Profiling of Environmental Contaminants in Water using GC/Q-TOF

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SETAC Helsinki 2019

POSTER TU172

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Introduction

The investigation of organic micropollutants is an important aspect of assessing environmental quality. The conventional approach to this monitoring involves analyzing a defined number of target compounds by mass spectrometry with the instrument operated in a selected data acquisition mode for targeted analytes. However, there is evidence that such an approach may significantly underestimate the exposure and risk of pollutants, compared to a more comprehensive untargeted screen.

Recent advances in mass spectrometry allows an increased scope of analysis, no longer sensitivity or selectivity limited when using high resolution accurate mass instruments operated in full spectrum acquisition mode. Accurate mass information enhances the amount of detail in the information collected and allows for the determination of both targeted and non-targeted components.

Experimental

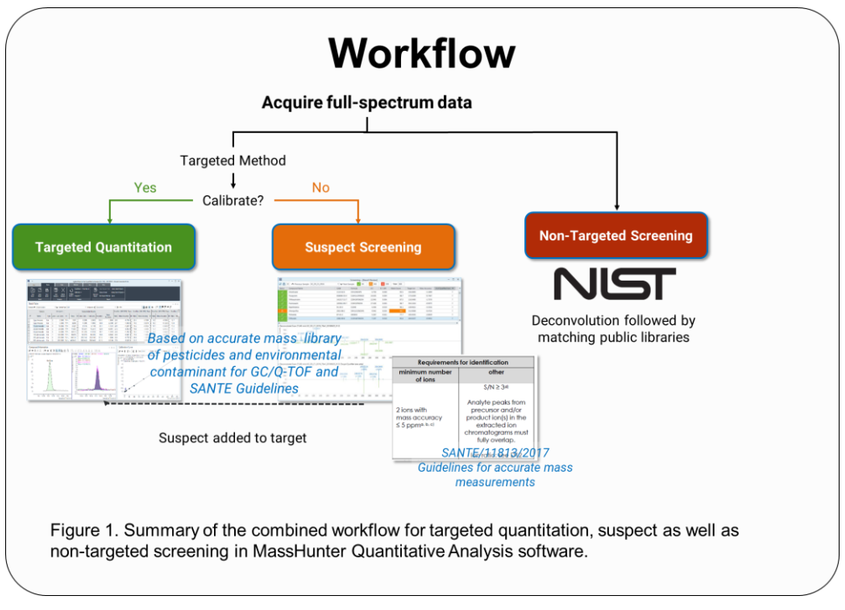


Figure 1. Summary of the combined workflow for targeted quantitation, suspect as well as non-targeted screening in MassHunter Quantitative Analysis software.

Surface Water Sampling

Sampling was carried out at locations throughout the Cache Slough Complex, located in the Sacramento-San Joaquin River Delta in Northern California

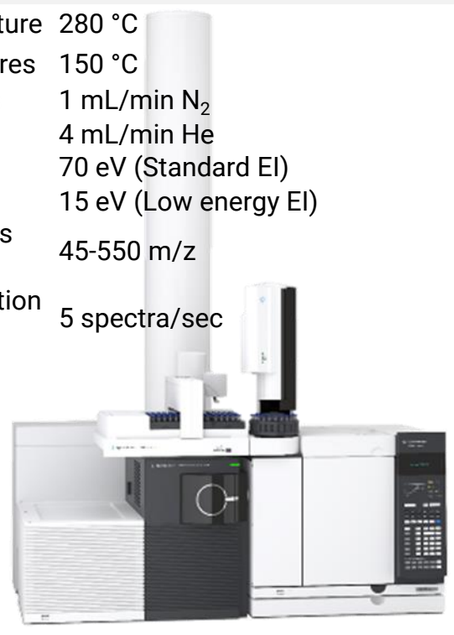
The main input of point-source micropollutants as well as diffuse pollutants is expected to be via Ulatis Creek.

All samples were cooled and stored in the dark at 4 °C until extraction. Surface waters (1L) were passed through a GF/F filter. The filtrate were passed through a polymeric solid phase extraction (SPE) cartridge. After drying for one hour, the cartridges were eluted with 10 mL of ethyl acetate.

