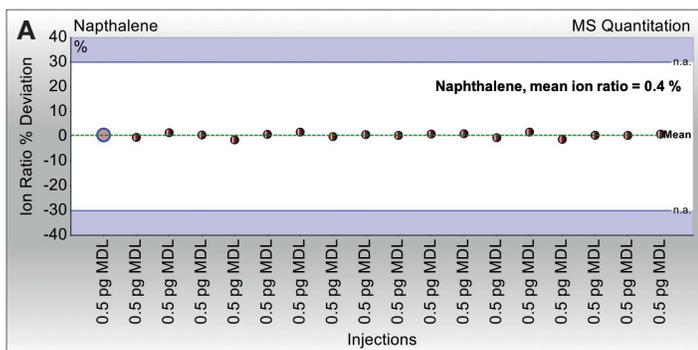
Figure 3. Graphs showing ion ratio consistency for selected PAHs and PCBs. (A) Naphthalene; (B) PCB 118, over n=18 replicate injections at the LOQ level. The average ion ratio % deviation calculated from the calibration range is displayed as a green dotted line in the center. The ±30% upper and lower ion ratio tolerance windows are also defined, and for all PAHs and PCBs the ion ratio % deviation for injections were within specification. This also illustrates how using Chromeleon CDS interactive charts allows the user to easily handle and interpret MS data.

Linearity

Linearity was determined using solvent standards at concentrations 0.1–500 pg/µL. The calibration of each compound was performed using the linear/average calibration factor function in Chromeleon CDS (AvCF) over three injections at each concentration level (Figure 4).

All compounds show excellent linear responses with coefficients of determination $R^2 \geq 0.995$, and average calibration factors %RSD across the calibration range being <13%. The R^2 values ranged from 0.9951 to 1.0000 with an average value of 0.999. (Appendix 4 – Table 4).
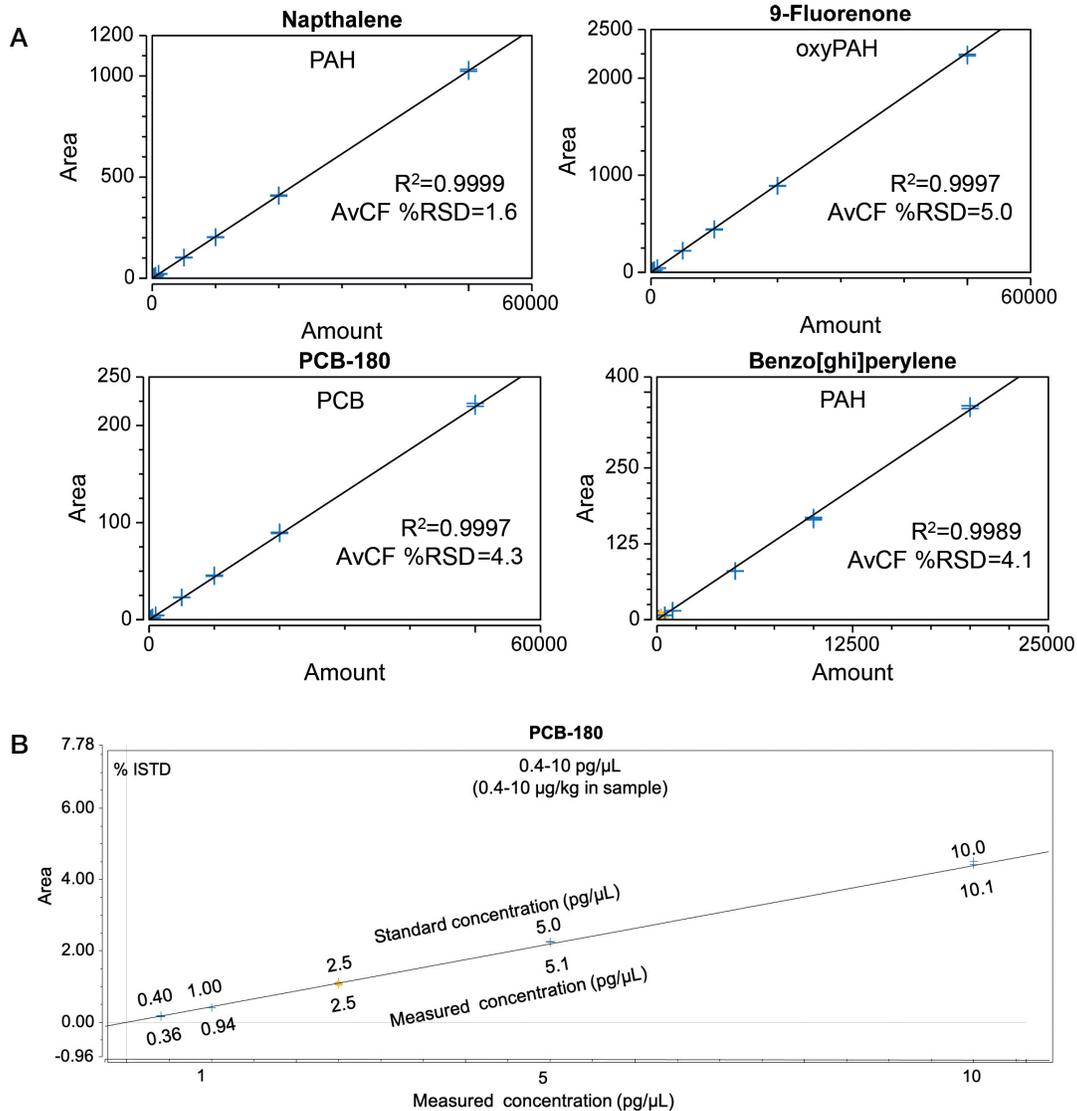
Figure 4. (A) Linearity of example PAHs and PCBs as demonstrated using solvent-based calibration curves ranging from 0.1 to 500 pg/µL (corresponding to 0.1–500 µg/kg in sample). Average calibration factor function (AvCF) was used in Chromeleon CDS and three replicate injections at each concentration with internal standard adjustment were performed. Coefficient of determination (R^2) and average calibration factor values (AvCF %RSD) are displayed. (B) A magnified region of the calibration for PCB 180 ranging from 0.4 to 10 pg/µL is shown (corresponding to 0.4–500 µg/kg in sample) showing excellent precision and accuracy for triplicate injections per point.

Recoveries

Seven replicate QuEChERS extractions, performed on soil spiked with deuterated internal standards at 50 ng/g added prior to extraction, were used to assess the compound recovery (details of sample preparation given in a recent application note (AN10720). Triphenyl phosphate at 100 ng/g was added post extraction and used as internal standard to adjust for potential injection variability (Appendix 5 – Table 5). All compounds show good recoveries with the average values of 79% (Appendix 5 – Table 5). Lower boiling point compounds, such as naphthalene-d$_8$, had lower recoveries that could be explained by losses during the solvent evaporation phase. Although the recovery of such compounds is low, precision of measurement over n=7 replicate extractions was

<15% RSD for all compounds and the majority being <5%. This clearly demonstrates that the QuEChERS extraction and dSPE procedure method is highly reproducible and therefore suitable for analytical testing laboratories. The total sample preparation time was <2 hours, which compared to typical Soxhlet extractions of 24–48 hours, and is a significant time (and cost) savings of 10–20×.

Quantification of PAHs and PCBs in QuEChERS soil extracts

Soil samples, extracted as described in AN10720, were analyzed for their native incurred residues. The quantitative performance of the method in terms of sensitivity and selectivity is highlighted below with examples of low level native incurred residues (Figure 5).

PAH — Phenanthrene	
Amount found in sample	1.3 µg/kg
Ion ratio % deviation	0.1%
Measured mass (m/z)	178.07771
Theoretical mass (m/z)	178.07770
Chemical formula	C$_{14}$H$_{10}$
Mass error (ppm)	0.1

PAH — Anthracene	
Amount found in sample	0.7 µg/kg
Ion ratio % deviation	5.6%
Measured mass (m/z)	178.07779
Theoretical mass (m/z)	178.07770
Chemical formula	C$_{14}$H$_{10}$
Mass error (ppm)	0.5

PCB — PCB 28	
Amount found in sample	0.6 µg/kg
Ion ratio % deviation	0.7%
Measured mass (m/z)	255.96074
Theoretical mass (m/z)	255.96078
Chemical formula	C$_{12}$H$_7$Cl$_3$
Mass error (ppm)	0.2

9-Fluorenone — oxyPAH	
Amount found in sample	0.8 µg/kg
Ion ratio % deviation	4.8%
Measured mass (m/z)	180.05698
Theoretical mass (m/z)	180.05697
Chemical formula	C$_{13}$H$_8$O
Mass error (ppm)	0.1

Figure 5. Examples of FS XIC chromatograms (quantification in black, and confirmation ions in blue) for phenanthrene in soil (top left), anthracene in soil (top right), PCB-28 in soil (bottom left), and 9-fluroenone in soil (bottom right). Below each of the FS XIC chromatograms the following is annotated: (i) amount found in sample as µg/kg, (ii) ion ratio deviation from the calibration average, (iii) measured mass (m/z), (iv) theoretical mass (m/z), (v) chemical formula, and (vi) mass error (ppm).

