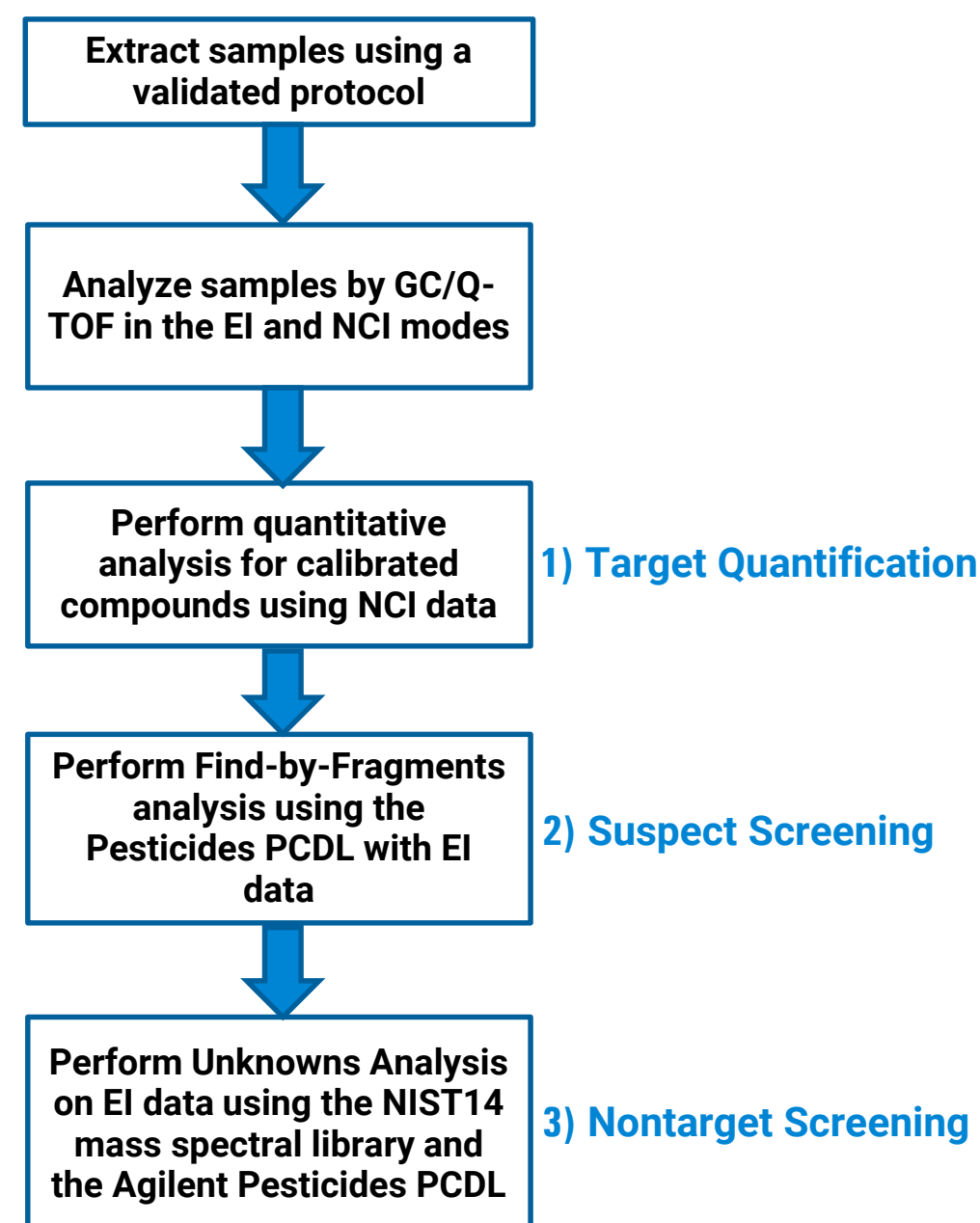


Introduction

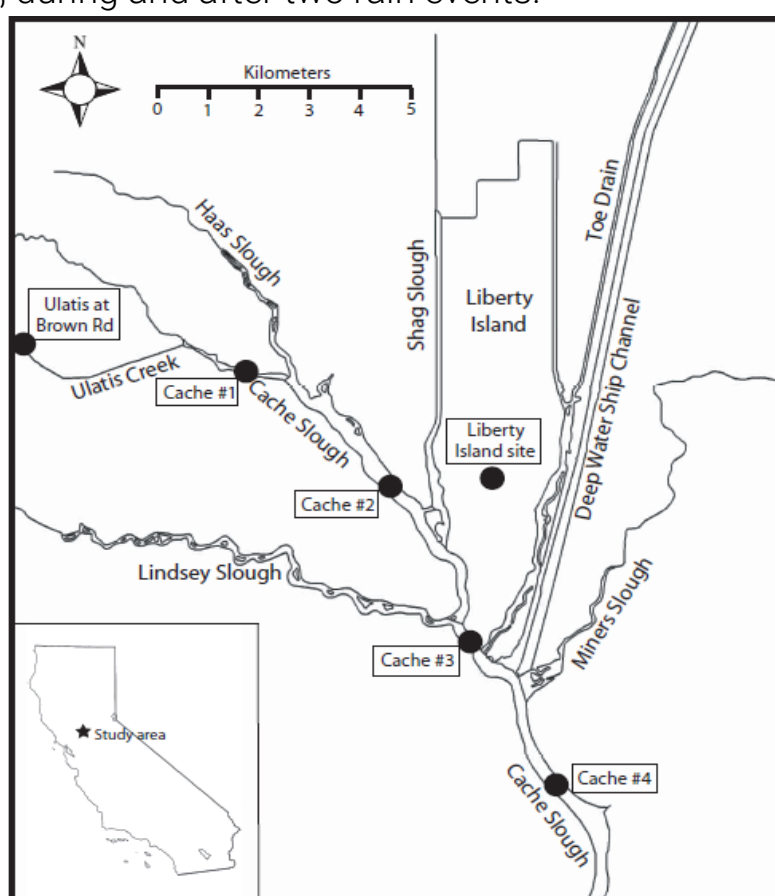
Three workflows for the analysis of pesticides and other environmental contaminants in water are discussed. [1,2]



Experimental

Water Sample Collection from the Cache Slough in the Sacramento-San Joaquin River Basin

1L samples taken in duplicate four times from six locations before, during and after two rain events.



Sample Extraction

Filter 1 L of water → Spike with two surrogates → SPE → Elute with EtOAc → Rinse bottle with DCM → Combine extracts → Reduce to 0.2 mL.

Spike filter with surrogates → Sonicate with hexane/acetone 1:1 (2 X 20 mL) → Combine & reduce to 0.2 mL.

GC/Q-TOF Analysis



Figure 1. Agilent 7250 GC/Q-TOF is shown. An Agilent 7200 GC/Q-TOF was used for this work.

Experimental

Instrument Conditions

Gas Chromatograph	Agilent 7890B
Mass Spectrometer	Agilent 7200 Q-TOF
Acquisition modes	NCI and EI (TOF only)
Injection	2.5 µL Splitless
Column	30 m x 0.25 mm x 0.25 µm HP-5MS
Oven Temp Program (NCI)	100°C (1 min), 15°C/min to 200°C, 3.8°C/min to 290°C, 10°C/min to 300°C (4 min)
Oven Temp Program (EI)	60°C (1 min), 40°C/min to 120°C, 5°C/min to 310°C