GC/MS Analysis

Agilent 7890 GC	
Parameter	**Value**
Inert flow path configuration	Mid-column backflush
Columns	Agilent HP-5ms UI, 2x15 m, 0.25 mm id, 0.25 µm film
Inlet	MMI, 4 mm UI liner single taper w wool
Injection volume	1 µL
Injection mode	Cold Splitless 60 °C for 0.2 minutes 600 °C/min to 300 °C, hold 330 °C, post run
Inlet flow (column 1)	1.0 mL/min (**Chlorpyrifos-methyl locked at 9.143 min**)
PUU flow (column 2)	column 1 flow + 0.2 mL/min
Oven temperature program	60 °C (hold 1 min) then 40 °C/min to 170 °C, then 10 °C/min to 310 °C (hold 3 min) **Run time 20.75 min**
Transfer line	280 °C
Midcolumn Backflush	
Timing	5 min duration during post-run
Oven temperature	310 °C
Aux EPC pressure	~50 psi
Inlet pressure	~2 psi

Agilent 7250 Q-TOF	
Parameter	**Value**
Source temperature	280 °C
Quad temperatures	150 °C
Collison cell gas flows	1 mL/min N_2 4 mL/min He
Electron energy	70 eV (Standard EI) 15 eV (Low energy EI)
Acquisition mass range	45-550 m/z
Spectral acquisition rate	5 spectra/sec



Results & Discussion

Target and Suspect Screening Results

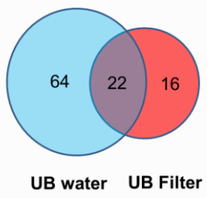
- Summary of targeted quantitation and suspect screening for UB site is shown in Table 2.
- Accurate mass of < 5ppm for two ions with high Library Match score, high coelution score (both >70) as well as S/N >3 was used as a criterium for compound identification.

Compound name	Frag ratio score	Mass diff (ppm)	Amount (ng/mL)	Compound name	Frag ratio score	Mass diff (ppm)	Amount (ng/mL)
2,4,6-Tribromoanisole	99.6	1.68	ID only	Malathion	94.5	0.98	7.9
2-Phenylphenol	86.2	0.59	ID only	Metalaxyl	90.4	0.59	11.6
Anthraquinone	93.7	2.35	ID only	Metolachlor	99.1	0.21	178
Atrazine	98.5	0.77	6.5	Metribuzin	97.4	2.98	ID only
Atrazine-desethyl	90.1	3.41	ID only	Myclobutanil	99.5	1.22	10
Atrazine-desisopropyl	94.4	2.42	ID only	N-(2,4-Dimethylphenyl)formamide	80.9	3.27	ID only
Azoxystrobin	99.9	0.89	95.1	Napropamide	90.7	0.47	11.5
BAM / Dichlorbenzamide	84.3	0.57	ID only	Nitrapyrin	72.2	2.84	ID only
Boscalid (Nicobifen)	99.8	0.03	ID only	Norflurazon	96.3	0.98	ID only
Bromacil	99.4	0.53	116.5	Norflurazon-desmethyl	94.7	0.75	ID only
Carvone	86.6	3.5	ID only	Octhilinone	94.3	1.06	ID only
Chlorantraniliprole	96.1	0.59	304.6	Omethoate	98.5	0.19	31.8
Chloroneb	96.1	0.57	ID only	Oryzalin	99.8	0.35	ID only
Chlorothalonil	99.9	0.83	7.3	Oxadiazon	99.9	0.78	ID only
Coumaphos	88.4	0.47	ID only	Oxyfluorfen	99.2	0.27	ID only
Cyprodinil	99.7	1.53	ID only	p,p'-DDE	99.8	1.41	1.9
DCPA / Chlorthal-dimethyl	99.4	2.06	ID only	PCP / Pentachlorophenol	72.8	1.35	3.1
DEET / Diethyltoluamide	99.7	1.47	ID only	Pendimethalin (Penoxalin)	99.8	0.54	ID only
Diazinon (Dimpylate)	86.5	0.86	265	Pentachloroanisole	89.8	0.09	ID only
Diazoxon	99.5	0.21	ID only	Phenanthrene	99.5	1.76	ID only
Dichlobenil	98.1	1.24	ID only	Phenothiazine	87.5	1.43	ID only
Difenoconazole(I)	95.7	1.32	26.1	Phosmet (Imidan)	80.6	1.79	ID only
Dimethenamid-P	99	1.11	ID only	Phthalide	94.5	2.81	ID only
Dimethoate	98.6	2.03	1048.1	Prodiamine	99.9	0.31	ID only
Disugran	67.9	2.44	ID only	Prometon	90.1	1.04	ID only
Dithiopyr	99.8	1.38	ID only	Propiconazole(I)	99.3	1.13	ID only
DiuronMetabolite[3,4-Dichlorophenylisocyanate]	100	0.64	ID only	Propiconazole(II)	99.4	0.42	ID only
Fenbuconazole	92.8	0.64	ID only	Propyzamide (Pronamide)	80.1	1.07	2.2
Fipronil	91.9	1.26	ID only	Pyraclostrobin	93.8	0.71	ID only
Fipronil sulfide	99.6	0.27	ID only	Pyrimethanil	88.6	2.26	ID only
Fipronil sulfone	99.9	0.06	ID only	Simazine	99.8	0.27	ID only
Flonicamid	89.1	0.73	ID only	Sulfentrazone	99.9	0.32	ID only
Flumioxazin	96.6	0.26	ID only	Tebuconazole(I)	91.4	1.03	ID only
Fluopyram	99.1	1.11	ID only	Tebuthiuron	90.4	0.89	ID only
Fluridone	96.1	1.43	ID only	Tetraconazole	84.3	1.74	ID only
Flurprimidol	92.6	2.3	ID only	Thanite	86.5	3.98	ID only
Flutolanil	78.5	0.34	ID only	Thiamethoxam	97.1	1.24	34.1
Fluxapyroxad	99.3	0.9	ID only	Triclosan	95.7	1.15	ID only
Fthalide	84.9	1.22	ID only	Trifloxystrobin	87	1.27	ID only
Hexazinone	84.4	1.89	ID only	Trifluralin	95.8	2.22	ID only
Indoxacarb	71.6	1.5	37.9	Tris(2-butoxyethyl)phosphate	96	2.02	ID only
Iprodione (Glycophen)	99.4	0.78	ID only	Tris(3-Chloropropyl)phosphate	98.6	2.63	ID only
Isoxaben	88.1	1.46	ID only	Tris(b-Chloropropyl)phosphate	99.1	0.9	ID only