In summary, the results obtained in these experiments demonstrate that a consolidated compound class method using a modified QuEChERS sample preparation can be used to quantify PAHs and PCBs in soils. In the case of PCB-28, low levels of incurred residues of 0.6 µg/kg were detected and quantified within an ion ratio deviation from the calibration of only 0.7% and a mass error of the theoretical exact mass of 0.2 ppm with minimal matrix interferences all while in FS.

Screening for additional soil contaminants

The advantages of acquiring data in FS with high resolution and accurate mass were leveraged through retrospective analysis of samples and additional screening of unknown contaminants with confirmation by chemical ionization (CI). The Compound Discoverer platform includes a streamlined workflow for GC EI data allowing for extraction, deconvolution, and putative identification of the unknowns based on mass spectral library matching (NIST 2017). The software first performed spectral deconvolution above a customizable signal to noise (S/N) followed by compounds detection and grouping to consider compounds that

elute at the same retention time (within ±6 s window). The deconvoluted spectra were then searched against mass spectral libraries (such as NIST), and the hits were scored based on the total score derived from a combination of library search index (SI) score and presence/absence of the molecular ions as well as percentage of fragment ions that can be explained from the NIST elemental composition. The use of a retention index acquired under the same conditions used for sample analysis helped to increase the confidence in compound identification. Compounds detected with NIST SI scores >750 can be seen in (Figure 6A). With the Compound Discoverer browser an overlaid XIC of the peak eluting at 10.95 min (m/z 136.07579) was identified as the top hit versus NIST library (Figure 6B). The peak was putatively identified as pyriproxyfen with a SI score of 953; however, the molecular ion of m/z 321.135945 was not observed, which demonstrates the requirement for additional chemical ionization and mass accuracy confirmation of molecular ions. Full results of the EI NIST matches for the deconvoluted data can be found in the (Appendix 6 – Table 6).
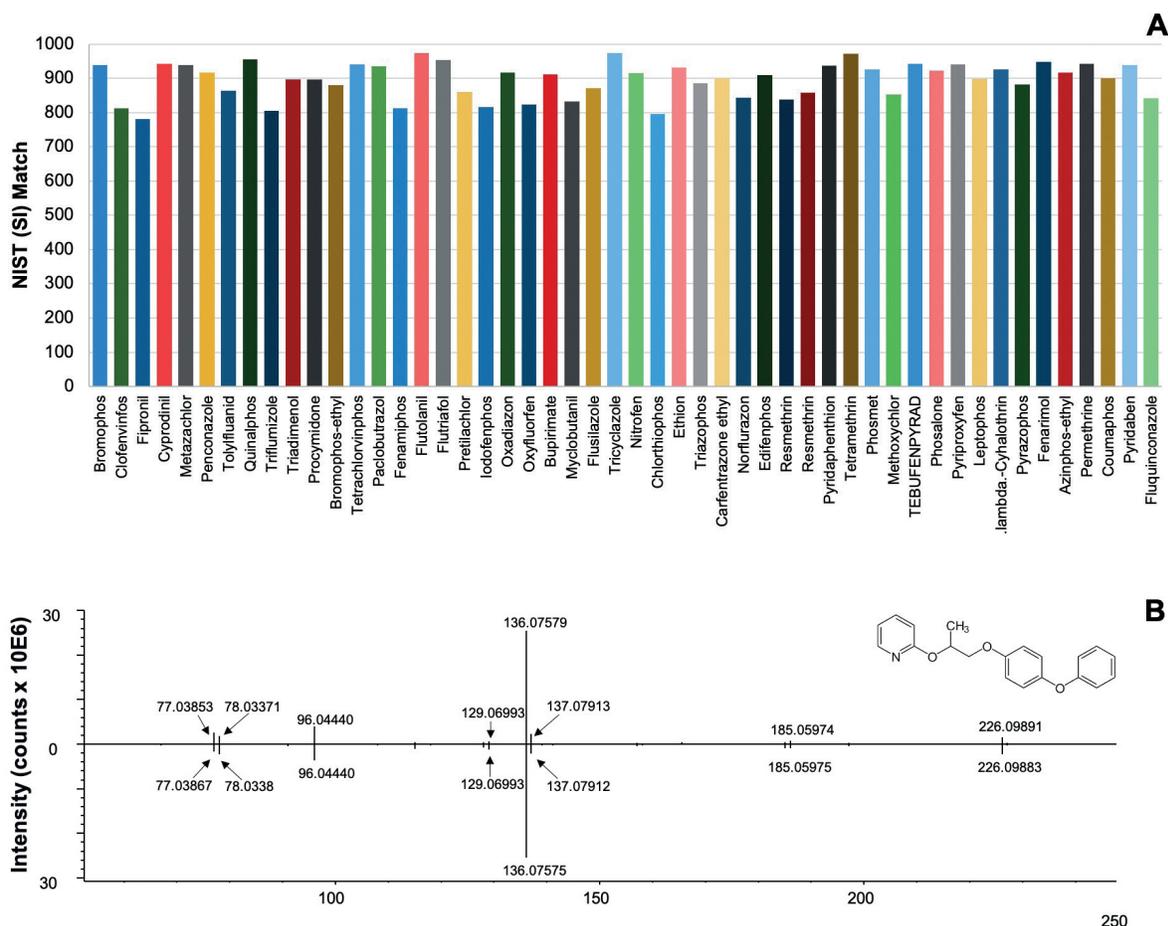

Figure 6. (A) Example NIST SI match scores for compounds detected in the deconvoluted EI spectra QuEChERS soil extract spiked at 100 pg/µL. (B) Compound Discoverer software EI spectrum of a spiked QuEChERS soil extract – deconvoluted versus NIST library of the peak eluting at 10.95 min (m/z 136.07579), with the structure of the top SI match pyriproxyfen from the result table.

Full-scan data for blank and spiked QuEChERS soil extracts (100 pg/µL) were analyzed with Compound Discoverer 3.2 software for putative identification of peaks. A complete workflow was used to identify compounds with a high degree of confidence using deconvoluted EI spectra based on search index scores (SI) and confirmation of the corresponding molecular ion and or adducts using positive chemical ionization. FS data was acquired using Chromeleon 7.3 in EI and PCI modes at 60,000 FWHM resolution and then imported in Compound Discoverer 3.2 software. The software was used to deconvolute, align, and filter the peaks to putatively identify the compounds using mass spectral library match (NIST 17). The power of the deconvolution algorithms become clear when overlaying both the FS TIC and deconvoluted spectra for analytes eluting in a crowded area of the chromatogram (Figure 7).

