Helping Contaminants Emerge: Non-targeted Analysis and Passive Sampling for Assessing Water Quality

P. Lee Ferguson[1], Gordon J. Getzinger[2], Jake C Ulrich[1],
Kirsten E. Overdahl[1], Jennifer Sun[4], Rebecca Sutton[4]

[1]Duke University, [2]ETH Zürich, [4]San Francisco

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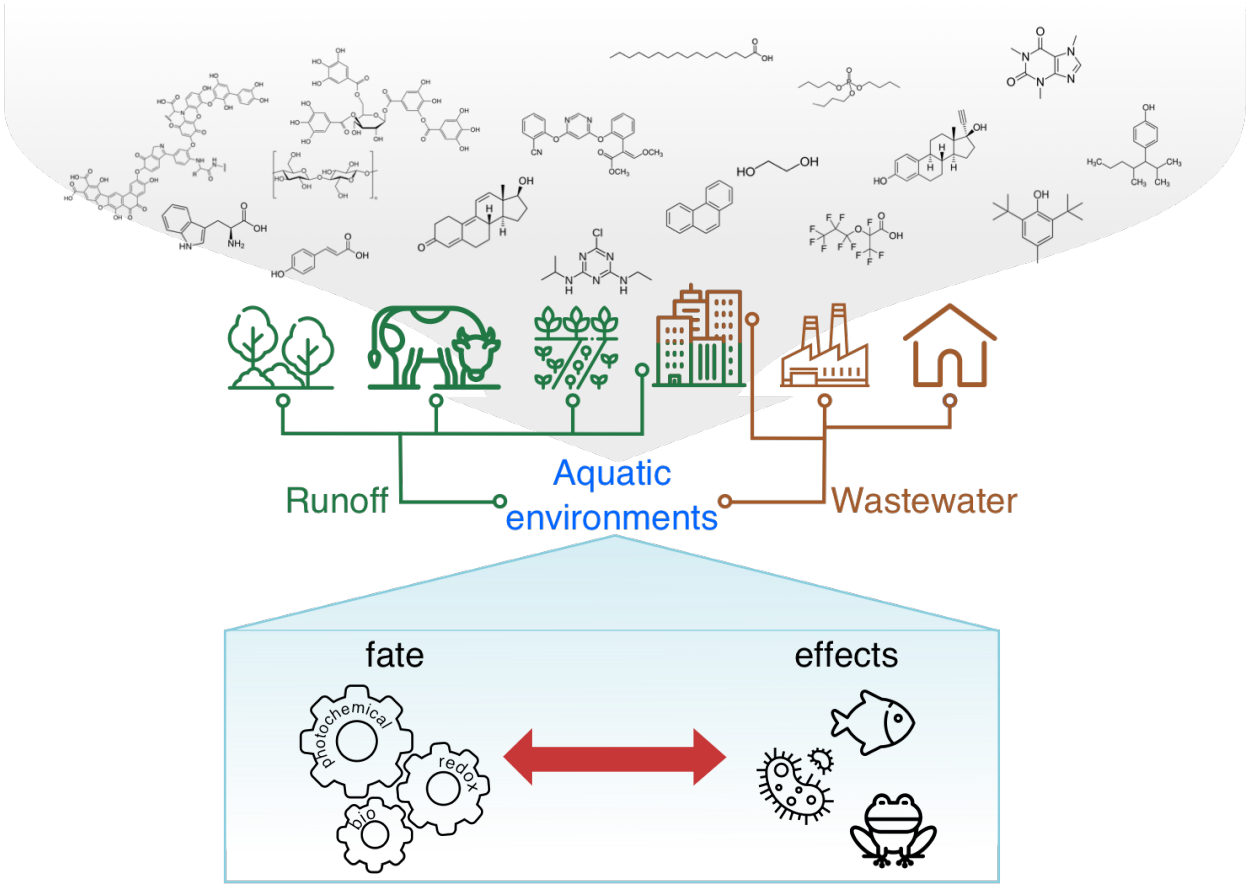
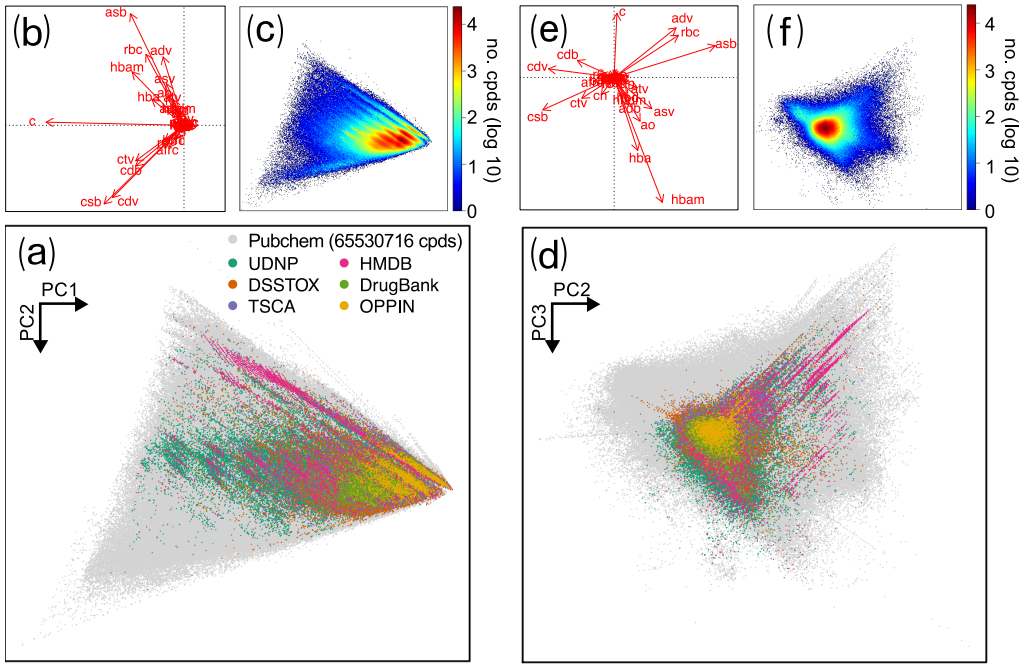
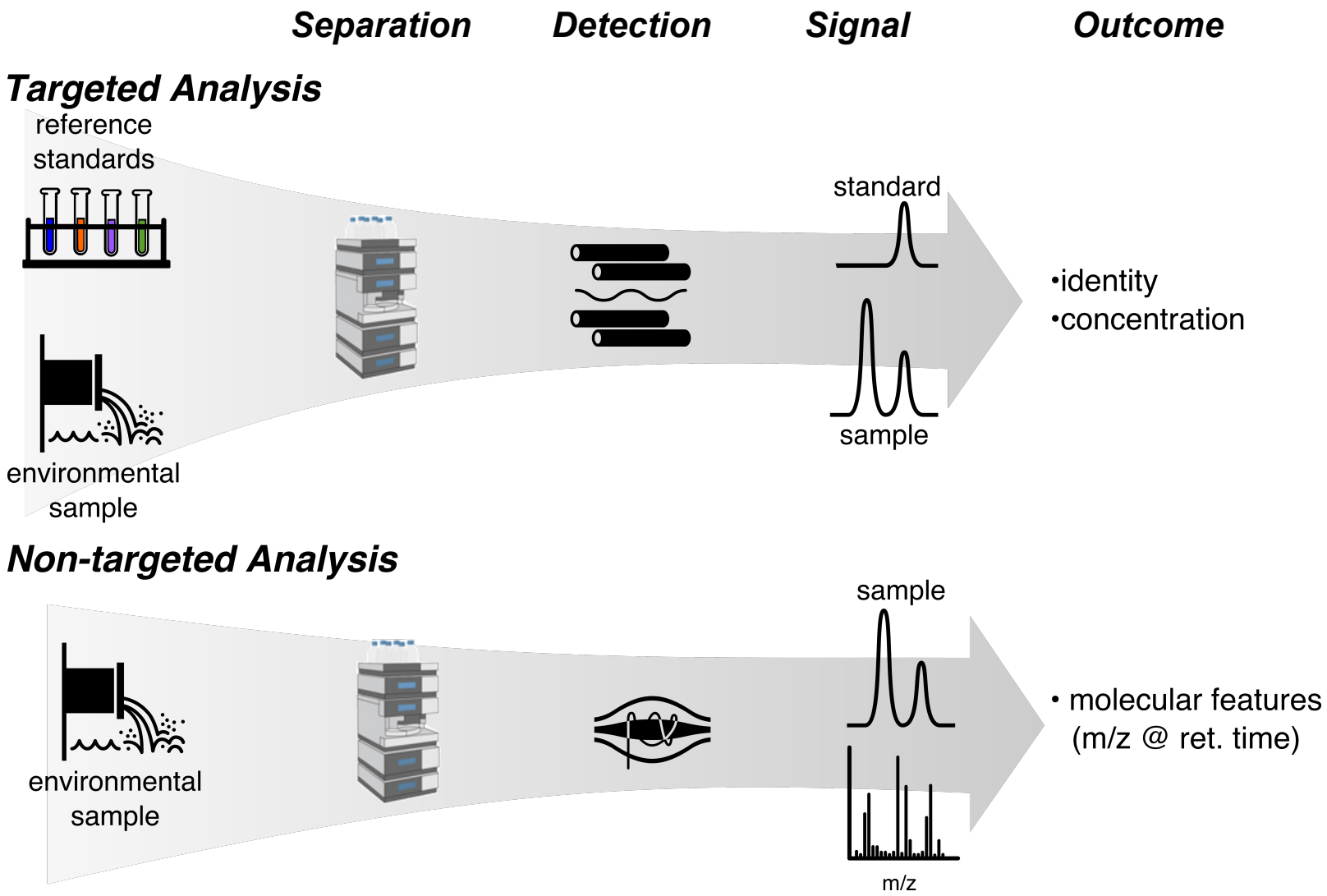
Which organic pollutants occur in environmental waters?