Mass Calibration	Automated after every other sample
Emission Current	35 µA EI; 90 µA NCI
NCI reagent gas	Methane (40%)

Results and Discussion

1) Target quantification: Validation Study using NCI GC/TOF

Table 1. Some compound validation results and number of times each compound was detected in 51 water samples.

Compound Name (No. times detected in 51 water samples)	MDL (ng/L)	Recovery Water Extraction	Recovery Filter Extraction
Bifenthrin (20)	0.2	73%	82%
Bioallethrin	0.1	76%	72%
Chlorothalonil (10)	0.6	94%	0%
Chlorpyrifos (40)	0.1	80%	62%
Cyfluthrin ¹ (18)	1.0	-	-
Cyhalothrin (18)	0.1	82%	82%
Cypermethrin (6)	1.0	85%	62%
Cyphenothrin	0.5	48%	81%
Deltamethrin (13)	1.0	96%	66%
Esfenvalerate (6)	0.1	93%	80%
Fipronil (51)	0.5	92%	77%
Fipronil amide (51)	0.1	98%	82%
Fipronil-desulfinyl (51)	0.2	77%	96%
Fipronil-desulfinyl amide (50)	0.2	88%	74%
Fipronil-sulfide (42)	0.1	79%	89%
Fipronil-sulfone (51)	0.2	91%	85%
Novaluron	0.05	48%	91%
Permethrin (2)	2.0	84%	80%
Phenothrin	5.0	47%	75%
Prallethrin	0.1	299%	36%
Tetramethrin	5.0	80%	205%

2) Suspect Screening Using Agilent Pesticides & Environmental Pollutants Personal Compound Database and Library (PCDL)