Confirmation of suspect contaminants using positive chemical ionization

Further confirmation used in the identification of compounds was achieved by assessing the PCI spectra to identify the elemental composition of the parent ion by looking at common adducts. In PCI experiments using methane as the reagent gas, three adducts are typically observed: $[M+H]^+$, $[M+C_2H_5]^+$, and $[M+C_3H_5]^+$. An example was shown for a peak at 9.44 min, which was identified as flutolanil versus the NIST library; however, the molecular ion m/z 323.11276 was not giving a significant response (Figure 8 A). When looking at the PCI data for this compound a significant boost in the molecular ion was observed with minimal mass error of 0.09 ppm (Figure 13B). Two additional adducts $[M+H]^+$ and $[M+C_2H_5]^+$ were also observed with ppm mass errors of -0.1 and -0.03 ppm respectively. Full results of the PCI confirmation can be found in Appendix 7 – Table 7.
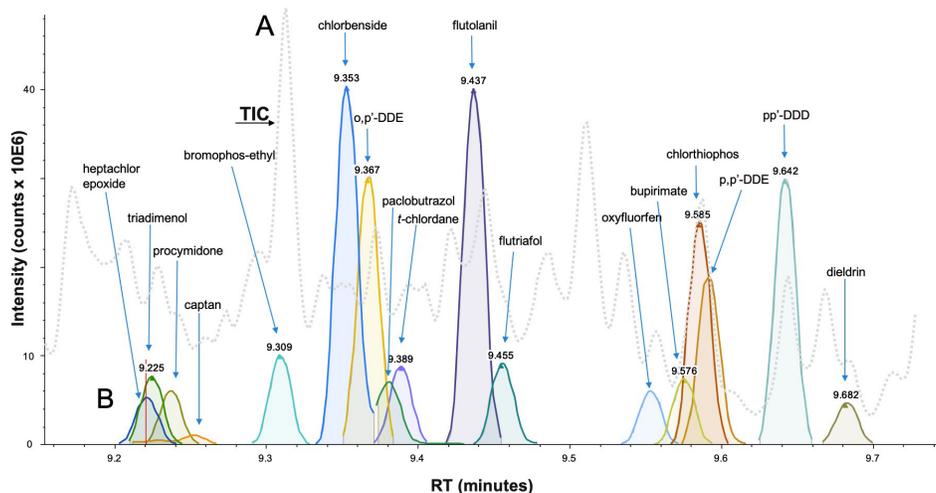
Figure 7. (A) Overlaid FS (m/z = 50–550) TIC for a soil QuEChERS extract spiked with pesticides at 100 pg/µL. (B) Compound Discoverer 3.2 software deconvoluted EI spectrum showing closely eluting compounds extracted from the complex TIC FS data.
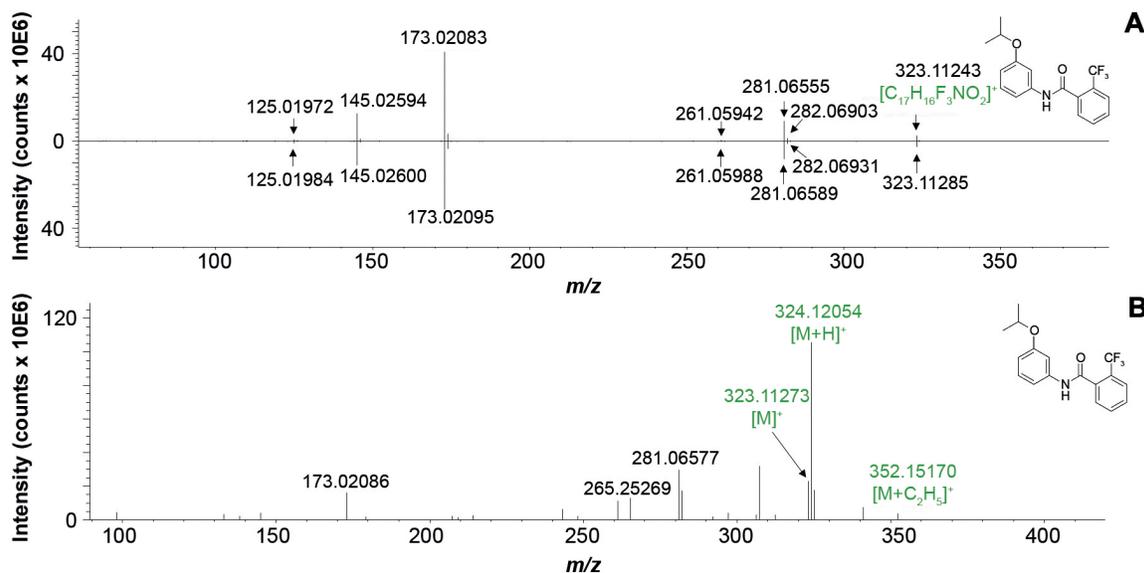
Figure 8. (A) Compound Discoverer software EI spectrum of a spiked QuEChERS soil extract – deconvoluted versus NIST library of the peak eluting at 9.437 min (m/z 323.11243), with the structure from the top SI match flutolanil from the result table. (B) PCI mass spectrum for flutolanil displaying adducts $[M+H]^+$ and $[M+C_2H_5]^+$ used for confirmation of this compound in conjunction with the EI data.

Conclusions

The results of the experiments presented demonstrate that modified QuEChERS methods and the TriPlus RSH autosampler in combination with the Orbitrap Exploris GC provides an ideal solution for **analytical testing laboratories looking to improve productivity and deliver confident results.**

- Comprehensive method consolidation with chromatographic separation and overall analytical performance was achieved for the analysis of PAHs and PCBs in soil in <20 min.

- Increased throughput of up to 20× can be realized by using a modified QuEChERS method compared to tradition Sohxlet extraction methods, saving cost and time.

- Femtogram level sensitivity was achieved using the Orbitrap Exploris GC, with the MDLs values calculated for 45 native compounds ranging from 115 to 475 fg OC (corresponding to 0.1–0.5 µg/kg in sample).

- LOQs ranged from 0.5 to 5.0 µg/kg in soil as determined from n=18 repeat injections of the lowest serially diluted matrix-matched standard that satisfied the acceptance criteria defined below:

  – Ion ratios within ±30% of the expected values calculated as an average across a calibration curve ranging from 0.1 to 500 pg/µL (equivalent to 0.4–5.0 µg/kg in sample)

  – Peak area repeatability of <15% RSD

- Linearity was achieved across a calibration range of 0.1–500 pg/µL (corresponding to 0.1–500 µg/kg in soil) showed coefficient of determination values of R^2 ≥0.995, and residuals <13%.

- All compounds show good recovery overall with the average internal standard recovery being 79%, and precision of the seven technical replicate extractions <5% RSD.

- Quantitative performance with soil samples was excellent as demonstrated by the closeness of the ion ratios and mass error compared to expected values when used for confirmation of low-level incurred residues in soil such as PAHs, PCBs, and oxyPAHs.

- Rapid change-over from EI (for spectral library search) to softer ionization such as PCI (for molecular ion confirmation using adduct information) is possible.

- The streamlined GC-EI data processing workflow with Compound Discoverer software allows for quick extraction, deconvolution, and identification of unknown compounds.

References

1. S.R. CEN/TR 16998:2016 ambient air –report on nitro-and oxy-PAHs - origin, toxicity, concentrations and measurement methods.

2. Sun, Z.; Zhu. Y.; Zhuo, S.; Liu, W, Z.; Zheng, E.Y.; Wang, X.; Xing. B.; Tao. S Occurrence of nitro- and oxy-PAHs in agricultural soils in eastern China and excess lifetime cancer risks from human exposure through soil ingestion. *Environ Int.* **2017**, *108*, 261-270.

3. Anderson, J.T.; Achten, C. Time to say Goodbye to the 16 EPA PAHs? Toward an up-to-date use of PACs for environmental purposes. *Polycyclic Aromatic Compounds* **2015**, *35*, 330–354.

4. Thermo Fisher Scientific (2017) Application note 21736: Ultra-inert low bleed GC columns with advanced silphenylene polymer technology. https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/an-21735-gc-ms-ultra-inert-columns-an21735-en.pdf

5. Hites, R.A. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. *Environ. Sci. Technology* **2004**, *38*, 945.

6. Guidance for the inventory of polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on POPs. [Online] http://chm.pops.int/Implementation/NationalImplementationPlans/Guidance/GuidancefortheinventoryofPBDEs/tabid/3171/Default.aspx (accessed May 8, 2018).

7. Fernandes, A.; White, S.; D'Silva, K.; Rose, M. Simultaneous determination of PCDDs, PCDFs, PCBs and PBDEs in food. *Talanta* **2004**, *63*, 1147–1155.

8. Thermo Fisher Scientific (2009) Technical note 51797: Timed SRM: improved capabilities for multi-target compound analysis. https://tools.thermofisher.com/content/sfs/brochures/AN51797-TimedSRM-Multitarget-Compound-Analysis.pdf

Appendix 1 – Table 1. Details of 45 native compounds analyzed, including compound type, CAS number, and calibration range

Native standard	Compound type	CAS Number	Calibration range (ng/mL)
Napthalene	PAH	91-20-3	
Benzo(b)thiophene	PASH	95-15-8	
Quinoline	PANH	91-22-5	
1-Indanone	PAOH	83-33-0	
2-Methylnapthalene	methylPAH	91-57-6	
1-Methylnapthalene	methylPAH	90-12-0	
Biphenyl	aromatic	92-52-4	
Acenaphthylene	PAH	208-96-8	
1-Ethylnapthalene	methylPAH	1127-76-0	
2-Ethylnapthalene	methylPAH	939-27-5	
Acenaphthene	PAH	83-32-9	
2,7-Dimethylnapthalene	methylPAH	582-16-1	
1,3-Dimethylnapthalene	methylPAH	575-41-7	
1,6-Dimethylnapthalene	methylPAH	575-43-9	
2,3-Dimethylnapthalene	methylPAH	581-40-8	
1,2-Dimethylnapthalene	methylPAH	573-98-8	
1,8-Dimethylnapthalene	methylPAH	569-41-5	
Dibenzofuran	PAOH	132-64-9	
Fluorene	PAH	86-73-7	
9-Fluorenone	oxyPAH	486-25-9	
Dibenzothiophene	PASH	132-65-0	
Phenanthrene	PAH	85-01-8	
Anthracene	PAH	120-12-7	0.1–500
Carbazole	PAOH	86-74-8	
PCB-28	PCB	7012-37-5	
PCB-52	PCB	35693-99-3	
9,10-Anthraquinone	PAOH	84-65-1	
Fluoranthene	PAH	206-44-0	
PCB-101	PCB	37680-73-2	
2-Methylanthraquinone	PAOH	84-54-8	
Pyrene	PAH	129-00-0	
PCB-118	PCB	31508-00-6	
PCB-153	PCB	35065-27-1	
PCB-138	PCB	35065-28-2	
Benzo[a]anthracene	PAH	56-55-3	
Chrysene	PAH	218-01-9	
PCB-180	PCB	35065-29-3	
Benzanthrone	oxyPAH	82-05-3	
5,12-Napthacenequinone	oxyPAH	1090-13-7	
Benzo[b]fluoranthene	PAH	205-99-2	
Benzo[k]fluoranthene	PAH	207-08-9	
Benzo[a]pyrene	PAH	50-32-8	
Indeno[1,2,3-cd]pyrene	PAH	193-39-5	
Dibenzo[a,h]anthracene	PAH	53-70-3	
Benzo[ghi]perylene	PAH	191-24-2	