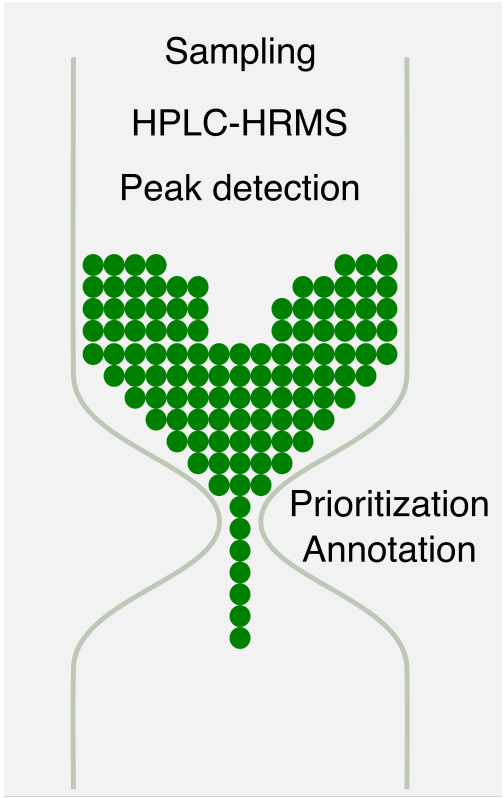


- Chemical space is vast. How can we assess which chemicals in commerce are important as emerging pollutants in the aquatic environment?
- Chemical use, production, and regulation lists are incomplete.
- (Bio)transformation makes prioritization more difficult and compound identification challenging.