Table 2. Target and suspect screening results summary from UB sampling site. Reported amounts are concentrations in the injected solution.

Target and Suspect Screening Results

- Extractions were performed from both water and filter particles. The majority of the contaminants were present in water extracts but few pollutants were also identified in filters extracts (Figure 3).
- Pollutants identified by targeted and suspect screening approach were compared across different sampling sites. The highest number of contaminants was identified in water extract from C2 site. About a half of all identified pollutants were in common between UB, C2 and C4 sampling sites (Figure 4A and B). Relative amounts of the identified contaminants across all sampling sites shown in Figure 4C.



Compounds uniquely identified in the UB filter extract:

Diphenylamine (DFA)
Hexachlorobenzene
Pentachloroaniline
Fluoranthene
Pyrene
Nonachlor-trans
p,p'-DDD
Dihexylphthalate
Bifenthrin
Chrysene
cis-Permethrin
trans-Permethrin
Benzo[b]fluoranthene
Benzo[a]pyrene
Dinonylphthalate
Indeno[1,2,3-cd]pyrene

Figure 3. Distribution of the contaminants between water and filter extracts from UB site.

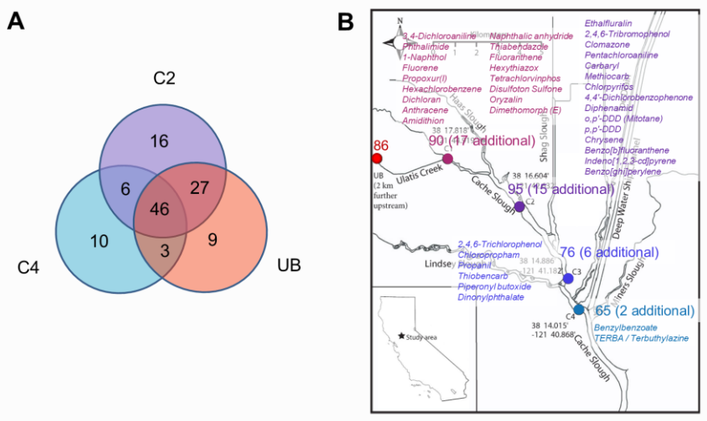
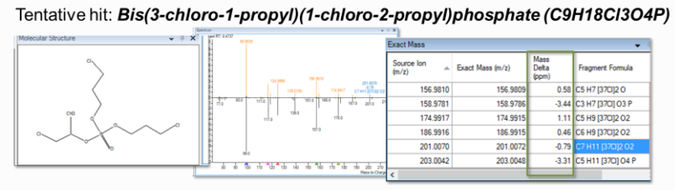


Figure 4. Geographic distribution of pollutants. Comparison of the identified contaminants between UB, C2 and C4 sites (A). Sampling map showing the number of identified pollutants as well as the new contaminants added to the flow stream from each site (B).