Appendix 2 – Table 2. Details of the 14 internal standards, including compound type, CAS number, and concentration (suffix "L" indicates mass-labeled)

Internal standard	Compound type	CAS Number	Concentration (ng/mL)
Napthalene-d-8	PAH	1146-65-2	
Dibenzofuran-d8	PAOH	93952-04-6	
9-Fluorenone-d8	oxyPAH	137219-34-2	
Pyrene-d-10	PAH	1718-52-1	
PCB-28L	PCB	7012-37-5	
PCB-52L	PCB	35693-99-3	
PCB-101L	PCB	37680-73-2	
PCB-118L	PCB	31508-00-6	100
PCB-153L	PCB	35065-27-1	
PCB-138L	PCB	35065-28-2	
PCB-180L	PCB	35065-29-3	
Quinoline-d7	PANH	34071-94-8	
o-Terphenyl	aromatic	84-15-1	
Perylene-d-12	PAH	1520-96-3	

Appendix 3 – Table 3. Method LOQs were determined from the lowest serially diluted spiked QuEChERS extract solution prepared as detailed in the experimental section, which pass the criteria. Eighteen replicate injections of each of the diluted standards ranging between 0.5 pg/µL and 5.0 pg/µL were performed. The criteria used to assess individual LOQs were (i) measured ion ratio (IR) ±30% compared to the target ion ratio calculated from the average ion ratio across the calibration range and (ii) peak area <15 % RSD.

Compound	Injected amount (pg OC)	Min IR % dev	Max IR % dev	Mean IR % dev	Peak area % RSD	LOQ (pg OC)	LOQ (µg/kg)
Napthalene	0.5	-1.4	1.7	0.4	4.5%	0.5	0.5
Benzo(b)thiophene	1.0	-0.8	-13.3	1.0	5.7%	1.0	1.0
Quinoline	1.0	10.9	-0.7	1.0	8.1%	1.0	1.0
1-Indanone	2.5	-10.9	13.0	2.6	6.2%	2.5	2.5
1-Methylnapthalene	0.5	6.9	10.3	8.8	2.2%	0.5	0.5
2-Methylnapthalene	0.5	4.6	7.3	6.0	2.2%	0.5	0.5
Acenaphthene	0.5	-5.8	13.5	4.4	5.6%	0.5	0.5
Acenaphthylene	0.5	-10.2	14.7	2.8	6.6%	0.5	0.5
Biphenyl	0.5	-12.0	1.6	-5.2	3.6%	0.5	0.5
1 & 2-Ethylnapthalene	0.5	-9.1	9.9	3.0	2.9%	0.5	0.5
2, 7-Dimethylnapthalene	0.5	5.6	14.7	10.0	2.2%	0.5	0.5
1,3 & 1,6-Dimethylnapthalene	0.5	10.4	17.5	13.7	3.3%	0.5	0.5
2,3-Dimethylnapthalene	0.5	-13.3	13.2	0.3	10.2%	0.5	0.5
1,2-Dimethylnapthalene	0.5	-24.2	16.1	-12.1	5.8%	0.5	0.5
1,8-Dimethylnapthalene	2.5	-12.5	11.3	-3.1	3.2%	2.5	2.5
Dibenzofuran	0.5	-13.9	2.1	-5.4	2.0%	0.5	0.5
Fluorene	1.0	11.1	5.4	1.0	6.5%	1.0	1.0
9-Fluorenone	1.0	9.1	-2.3	1.0	5.3%	1.0	1.0
Dibenzothiophene	1.0	9.7	-4.4	1.0	5.4%	1.0	1.0
Phenanthrene	0.5	-13.3	2.9	-5.6	2.6%	0.5	0.5
Anthracene	1.0	11.5	0.8	1.0	5.5%	1.0	1.0
Carbazole	1.0	11.3	-1.0	1.0	8.3%	1.0	1.0
PCB-28	2.5	-11.7	9.5	-3.6	3.7%	2.5	2.5
PCB-52	1.0	12.1	0.4	1.0	6.6%	1.0	1.0

Appendix 3 – Table 3 continued. Method LOQs were determined from the lowest serially diluted spiked QuEChERS extract solution prepared as detailed in the experimental section, which pass the criteria. Eighteen replicate injections of each of the diluted standards ranging between 0.5 pg/µL and 5.0 pg/µL were performed. The criteria used to assess individual LOQs were (i) measured ion ratio ±30% compared to the target ion ratio calculated from the average ion ratio across the calibration range and (ii) peak area <15 % RSD.

Compound	Injected amount (pg OC)	Min IR % dev	Max IR % dev	Mean IR % dev	Peak area % RSD	LOQ (pg OC)	LOQ (µg/kg)
9, 10-Anthraquinone	1.0	14.6	8.8	1.0	6.1%	1.0	1.0
Fluoranthene	0.5	-11.3	13.7	4.5	6.7%	0.5	0.5
PCB-101	0.5	-27.9	15.3	-12.9	8.3%	0.5	0.5
2-Methylanthraquinone	1.0	13.5	-1.4	1.0	8.4%	1.0	1.0
Pyrene	0.5	-12.2	2.6	-4.1	3.6%	0.5	0.5
PCB-118	0.5	-20.4	17.8	-0.3	7.0%	0.5	0.5
PCB-153	1.0	19.5	1.5	1.0	6.6%	1.0	1.0
PCB-138	1.0	13.2	1.2	1.0	9.4%	1.0	1.0
Benzo[a]anthracene	1.0	6.8	-0.6	1.0	7.1%	1.0	1.0
Chrysene	1.0	10.7	0.0	1.0	7.7%	1.0	1.0
PCB-180	0.5	-24.2	24.7	-4.5	9.5%	0.5	0.5
Benzanthrone	2.5	-12.3	12.0	1.3	6.3%	2.5	2.5
5, 12-Napthacenequinone	2.5	-12.2	12.8	0.4	8.1%	2.5	2.5
Benzo[b]fluoranthene	1.0	6.3	-2.7	1.0	7.2%	1.0	1.0
Benzo[k]fluoranthene	1.0	7.6	-3.9	1.0	10.1%	1.0	1.0
Benzo[a]pyrene	1.0	8.3	-3.1	1.0	9.1%	1.0	1.0
Indeno[1,2,3-cd]pyrene	1.0	-7.8	-14.6	1.0	8.3%	1.0	1.0
Dibenzo[a,h]anthracene	2.5	-6.4	9.6	1.4	4.6%	2.5	2.5
Benzo[ghi]perylene	2.5	-9.9	11.8	-0.2	3.0%	2.5	2.5

Appendix 4 – Table 4. Coefficient of determination (R^2) and residual average response factor (% RSD)

Compound	Compound type	R^2	AVCF % RSD
Naphthalene	PAH	0.9999	1.6
Acenaphthylene	PAH	0.9987	5.4
Acenaphthene	PAH	0.9995	4.0
Biphenyl	PAH	0.9998	2.6
Fluorene	PAH	0.9981	9.0
Phenanthrene	PAH	0.9995	3.8
Anthracene	PAH	0.9981	4.3
Fluoranthene	PAH	0.9998	3.0
Pyrene	PAH	0.9997	3.2
Benzo[a]anthracene	PAH	0.9999	1.7
Chrysene	PAH	0.9997	3.1
Benzo[b]fluoranthene	PAH	0.9998	2.6
Benzo[k]fluoranthene	PAH	0.9994	4.5
Benzo[a]pyrene	PAH	0.9987	5.4
Indeno[1,2,3-cd]pyrene	PAH	0.9964	9.3
Dibenzo[a,h]anthracene	PAH	0.9978	7.3
Benzo[ghi]perylene	PAH	0.9989	5.1
1-Methylnapthalene	methylPAH	1.0000	1.1
2-Methylnapthalene	methylPAH	0.9999	1.8