Targeted vs. Non-targeted analysis

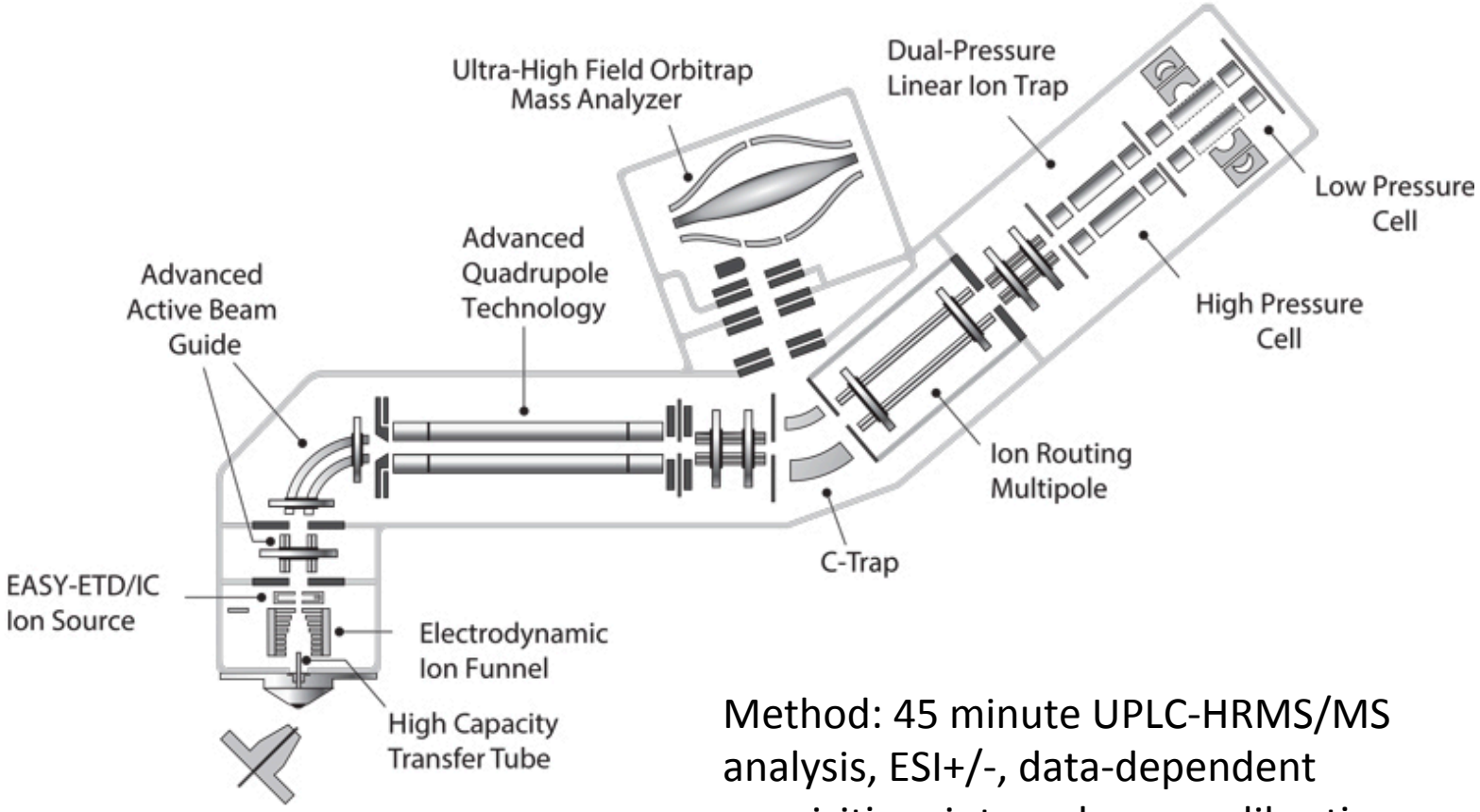




Chemical Information

Ultra-high resolution mass spectrometry for non-targeted analysis

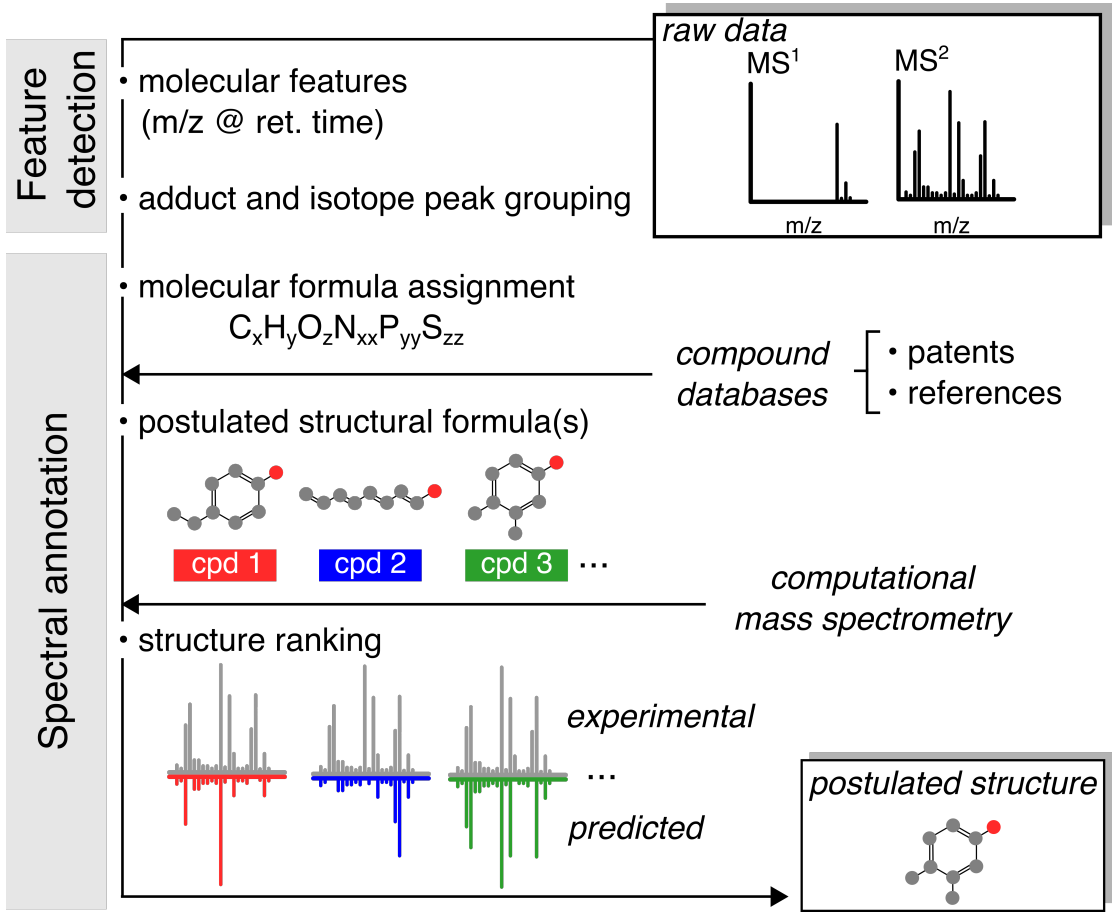
- Orbitrap Fusion Lumos mass spectrometer
- Critical resolution (500,000) and mass accuracy (< 1 ppm)
- Ultra-fast data-dependent MS/MS maximizes data acquisition rate
- MS^3 capability for structural characterization
- Ion funnel gives maximum sensitivity



Method: 45 minute UPLC-HRMS/MS analysis, ESI+/-, data-dependent acquisition, internal mass calibration

Data analysis: The hard part!

Overall non-targeted analysis workflow:



Objectives

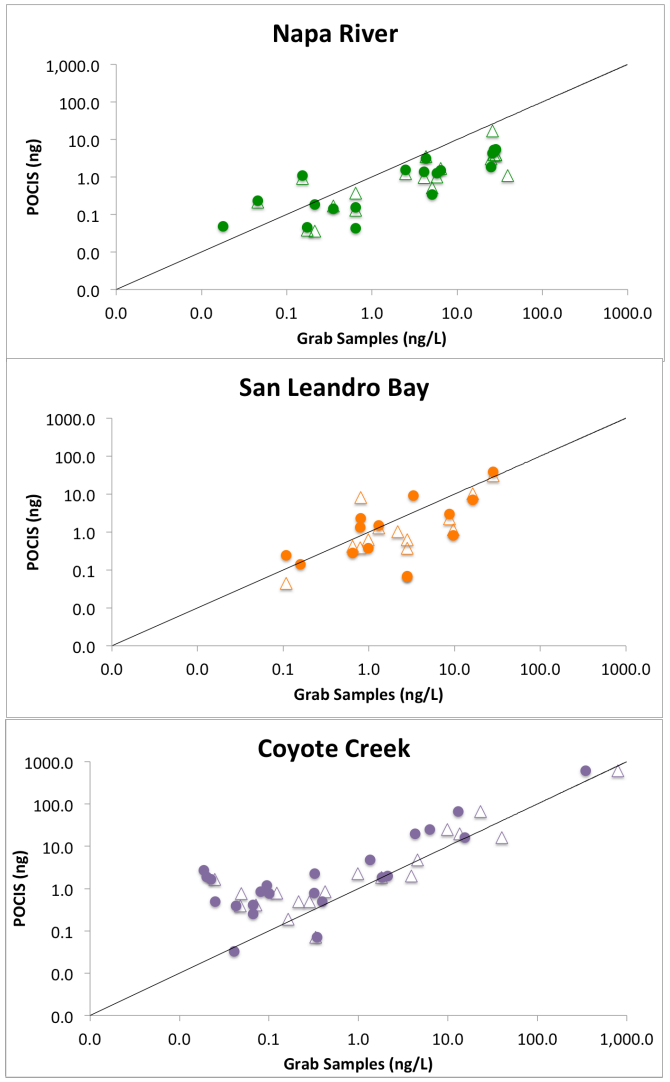
- Utilize high-resolution mass spectrometry strategies to identify non-targeted polar organic pollutants in San Francisco Bay waters.
- Assess the performance of passive sampling vs. grab sampling strategies for non-targeted analysis of organic pollutants in Bay waters.
- Examine differences in organic pollutant occurrence and abundance among Bay waters with various pollutant sources.
- Perform reconnaissance of emerging contaminant occurrence in drinking water sources within three watersheds of North Carolina.

Emerging pollutants in SF Bay waters

- Ambient Bay sample collection:
  - Three sites were sampled: San Leandro Bay (March 2016), Napa River (April 2016), and Coyote Creek (Aug/ Sept. 2016)
  - POCIS were deployed for one month at each site.
  - Grab samples (4L volume, one collected in triplicate) were taken at sites on POCIS deployent & retrieval.
  - Field blanks collected for POCIS and grab samples.
- Four WWTP effluent grab samples were collected. Sampling sites were located near the San Leandro Bay and Coyote Creek sites