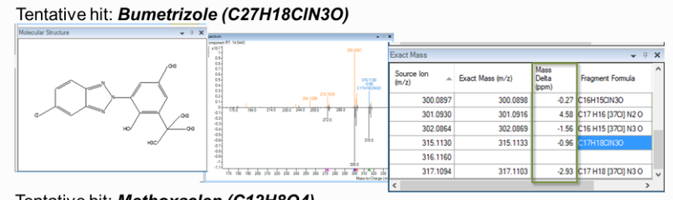
Non-Targeted Screening Results

- A number of pollutants were tentatively identified in water extracts using Unknowns Analysis and NIST17.L library. Examples from UB site are shown in Figure 5.
- Some of the tentative hits were rejected due to large mass error, and therefore were subjects for further structure elucidation using MS/MS. An example is shown in Figure 6. To identify the compound, first, the molecular ion was confirmed using low electron energy setting (12 eV). Further, MS/MS was performed using tentative molecular ion as a precursor to propose a structure (Figure 6B).

Tentative hit: ***Bis(3-chloro-1-propyl)(1-chloro-2-propyl)phosphate (C9H18Cl3O4P)***



Tentative hit: ***Bumetrizole (C27H18ClN3O)***



Tentative hit: ***Methoxsalen (C12H8O4)***

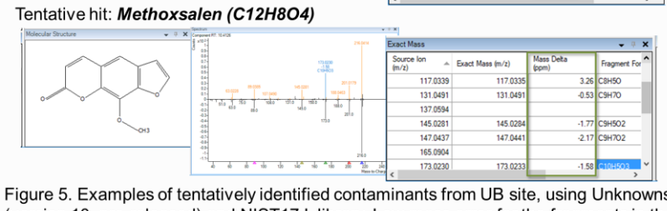
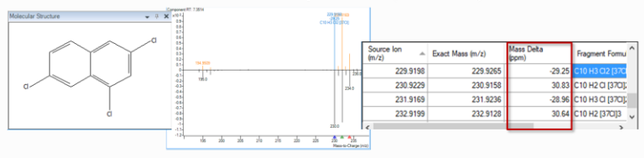
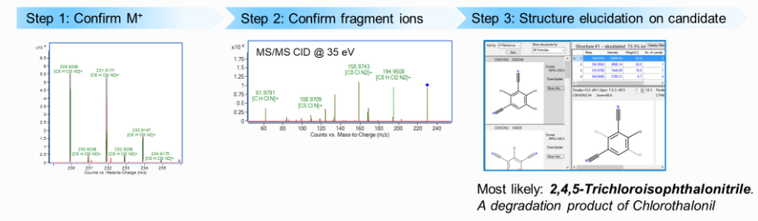


Figure 5. Examples of tentatively identified contaminants from UB site, using Unknowns Analysis (version 10, pre-released) and NIST17.L library. Low mass error for the fragments in the deconvoluted spectrum provides additional point for confirmation of the molecular formula of the hit.

A Tentative NIST17 hit: ***1,3,7-trichloronaphthalene (C10H5Cl3)***



B



Most likely: ***2,4,5-Trichloroisophthalonitrile***.
A degradation product of Chlorothalonil

Figure 6. Identity confirmation and structure elucidation of one of the tentative hits. Significant mass error suggested incorrect identity of the compound (A). The compound was identified using Molecular Structure Correlator tool with accurate mass product ion spectrum as an input (B).

Conclusions

A comprehensive workflow that includes targeted quantitation, suspect screening as well as a non-targeted approach was applied to screen for environmental pollutants in water samples.

An accurate mass GC/Q-TOF library was used to successfully screen pesticides and environmental contaminants.

Low energy EI and accurate mass MS/MS facilitate untargeted screening and structure elucidation of unknowns.

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