Appendix 4 – Table 4 continued. Coefficient of determination (R²) and residual average response factor (% RSD)

Compound	Compound type	R²	AVCF % RSD
2, 7-Dimethylnapthalene	methylPAH	0.9999	1.5
1,3 & 1,6-Dimethylnapthalene	methylPAH	0.9999	2.0
2,3-Dimethylnapthalene	methylPAH	0.9999	1.8
1,2-Dimethylnapthalene	methylPAH	0.9993	4.5
1,8-Dimethylnapthalene	methylPAH	0.9998	2.6
PCB-28	PCB	0.9997	2.5
PCB-52	PCB	0.9991	2.8
PCB-101	PCB	0.9998	3.2
PCB-118	PCB	0.9998	3.7
PCB-153	PCB	0.9998	1.6
PCB-138	PCB	0.9991	2.8
PCB-180	PCB	0.9997	4.3
Benzo(b)thiophene	PASH	0.9998	3.2
Dibenzothiophene	PASH	0.9988	3.7
1 & 2-Ethylnapthalene	ethylPAH	0.9996	3.7
Quinoline	PANH	0.9988	4.0
1-Indanone	PAOH	0.9993	4.7
Dibenzofuran	PAOH	0.9993	5.3
Carbazole	PAOH	0.9980	4.7
9, 10-Anthraquinone	PAOH	0.9951	12.9
2-Methylanthraquinone	PAOH	0.9981	6.5
9-Fluorenone	oxyPAH	0.9997	5.0
Benzanthrone	oxyPAH	0.9985	6.0
5, 12-Napthacenequinone	oxyPAH	0.9963	9.6
	Min	**0.9951**	**1.1**
	Max	**1.0000**	**12.9**
	Mean	**0.9991**	**4.2**

Appendix 5 – Table 5. QuEChERS soil extraction IS % recovery data

Compound	Extraction internal standard spiked recovery %							Mean	STDEV	% RSD
	1	2	3	4	5	6	7			
Napthalene d8	70.6	69.3	68.4	69.1	69.1	71.0	64.8	69	2.015	2.9%
Quinoline d7	72.0	71.7	69.9	74.8	72.4	71.9	69.3	72	1.792	2.5%
Dibenzofuran d8	82.0	82.8	80.4	80.7	79.8	82.4	77.4	81	1.847	2.3%
9-Fluorenone d8	81.8	81.4	78.2	82.5	79.1	79.9	78.7	80	1.676	2.1%
PCB 28L	89.2	89.5	90.9	93.7	86.0	92.7	91.2	91	2.546	2.8%
PCB 52L	89.7	88.5	87.0	85.2	85.1	86.5	83.8	87	2.063	2.4%
PCB 101L	85.2	82.6	82.7	78.0	81.6	79.5	80.3	81	2.375	2.9%
Pyrene d10	92.9	91.0	90.0	86.7	88.7	86.0	85.7	89	2.734	3.1%
PCB 118L	83.9	82.1	80.0	78.8	80.0	79.3	77.8	80	2.067	2.6%
PCB 153L	83.0	82.1	78.2	76.9	79.0	77.0	76.1	79	2.685	3.4%
PCB 138L	84.9	83.5	82.6	78.1	82.2	81.9	80.5	82	2.168	2.6%
PCB 180L	75.2	73.8	71.3	68.8	71.9	72.3	70.8	72	2.0735	2.9%
Perylene d12	63.6	63.6	62.3	64.4	66.7	70.4	68.1	66	2.9116	4.4%

Appendix 6 – Table 6. Compound Discoverer 3.2 software QuEChERS soil extract deconvoluted EI data NIST search index

Compound name	Reference RT [min]	Measured (m/z)	NIST formula	NIST theoretical (m/z)	Mass error (ppm)	Area	Calculated RI	RI Delta	NIST formula	Score	SI	RSI
Benzyl alcohol	4.466	79.05409	C6H7	79.05423	1.78	16069986	1039	5	C7H8O	95.7	937	987
Mevinphos	6.543	127.01549	C2H8O4P	127.01547	0.13	17076195	1429	16	C7H13O6P	99	960	962
Pebulate	6.729	128.10695	C7H14NO	128.10699	0.32	8595860	1469	0	C10H21NOS	95.2	895	936
Phthalimide	6.788	147.03149	C8H5NO2	147.03148	0.10	1242332	1482	0	C8H5NO2	99.4	968	968
Methacrifos	6.874	180.00058	C5H9O3PS	180.00045	0.71	6569371	1501	6	C7H13O5PS	98.5	931	932
Chloroneb	6.945	190.96625	C7H5Cl2O2	190.96611	0.72	17004439	1517	0	C8H8Cl2O2	98.2	960	981
Benzene, pentachloro-	7.084	249.84847	C6HCl5	249.84859	0.50	24762934	1549	0	C6HCl5	94.2	943	973
Tecnazene	7.384	202.87970	C5HCl4	202.87974	0.18	4337238	1609	0	C6HCl4NO2	94.3	975	988
Propachlor	7.411	120.08082	C8H10N	120.08078	0.36	9254651	1612	0	C11H14ClNO	97.2	938	964
Diphenylamine	7.501	169.08841	C12H11N	169.0886	1.13	24878507	1624	2	C12H11N	95.6	954	983
Cycloate	7.537	83.08540	C6H11	83.08553	1.48	12902977	1628	8	C11H21NOS	96.4	859	874
Chlorpropham	7.587	127.01830	C6H6ClN	127.01833	0.20	9390559	1634	0	C10H12ClNO2	97.9	953	976
Trifluralin	7.590	264.02240	C8H5F3N3O4	264.02267	1.01	10518127	1635	0	C13H16F3N3O4	96.9	855	860
Benfluralin	7.612	292.05356	C10H9F3N3O4	292.05397	1.40	11572988	1637	0	C13H16F3N3O4	98.3	915	924
Sulfotep	7.640	293.99060	C6H16O5P2S2	293.99089	0.98	5705056	1641	0	C8H20O5P2S2	98.9	945	948
Phorate	7.764	75.02623	C3H7S	75.0263	0.89	9945770	1656	0	C7H17O2PS3	93.4	858	914
Pentachloroanisole	7.934	264.83575	C6Cl5O	264.83568	0.28	10759890	1677	0	C7H3Cl5O	98.6	950	954
Botran	7.936	123.99490	C6H3ClN	123.99485	0.35	2725458	1677	0	C6H4Cl2N2O2	96	886	907
Atrazine	7.963	200.06975	C7H11ClN5	200.06975	0.00	8074011	1681	67	C8H14ClN5	97.5	947	948
Clomazone	8.022	125.01531	C7H6Cl	125.01525	0.41	24300346	1688	0	C12H14ClNO2	95.9	884	907
Terbuthylazine	8.073	214.08533	C8H13ClN5	214.0854	0.34	9737849	1694	82	C9H16ClN5	98.5	969	969
Diazinone	8.102	137.07097	C7H9N2O	137.07094	0.22	13998989	1698	90	C12H21N2O3PS	98.5	924	926
Propyzamide	8.113	172.95569	C7H3Cl2O	172.95555	0.82	17602860	1699	85	C12H11Cl2NO	98.2	942	944
Fonofos	8.148	108.98717	C2H6OPS	108.98715	0.17	23490821	1708	73	C10H15OPS2	98.3	950	956
Pyrimethanil	8.177	198.10248	C12H12N3	198.10257	0.48	45520948	1715	0	C12H13N3	94.9	918	978
Isazophos	8.203	118.98820	C2H2ClN3O	118.98809	0.90	9010911	1722	0	C9H17ClN3O3PS	98.1	905	915
Disulfoton	8.221	88.03407	C4H8S	88.03412	0.56	8860789	1727	0	C8H19O2PS3	97.2	921	951
Chlorothalonil	8.239	265.87787	C8Cl4N2	265.87806	0.72	19236284	1732	0	C8Cl4N2	97.1	966	971
Anthracene	8.252	178.07787	C14H10	178.0777	0.93	764555	1736	70	C14H10	97.8	909	914
Triallate	8.287	268.03238	C10H16Cl2NOS	268.03242	0.14	6379150	1745	80	C10H16Cl3NOS	97.4	896	897
Dibutyl phthalate	8.386	149.02332	C8H5O3	149.02332	0.03	5881147	1772	181	C16H22O4	98.1	915	916
Propanil	8.464	160.97940	C6H5Cl2N	160.97936	0.28	19471408	1793	0	C9H9Cl2NO	98.7	955	960
Chloropyriphos-methyl	8.514	285.92539	C7H7Cl2NO3PS	285.92558	0.69	20128971	1807	72	C7H7Cl3NO3PS	97.9	940	941
Transfluthrin	8.523	163.01637	C7H3F4	163.01654	1.02	11807916	1809	0	C15H12Cl2F4O2	97.3	897	927
Vinclozoline	8.526	212.00269	C10H8Cl2N	212.00283	0.68	3926786	1810	0	C12H9Cl2NO3	97.6	921	942
Alachlor	8.561	160.11224	C11H14N	160.11208	1.05	8630775	1820	74	C14H20ClNO2	92.8	849	907
Tolclofos-methyl	8.570	264.98505	C9H11ClO3PS	264.98496	0.34	30985887	1822	74	C9H11Cl2O3PS	97	848	848
Fenchlorphos	8.643	284.93015	C8H8Cl2O3PS	284.93033	0.66	22859648	1843	0	C8H8Cl3O3PS	97.4	887	973
Pirimiphos methyl	8.682	290.07211	C10H17N3O3PS	290.07228	0.56	12041239	1853	79	C11H20N3O3PS	98.1	913	914
Fenitrothion	8.726	260.01404	C9H11NO4PS	260.01409	0.20	6776685	1866	0	C9H12NO5PS	97.7	911	918
Malathion	8.755	124.98213	C2H6O2PS	124.98206	0.55	9227531	1874	0	C10H19O6PS2	99	953	954
Linuron	8.786	61.05217	C2H7NO	61.05222	0.67	996941	1882	0	C9H10Cl2N2O2	93.7	754	767
Dichlofluanid	8.801	123.01375	C6H5NS	123.01372	0.22	10765859	1886	71	C9H11Cl2FN2O2S2	98.3	923	924