Target Analyte Quantitation

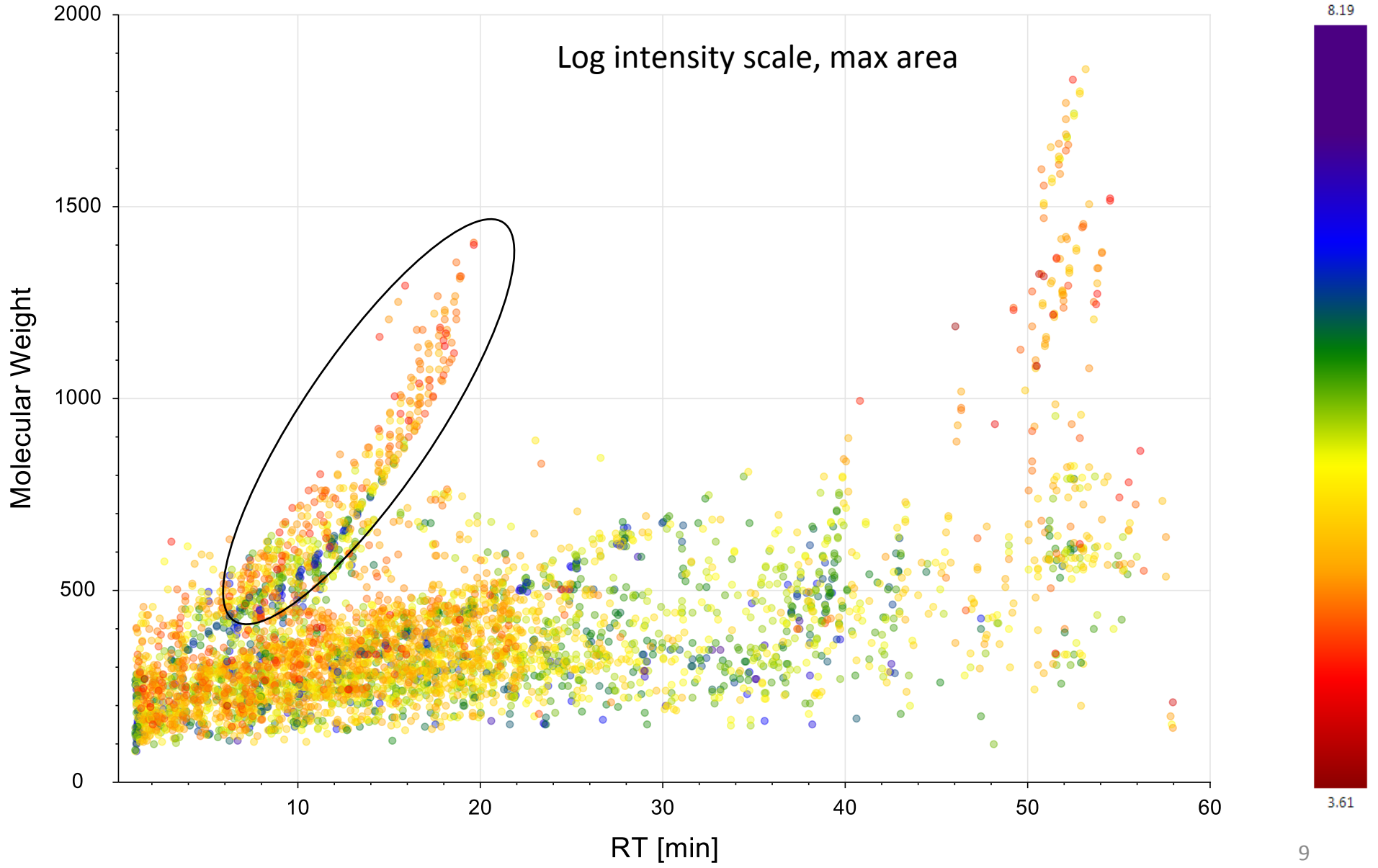
Concentrations in ng/L	Detection Limit	Napa River Deploy	Napa River Retrieval	San Leandro Bay Field Blank	San Leandro Bay Deploy	San Leandro Bay Retrieval	Coyote Creek Deploy	Coyote Creek Retrieval	WWTP Site A	WWTP Site B	WWTP Site C	WWTP Site D	WWTP Site D Field Blank
Agrochemicals:													
Allethrin	1.2				1.33 ± 0.13								
Atrazine	0.06		1.10 ± 0.072									0.296	
Azoxystrobin	0.6	3.09	3.51 ± 0.28								0.68 ± 0.29	3.30	
Benomyl	0.06								23.3				
Carbaryl	0.6	5.33	3.87 ± 0.27			0.628 ± 0.074	0.07						
Carbendazim	0.06	1.39	0.964	0.884 ± 0.38	2.97 ± 0.74	2.21 ± 0.28	6.29 ± 0.14	9.82 ± 0.15	86.6	39.2	40.5 ± 2.1	75.0	
Deet	0.6	1.82	2.98 ± 0.033	0.875 ± 0.37	7.13 ± 0.84	10.4 ± 1.8	4.31 ± 0.43	13.6 ± 0.84	264	61.3	65.0 ± 0.58	13.1	
Fluoxastrobin	0.06	1.10	0.913 ± 0.057	1.70 ± 0.28			0.40	0.29 ± 0.19		0.13	0.14		1.73
Fluridone	0.6	1.52	1.21 ± 0.019				1.83 ± 0.074	1.81 ± 0.20	1.56		3.30 ± 0.18	6.13	
Imazapyr	0.6								1.10				
Metalaxyl	0.06						0.07				0.17		
Prometon	0.06	0.34	0.512 ± 0.012	0.494 ± 0.019	1.47 ± 0.030	1.29 ± 0.074	0.319 ± 0.017	0.12 ± 0.12		0.61	0.42 ± 0.079	5.40	
Simazine	0.6	5.41	3.96 ± 0.20			0.63 ± 0.074						0.98	
Sulfapyridine	0.6						1.36 ± 0.71	4.59 ± 1.1	50.4	49.5	144 ± 4.9	126	
Tertbutylazin-desethyl	0.6	5.41	3.95 ± 0.20									0.979	
Propiconazole	0.6	0.14		3.03 ± 0.331	2.28 ± 0.12	8.14 ± 0.54						4.05	2.38
Pharmaceuticals:													
Carbamazepine	0.6	1.27	1.00 ± 0.11		0.822 ± 0.10	1.16 ± 0.067	13.1 ± 0.12	23.1 ± 1.1	107	125	101 ± 2.0	128	
Cetirizine	0.6	1.50	1.70 ± 0.24			1.03 ± 0.40	15.5 ± 0.41	39.9 ± 1.3	241	440	475 ± 24	454	
cis-Diltiazem	0.06	0.19		0.132 ± 0.007			0.33	0.98 ± 1.3		21.1	46.7 ± 4.1	45.0	
Citalopram	0.06	0.045		0.180 ± 0.014			0.095 ± 0.10			51.4	58.0 ± 0.92		
Dextromethorphan	0.06	0.02								18.3	23.2 ± 0.78		
Diphenhydramine	0.06	0.048		0.086 ± 0.009					0.12	18.8	34.8 ± 3.2	0.508	
Genistein	1.2				9.15 ± 0.11								
Irbesartan	0.6	0.04					2.11 ± 0.21	3.92 ± 0.98	26.3	24.1	70.2 ± 0.31	64.1	
Pramoxine	0.06	0.23	0.215 ± 0.016	0.543 ± 0.024				0.21 ± 0.32	3.68	6.58	0.40 ± 0.32	0.092	
Propanolol	0.06	0.29	0.179 ± 0.013	0.51 ± 0.029						16.4		0.093	
Rosuvastatin	0.6								49.1		1.65 ± 0.41	5.94	
Trimethoprim	0.06	0.16	0.131					0.43	41.0	3.81	5.67 ± 0.52	9.49	
Verapamil	0.6	0.10								7.05	7.72 ± 1.0	5.27	
Benzotriazole	0.06	4.28	16.9 ± 1.6	0.395 ± 0.021	38.1 ± 1.7	30.7 ± 3.7	346 ± 36	792 ± 9.4	1252	701	606 ± 12	1443	



- A variety of agrochemicals and pharmaceutical compounds were detected in WWTP effluents and Bay waters at typically ppt levels.
- Benzotriazole was the most abundant targeted micropollutant in Bay water (Coyote Creek), consistent with high levels in WWTP effluent.
- Target analyte levels in POCIS extracts generally correlated with water concentrations (grab samples) for all sites.