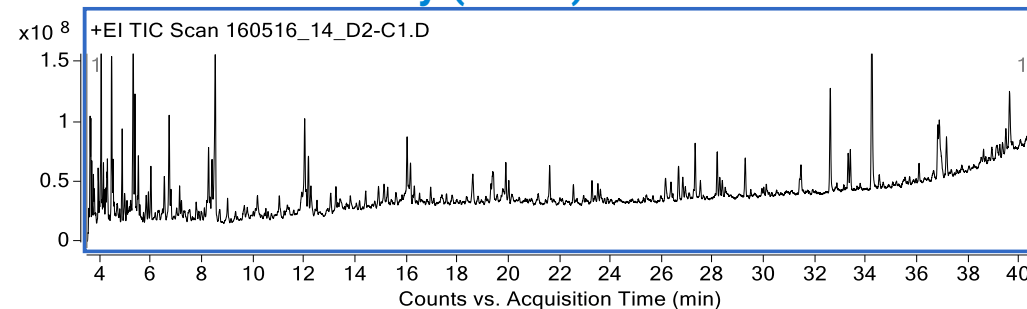


Figure 2. Chromatogram of Cache Slough water extract.

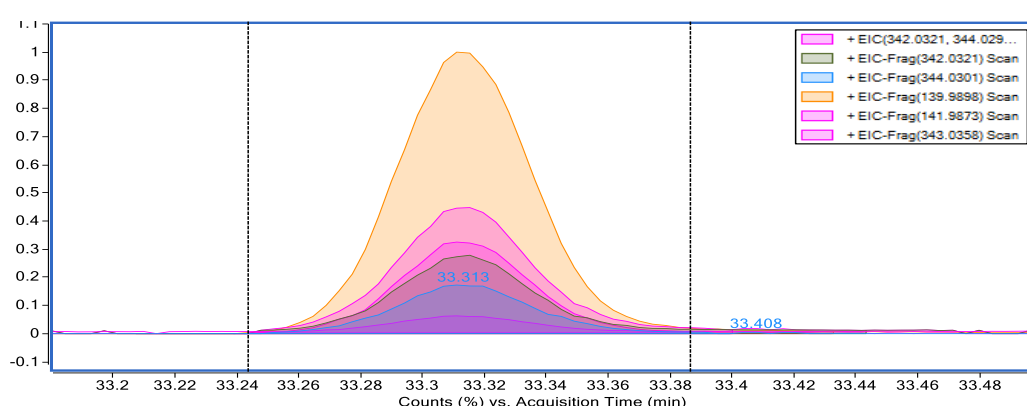


Figure 3. Coelution plot of 6 EICs for ions characteristic of Boscalid.

ID Techniques Applied	Best	Name	Formula	Mass (Tgt)	Diff (ppm)	RT	RT (Tgt)	RT Diff	Notes
FF-FragConfirm	99.61	Boscalid (Nicobifen)	C18 H12 Cl2 N2 O	342.032	1.48	33.312	33.312	0.000	Forensic and Toxicology drug; Pesticide; Herbicide; Veterinary drug
	99.57								
	99.73								
	99.64								
	100								

Figure 4. Find by Formula 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.

Results and Discussion

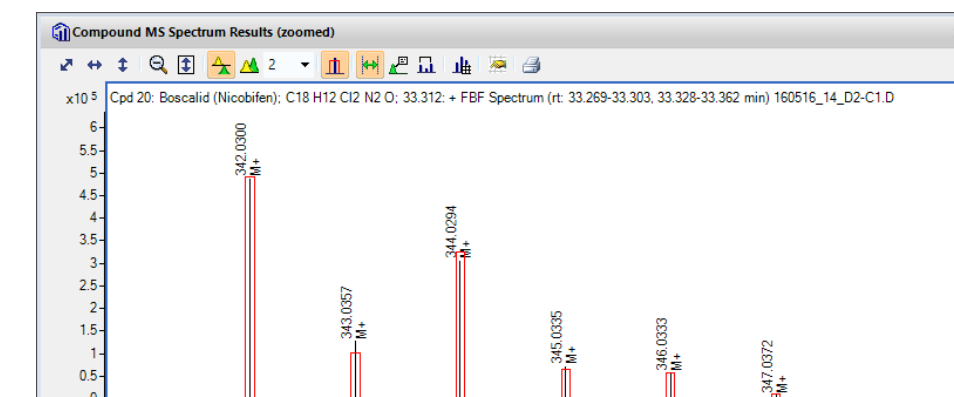


Figure 5. Theoretical (red rectangles) and measured molecular ion isotope pattern for boscalid found in a Cache Slough water extract.

Suspect Screening 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.