Appendix 6 – Table 6 continued. Compound Discoverer 3.2 software QuEChERS soil extract deconvoluted EI data NIST search index

Compound name	Reference RT [min]	Measured (m/z)	NIST formula	NIST theoretical (m/z)	Mass error (ppm)	Area	Calculated RI	RI Delta	NIST formula	Score	SI	RSI
Pentachlorothioanisole	8.839	295.83633	C7H3Cl5S	295.83631	0.08	10450278	1897	58	C7H3Cl5S	98.1	937	954
Parathion	8.894	96.95074	H2O2PS	96.95076	0.27	4484103	1913	75	C10H14NO5PS	97.9	907	912
DCPA	8.901	300.87985	C9H3Cl4O3	300.88013	0.93	23819724	1915	72	C10H6Cl4O4	98.5	944	947
Triadimefon	8.918	208.02710	C9H7ClN3O	208.02722	0.56	4235155	1919	77	C14H16ClN3O2	97.7	896	898
9,10-Anthracenedione	8.949	208.05202	C14H8O2	208.05188	0.65	8399424	1928	55	C14H8O2	97.5	903	919
Pirimiphos ethyl	8.956	168.05891	C7H10N3S	168.05899	0.48	9261908	1930	0	C13H24N3O3PS	98.4	928	945
Isopropalin	9.011	238.08212	C10H12N3O4	238.08223	0.46	11131988	1946	0	C15H23N3O4	97.8	892	902
Bromophos	9.027	330.87711	C8H8BrClO3PS	330.87687	0.72	18301347	1951	68	C8H8BrCl2O3PS	97.9	938	949
Clofenvinfos	9.060	266.93747	C8H6Cl2O4P	266.93753	0.22	423034	1960	0	C12H14Cl3O4P	94.6	813	831
Fipronil	9.080	366.94272	C11H4Cl2F3N4OS	366.94295	0.62	1478777	1966	0	C12H4Cl2F6N4OS	95.6	781	781
Cyprodinil	9.093	224.11832	C14H14N3	224.11822	0.41	40372063	1969	0	C14H15N3	97.3	943	971
Metazachlor	9.117	132.08084	C9H10N	132.08078	0.50	11264282	1976	68	C14H16ClN3O	98.6	939	941
Penconazole	9.137	158.97646	C7H5Cl2	158.97628	1.09	18713951	1982	74	C13H15Cl2N3	98.3	917	918
Tolylfluanid	9.161	137.02948	C3H12Cl2F	137.02946	0.15	13660572	1989	74	C10H13Cl2FN2O2S2	96.6	864	894
Quinalphos	9.201	146.04755	C8H6N2O	146.04746	0.56	10014184	2000	77	C12H15N2O3PS	98.4	956	959
Triflumizole	9.214	205.99829	C8H4ClF3N	205.99789	1.96	3132804	2004	83	C15H15ClF3N3O	96	805	806
Triadimenol	9.225	112.05049	C4H6N3O	112.05054	0.42	8170623	2008	78	C14H18ClN3O2	97.9	897	897
Procymidone	9.238	96.05702	C6H8O	96.05697	0.58	6299842	2012	0	C13H11Cl2NO2	96.9	897	916
Bromophos-ethyl	9.309	302.84604	C7H4BrCl2O2S	302.84574	0.97	10486942	2034	0	C10H12BrCl2O3PS	96.8	880	888
Tetrachlorvinphos	9.342	328.92981	C10H9Cl3O4P	328.92985	0.13	8515425	2044	0	C10H9Cl4O4P	97.8	940	952
Paclobutrazol	9.382	125.01531	C7H6Cl	125.01525	0.41	7793995	2057	0	C15H20ClN3O	98.5	935	979
Fenamiphos	9.417	55.05417	C4H7	55.05423	1.11	8959158	2068	0	C13H22NO3PS	93.4	813	896
Flutolanil	9.437	173.02083	C8H4F3O	173.02088	0.27	42560841	2074	0	C17H16F3NO2	99.5	974	976
Flutriafol	9.455	123.02410	C7H4FO	123.02407	0.26	9903083	2080	50	C16H13F2N3O	98.5	953	960
Pretilachlor	9.508	162.12763	C11H16N	162.12773	0.62	10905234	2096	0	C17H26ClNO2	95.3	860	902
Iodofenphos	9.510	376.86569	C8H8ClIO3PS	376.86595	0.68	21511075	2097	61	C8H8Cl2IO3PS	93.1	816	857
Oxadiazon	9.530	174.95873	C6H3Cl2NO	174.95862	0.60	11688803	2103	0	C15H18Cl2N2O3	98.3	916	918
Oxyfluorfen	9.554	252.03917	C13H7F3O2	252.03927	0.38	6287263	2111	85	C15H11ClF3NO4	95.9	824	826
Bupirimate	9.576	208.14444	C11H18N3O	208.14444	0.01	7679148	2118	0	C13H24N4O3S	98.2	911	915
Myclobutanil	9.583	179.02463	C8H6ClN3	179.02448	0.85	7298452	2120	0	C15H17ClN4	96.1	832	891
Flusilazole	9.592	233.05919	C13H11F2Si	233.05926	0.30	20153005	2123	73	C16H15F2N3Si	90.3	871	891
Tricyclazole	9.614	189.03554	C9H7N3S	189.03552	0.10	3484770	2129	43	C9H7N3S	97.1	973	981
Nitrofen	9.759	282.97965	C12H7Cl2NO3	282.97975	0.37	4113285	2175	60	C12H7Cl2NO3	97	915	922
Chlorthiophos	9.782	268.92563	C7H7ClO3PS2	268.92573	0.36	4905455	2182	0	C11H15Cl2O3PS2	95.5	796	815
Ethion	9.837	230.97318	C5H12O2PS3	230.97315	0.09	17039535	2199	73	C9H22O4P2S4	98.1	932	970
Triazophos	9.934	162.06630	C8H8N3O	162.06619	0.68	4817402	2229	75	C12H16N3O3PS	97.6	886	887
Carfentrazone ethyl	9.974	312.05896	C13H9F3N3O3	312.05905	0.29	7221687	2242	0	C15H14Cl2F3N3O3	97.9	900	922
Norflurazon	10.055	303.03787	C12H9ClF3N3O	303.03808	0.67	5679397	2267	0	C12H9ClF3N3O	96.9	843	845
Carbophenothion	10.062	156.98746	C6H6OPS	156.98715	1.97	11686197	2269	62	C11H16ClO2PS3	98.4	941	946
Edifenphos	10.102	109.01067	C6H5S	109.01065	0.17	11653922	2282	0	C14H15O2PS2	94.3	910	920
Resmethrin	10.214	128.06212	C10H8	128.06205	0.53	3084053	2315	0	C22H26O3	96.4	838	852
Pyridaphenthion	10.422	199.08656	C12H11N2O	199.08659	0.13	4151296	2375	0	C14H17N2O4PS	98.8	937	942
Tetramethrin	10.481	164.07062	C9H10NO2	164.07061	0.08	16344579	2392	0	C19H25NO4	99.4	972	976
Phosmet	10.539	160.03935	C9H6NO2	160.0393	0.30	28822343	2408	0	C11H12NO4PS2	98.4	926	986