Non-targeted analysis: Data set characteristics

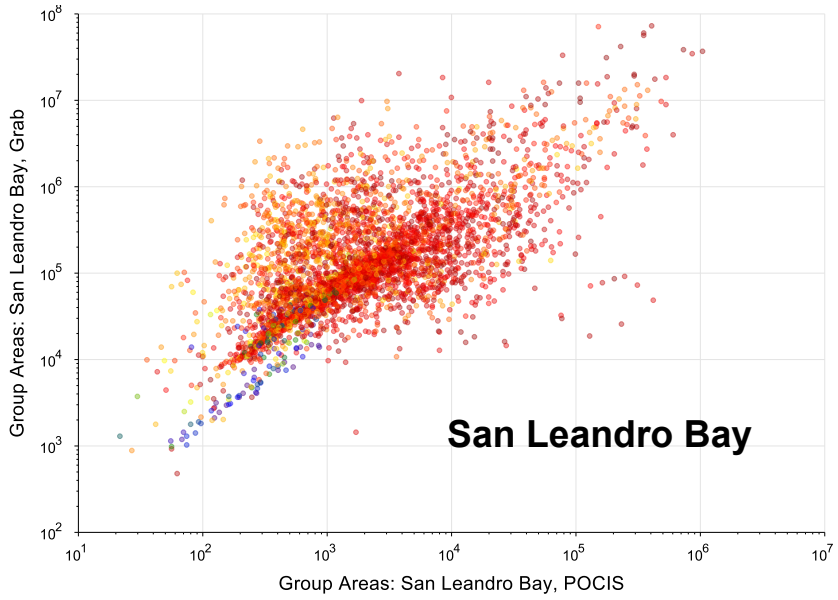
Total # compounds: **4965**
Not on target list: **4630**

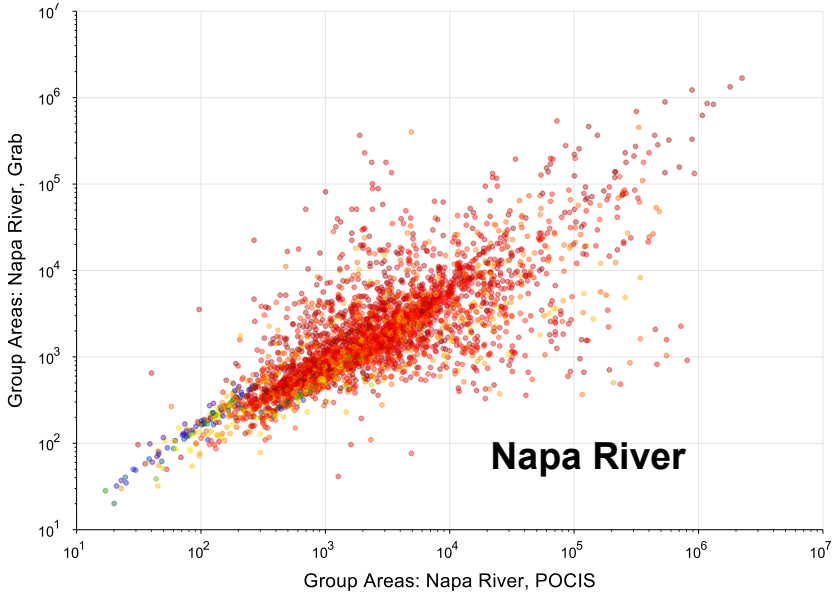


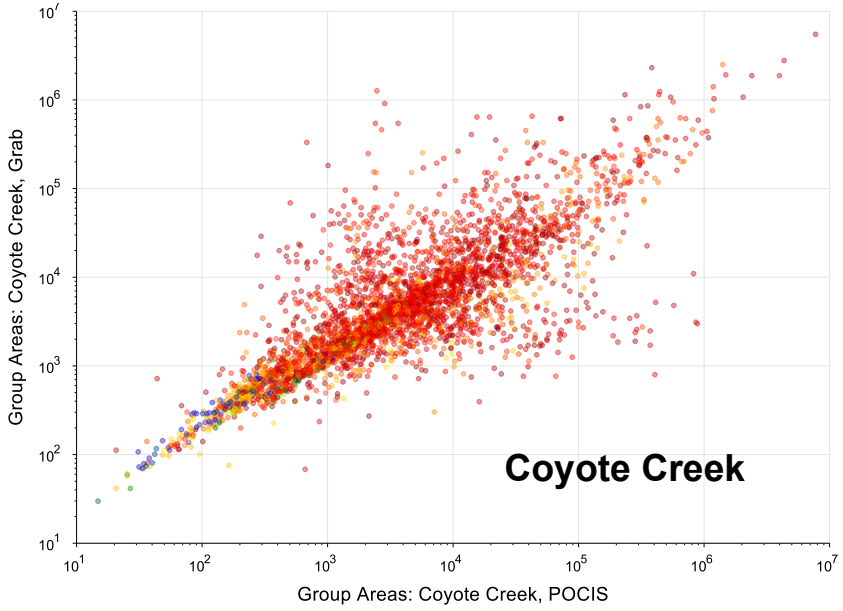
Non-targeted analysis data overview: POCIS vs. Grab samples