3) Nontarget Screening using Agilent Unknowns Analysis

MassHunter Unknowns Analysis:

- Deconvolutes spectra in the chromatogram
- Searches libraries for tentative identification (NIST was used)
- Searches the PCDL for matches. Component RT must match PCDL

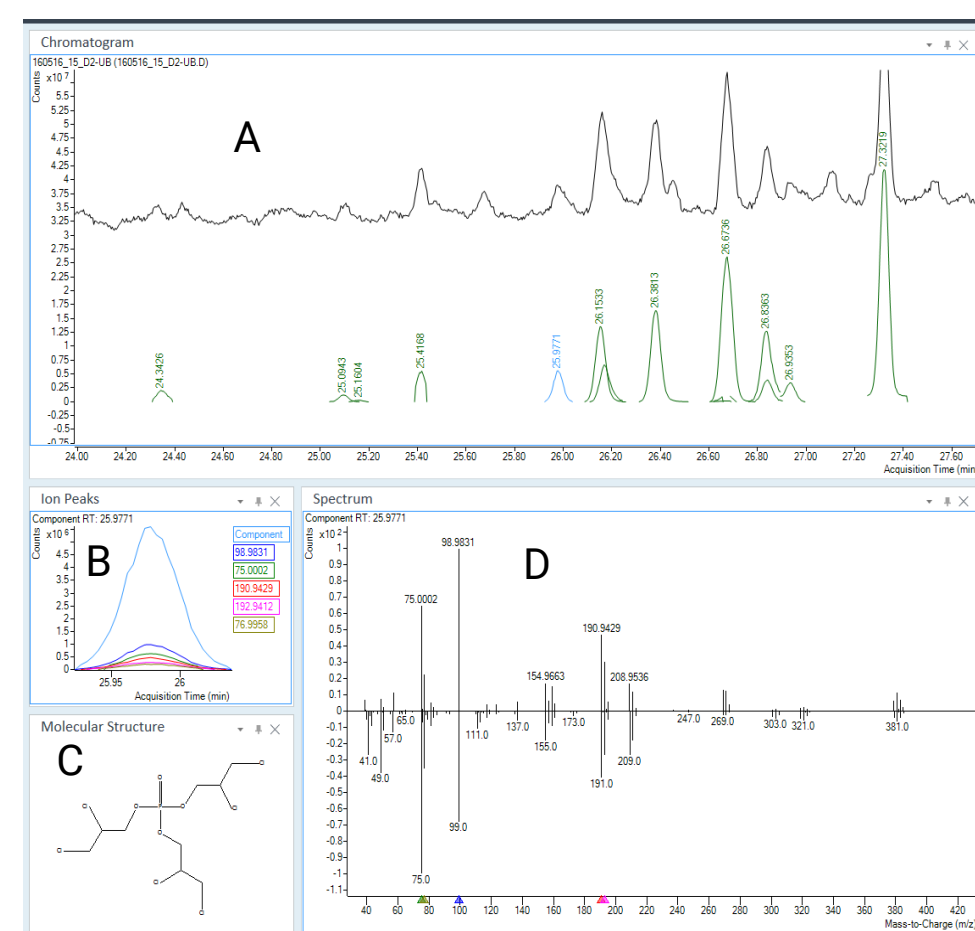


Figure 6. Unknowns Analysis results for a Cache Slough water extract showing the fire retardant tris(2,3-dichloropropyl) phosphate. A) TIC (black) and deconvoluted components [green (blue, peak for which results are displayed)], B) plots of significant EICs overlaid with the component plot, C) molecular structure, D) component spectrum (top) positioned head-to-tail with the library spectrum.

Nontarget Screening Results

- 45 compounds tentatively identified
- 19 were also found by suspect screening
- 36 were tentatively confirmed by matching RT to PCDL
- 9 without RT confirmation, but had NIST score >80
- 2 also found by LC/Q-TOF

Conclusions

Three workflows used to identify pesticides and environmental pollutants in 51 river water samples.

- Quant method validated for 21 pesticide targets using NCI GC/Q-TOF. 15 found in at least two water samples.
- Suspect Screening tentatively identified 41 additional pesticides and environmental pollutants. 24 also found by LC/Q-TOF. 17 found only by GC/Q-TOF.
- Nontarget analysis used MassHunter Unknowns Analysis software. 45 compounds tentatively identified, 36 with verified retention times. Pesticides, transformation products, organophosphates and other classes of water pollutants were found this way.

References

- [1] Moschet, C.; et al. LC- and GC-QTOF-MS as Complementary Tools for a Comprehensive Micropollutant Analysis in Aquatic Systems. *Environ. Sci. Technol.* 2017, 51(3), 1553–1561.
- [2] Moschet, C., Anumol, T., Wylie, P., and Young, T. GC/Q-TOF workflows for comprehensive pesticide analysis, *Agilent Technologies Application note*, Publication number 5991-9132EN, March 2018.