Appendix 6 – Table 6 continued. Compound Discoverer 3.2 software QuEChERS soil extract deconvoluted EI data NIST search index

Compound name	Reference RT [min]	Measured (m/z)	NIST formula	NIST theoretical (m/z)	Mass error (ppm)	Area	Calculated RI	RI Delta	NIST formula	Score	SI	RSI
Methoxychlor	10.574	227.10657	C15H15O2	227.10666	0.39	20536768	2417	69	C16H15Cl3O2	94.2	852	895
Tebufenpyrad	10.609	171.03200	C6H8N2O2P	171.03179	1.22	13061973	2426	76	C18H24ClN3O	96.7	942	956
Phosalone	10.852	182.00035	C8H5ClNO2	182.00033	0.10	11687589	2490	0	C12H15ClNO4PS2	97	922	938
Pyriproxyfen	10.883	136.07579	C8H10NO	136.07569	0.73	30668503	2498	71	C20H19NO3	97.9	940	953
Leptophos	10.885	171.00285	C7H8OPS	171.0028	0.32	13220533	2499	51	C13H10BrCl2O2PS	95.6	899	913
.lambda.-Cyhalothrin	10.921	181.06485	C13H9O	181.06479	0.33	12337809	2507	85	C23H19ClF3NO3	98.2	925	928
Pyrazophos	11.064	221.07954	C10H11N3O3	221.07949	0.24	6802604	2540	0	C14H20N3O5PS	97.6	881	923
Fenarimol	11.177	138.99460	C7H4ClO	138.99452	0.57	7620002	2567	52	C17H12Cl2N2O	97.9	947	950
Azinphos-ethyl	11.214	132.04440	C8H6NO	132.04439	0.10	6897902	2575	0	C12H16N3O3PS2	97.7	916	960
Permethrine	11.503	183.08044	C13H11O	183.08044	0.02	14135701	2639	0	C21H20Cl2O3	98.8	942	952
Pyridaben	11.578	147.11690	C11H15	147.11683	0.48	25077978	2655	0	C19H25ClN2OS	98.5	938	944
Fluquinconazole	11.583	340.03946	C16H8ClFN5O	340.03959	0.39	19132298	2656	62	C16H8Cl2FN5O	87.6	842	941

Appendix 7 – Table 7. Compound Discoverer 3.2 software QuEChERS soil extract PCI confirmation data for [M+], [M+H], [M+C$_2$H$_5$], and [C$_3$H$_5$] with associated ppm mass error (where detected)

Name	Reference RT [min]	NIST Formula	[M]$^+$	Mass error (ppm)	[M+H]$^+$	Mass error (ppm)	[M+C$_2$H$_5$]$^+$	Mass error (ppm)	[M+C$_3$H$_5$]$^+$	Mass error (ppm)
Benzyl alcohol	4.466	C7H8O	108.05697	0.83	109.06534	0.88	137.09664	0.19	149.09664	0.04
Mevinphos	6.543	C7H13O6P	224.04443		225.05280	-0.16	253.08410	-1.36	265.08410	
Pebulate	6.729	C10H21NOS	203.13384		204.14221	0.68	232.17351	0.33	244.17351	
Phthalimide	6.788	C8H5NO2	147.03148		148.03986	-0.22	176.07116		188.07116	
Methacrifos	6.874	C7H13O5PS	240.02158	0.06	241.02996	0.15	269.06126	-0.25	281.06126	-0.2
Chloroneb	6.945	C8H8Cl2O2	205.98959	0.5	206.99796	1.42	235.02926	-0.26	247.02926	
Benzene, pentachloro-	7.084	C6HCl5	247.85154	0.21	248.85992	2.63	276.89122		288.89122	
Tecnazene	7.384	C6HCl4NO2	258.87559	0.53	259.88397	0.74	287.91527		299.91527	
Propachlor	7.411	C11H14ClNO	211.07584	0.39	212.08422	0.24	240.11552	0.50	252.11552	-1.15
Diphenylamine	7.501	C12H11N	169.08860	0.65	170.09698	0.19	198.12828	0.50	210.12828	0.57
Cycloate	7.537	C11H21NOS	215.13384		216.14221	0.45	244.17351	0.13	256.17351	
Chlorpropham	7.587	C10H12ClNO2	213.05511	0.21	214.06348	1.39	242.09478		254.09478	
Trifluralin	7.590	C13H16F3N3O4	335.10874	-0.34	336.11712	-0.14	364.14842		376.14842	
Benfluralin	7.612	C13H16F3N3O4	335.10874	-0.34	336.11712	-0.14	364.14842		376.14842	
Sulfotep	7.640	C8H20O5P2S2	322.02219	-0.02	323.03057	-0.46	351.06187	-0.25	363.06187	-0.04
Phorate	7.764	C7H17O2PS3	260.01228	-0.24	261.02066	0.10	289.05196		301.05196	
Pentachloroanisole	7.934	C7H3Cl5O	277.86210	-0.02	278.87048	2.27	306.90178		318.90178	
Botran	7.936	C6H4Cl2N2O2	205.96443	0.34	206.97281	0.94	235.00411		247.00411	
Atrazine	7.963	C8H14ClN5	215.09322	0.46	216.10160	0.44	244.13290	-0.01	256.13290	0.45
Clomazone	8.022	C12H14ClNO2	239.07076		240.07913	0.11	268.11043	0.43	280.11043	-1.17
Terbuthylazine	8.073	C9H16ClN5	229.10887	0.34	230.11725	0.10	258.14855	-0.37	270.14855	-0.27
Diazinone	8.102	C12H21N2O3PS	304.10050	-0.09	305.10888	-0.84	333.14018	-0.37	345.14018	-0.62
Propyzamide	8.113	C12H11Cl2NO	255.02122	0.43	256.02960	-0.02	284.06090	0.84	296.06090	-1.29
Fonofos	8.148	C10H15OPS2	246.02964	-0.11	247.03802	-0.26	275.06932	-0.40	287.06932	-0.41
Pyrimethanil	8.177	C12H13N3	199.11040	0.99	200.11878	0.17	228.15008	-0.11	240.15008	-0.28

Appendix 7 – Table 7 continued. Compound Discoverer 3.2 software QuEChERS soil extract PCI confirmation data for [M+], [M+H], [M+C₃H₅], and [C₃H₅] with associated ppm mass error (where detected)

Name	Reference RT [min]	NIST Formula	[M]⁺	Mass error (ppm)	[M+H]⁺	Mass error (ppm)	[M+C₂H₅]⁺	Mass error (ppm)	[M+C₃H₅]⁺	Mass error (ppm)
Isazophos	8.203	C9H17ClN3O3PS	313.04113	-0.09	314.04950	-0.37	342.08080	-0.17	354.08080	-0.17
Disulfoton	8.221	C8H19O2PS3	274.02793	-0.74	275.03631	-0.28	303.06761		315.06761	
Chlorothalonil	8.239	C8Cl4N2	263.88101	-0.22	264.88939	1.09	292.92069	-0.58	304.92069	
Anthracene	8.252	C14H10	178.07770	0.03	179.08608	-0.18	207.11738		219.11738	
Triallate	8.287	C10H16Cl3NOS	303.00127		304.00965	-0.33	332.04095	-0.07	344.04095	
Dibutyl phthalate	8.386	C16H22O4	278.15126		279.15964	-0.06	307.19094		319.19094	
Propanil	8.464	C9H9Cl2NO	217.00557	0.06	218.01395	0.21	246.04525	-0.82	258.04525	
Chloropyriphos-methyl	8.514	C7H7Cl3NO3PS	320.89443	0.46	321.90281	-0.29	349.93411	-0.20	361.93411	0.03
Transfluthrin	8.523	C15H12Cl2F4O2	370.01450	-0.04	371.02288	-0.40	399.05418	0.74	411.05418	
Vinclozoline	8.526	C12H9Cl2NO3	284.99540	-0.55	286.00378	1.29	314.03508	-0.34	326.03508	
Alachlor	8.561	C14H20ClNO2	269.11771	0.16	270.12608	0.20	298.15738	0.21	310.15738	
Tolclofos-methyl	8.570	C9H11Cl2O3PS	299.95381		300.96218	-0.21	328.99349	-0.28	340.99349	-0.27
Fenchlorphos	8.643	C8H8Cl3O3PS	319.89919		320.90756	0.10	348.93886	-0.27	360.93886	0.08
Pirimiphos methyl	8.682	C11H20N3O3PS	305.09575	0.41	306.10413	-0.16	334.13543	0.22	346.13543	0.32
Fenitrothion	8.726	C9H12NO5PS	277.01683	0.42	278.02521	0.25	306.05651	0.30	318.05651	
Malathion	8.755	C10H19O6PS2	330.03552		331.04389	0.02	359.07519	-0.50	371.07519	
Linuron	8.786	C9H10Cl2N2O2	248.01138	0.08	249.01976	0.48	277.05106		289.05106	
Dichlofluanid	8.801	C9H11Cl2FN2O2S2	331.96175	-0.08	332.97013	0.39	361.00143		373.00143	
Pentachlorothioanisole	8.839	C7H3Cl5S	293.83926	0.23	294.84764	1.63	322.87894	0.30	334.87894	-0.4
Parathion	8.894	C10H14NO5PS	291.03248	0.27	292.04086	0.35	320.07216		332.07216	
DCPA	8.901	C10H6Cl4O4	329.90147	0.33	330.90985	0.37	358.94115	-0.89	370.94115	
Triadimefon	8.918	C14H16ClN3O2	293.09256		294.10093	-0.06	322.13223	2.74	334.13223	
9,10-Anthracenedione	8.949	C14H8O2	208.05188	0.71	209.06026	0.86	237.09156	0.33	249.09156	
Pirimiphos ethyl	8.956	C13H24N3O3PS	333.12705	0.24	334.13543	-0.34	362.16673	0.27	374.16673	-0.1
Isopropalin	9.011	C15H23N3O4	309.16831		310.17668	0.45	338.20798		350.20798	
Bromophos	9.027	C8H8BrCl2O3PS	363.84867		364.85705	0.54	392.88835	0.33	404.88835	0.92
Clofenvinfos	9.060	C12H14Cl3O4P	357.96898		358.97736	-0.11	387.00866		399.00866	
Fipronil	9.080	C12H4Cl2F6N4OS	435.93816		436.94653	-0.10	464.97783		476.97783	
Cyprodinil	9.093	C14H15N3	225.12605	1.74	226.13443	0.40	254.16573	-0.07	266.16573	0.2
Metazachlor	9.117	C14H16ClN3O	277.09764	0.86	278.10602	-0.23	306.13732		318.13732	
Penconazole	9.137	C13H15Cl2N3	283.06375		284.07213	-0.10	312.10343		324.10343	
Tolylfluanid	9.161	C10H13Cl2FN2O2S2	345.97740	-1.96	346.98578	-0.07	375.01708		387.01708	
Quinalphos	9.201	C12H15N2O3PS	298.05355	-0.05	299.06193	-0.10	327.09323	-0.16	339.09323	-0.31
Triflumizole	9.214	C15H15ClF3N3O	345.08503		346.09340	-0.31	374.12470		386.12470	
Triadimenol	9.225	C14H18ClN3O2	295.10821		296.11658	-0.77	324.14788		336.14788	
Procymidone	9.238	C13H11Cl2NO2	283.01614	-0.08	284.02451	-0.17	312.05581	-0.39	324.05581	-0.16
Bromophos-ethyl	9.309	C10H12BrCl2O3PS	391.87997		392.88835	0.04	420.91965	0.36	432.91965	1.75
Tetrachlorvinphos	9.342	C10H9Cl4O4P	363.89871		364.90708	-0.21	392.93838		404.93838	
Paclobutrazol	9.382	C15H20ClN3O	293.12894		294.13732	-0.13	322.16862		334.16862	
Fenamiphos	9.417	C13H22NO3PS	303.10525	-0.3	304.11363	1.41	332.14493	1.84	344.14493	
Flutolanil	9.437	C17H16F3NO2	323.11276	0.09	324.12114	-0.09	352.15244	0.03	364.15244	
Flutriafol	9.455	C16H13F2N3O	301.10212		302.11050	-0.37	330.14180		342.14180	

Appendix 7 – Table 7 continued. Compound Discoverer 3.2 software QuEChERS soil extract PCI confirmation data for [M+], [M+H], [M+C₃H₅], and [C₃H₅] with associated ppm mass error (where detected)

Name	Reference RT [min]	NIST Formula	[M]⁺	Mass error (ppm)	[M+H]⁺	Mass error (ppm)	[M+C₂H₅]⁺	Mass error (ppm)	[M+C₃H₅]⁺	Mass error (ppm)
Pretilachlor	9.508	C17H26ClNO2	311.16466	-0.66	312.17303	-0.06	340.20434	0.50	352.20434	0.62
Iodofenphos	9.510	C8H8Cl2IO3PS	411.83480		412.84318	-0.04	440.87448	-0.26	452.87448	-0.01
Oxadiazon	9.530	C15H18Cl2N2O3	344.06890	0.02	345.07728	-0.12	373.10858	1.81	385.10858	
Oxyfluorfen	9.554	C15H11ClF3NO4	361.03232	-1.34	362.04070	-0.02	390.07200		402.07200	
Bupirimate	9.576	C13H24N4O3S	316.15636	0.13	317.16474	-0.03	345.19604	-0.51	357.19604	-0.47
Myclobutanil	9.583	C15H17ClN4	288.11363		289.12200	-0.26	317.15330		329.15330	
Flusilazole	9.592	C16H15F2N3Si	315.09978	0.35	316.10816	0.20	344.13946	1.59	356.13946	
Tricyclazole	9.614	C9H7N3S	189.03552	0.96	190.04390	0.70	218.07520		230.07520	
Nitrofen	9.759	C12H7Cl2NO3	282.97975	-0.57	283.98813	-1.32	312.01943		324.01943	
Chlorthiophos	9.782	C11H15Cl2O3PS2	359.95718	0.17	360.96556	0.28	388.99686	0.22	400.99686	-0.33
Ethion	9.837	C9H22O4P2S4	383.98707	0.19	384.99544	0.29	413.02674		425.02674	
Triazophos	9.934	C12H16N3O3PS	313.06445	-1.35	314.07283	0.18	342.10413	0.02	354.10413	
Carfentrazone ethyl	9.974	C15H14Cl2F3N3O3	411.03588	0.16	412.04426	0.15	440.07556	2.15	452.07556	
Norflurazon	10.055	C12H9ClF3N3O	303.03808	0.52	304.04645	0.41	332.07775	-0.37	344.07775	
Edifenphos	10.102	C14H15O2PS2	310.02456	-0.21	311.03294	0.33	339.06424		351.06424	
Resmethrin	10.214	C22H26O3	338.18765	0.5	339.19602	0.40	367.22732		379.22732	
Resmethrin	10.258	C22H26O3	338.18765	0.5	339.19602	0.40	367.22732		379.22732	
Pyridaphenthion	10.422	C14H17N2O4PS	340.06412	-0.63	341.07249	-0.09	369.10379	-0.99	381.10379	
Tetramethrin	10.481	C19H25NO4	331.17781		332.18619	-0.34	360.21749		372.21749	
Phosmet	10.539	C11H12NO4PS2	316.99399		318.00236	-0.14	346.03366		358.03366	
Methoxychlor	10.574	C16H15Cl3O2	344.01321		345.02159	0.14	373.05289	0.86	385.05289	0.23
Tebufenpyrad	10.609	C18H24ClN3O	333.16024	0.15	334.16862	0.22	362.19992	-0.37	374.19992	
Phosalone	10.852	C12H15ClNO4PS2	366.98632	-0.29	367.99469	0.32	396.02599		408.02599	
Pyriproxyfen	10.883	C20H19NO3	321.13595		322.14432	-0.09	350.17562		362.17562	
Leptophos	10.885	C13H10BrCl2O2PS	409.86941		410.87778	0.22	438.90908	0.15	450.90908	
.lambda.-Cyhalothrin	10.921	C23H19ClF3NO3	449.10001		450.10838	-0.05	478.13968		490.13968	
Pyrazophos	11.064	C14H20N3O5PS	373.08558	-1.03	374.09396	0.10	402.12526	0.09	414.12526	
Fenarimol	11.177	C17H12Cl2N2O	330.03212	-1.22	331.04050	-0.52	359.07180		371.07180	
Azinphos-ethyl	11.214	C12H16N3O3PS2	345.03652		346.04490	-0.31	374.07620		386.07620	
Permethrine	11.503	C21H20Cl2O3	390.07840		391.08678	0.07	419.11808		431.11808	
Coumaphos	11.563	C14H16ClO5PS	362.01391	0.55	363.02229	0.56	391.05359	-0.88	403.05359	
Pyridaben	11.578	C19H25ClN2OS	364.13706	-1.4	365.14544	0.55	393.17674		405.17674	
Fluquinconazole	11.583	C16H8Cl2FN5O	375.00845		376.01682	0.86	404.04812	-0.67	416.04812	

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