How well do POCIS extract intensities correlate with intensities of compounds in grab samples?

- High MW, low abundance compounds correlate well at each location.
- Poor correlation is observed for higher abundance compounds in all locations.
- San Leandro Bay POCIS data underpredicts abundance in grab samples





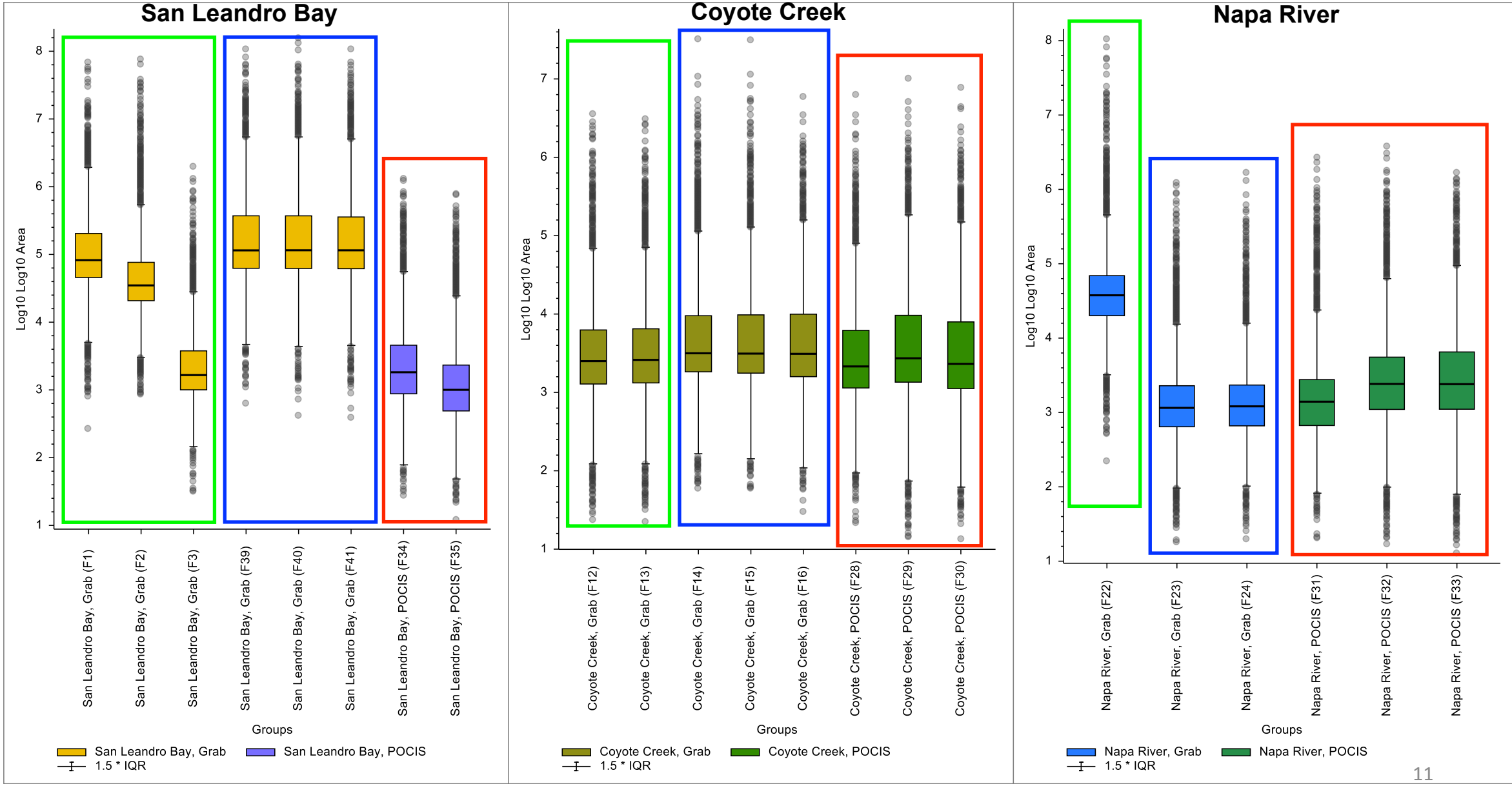


Non-targeted analysis data overview: POCIS and grab sample compound abundance by site

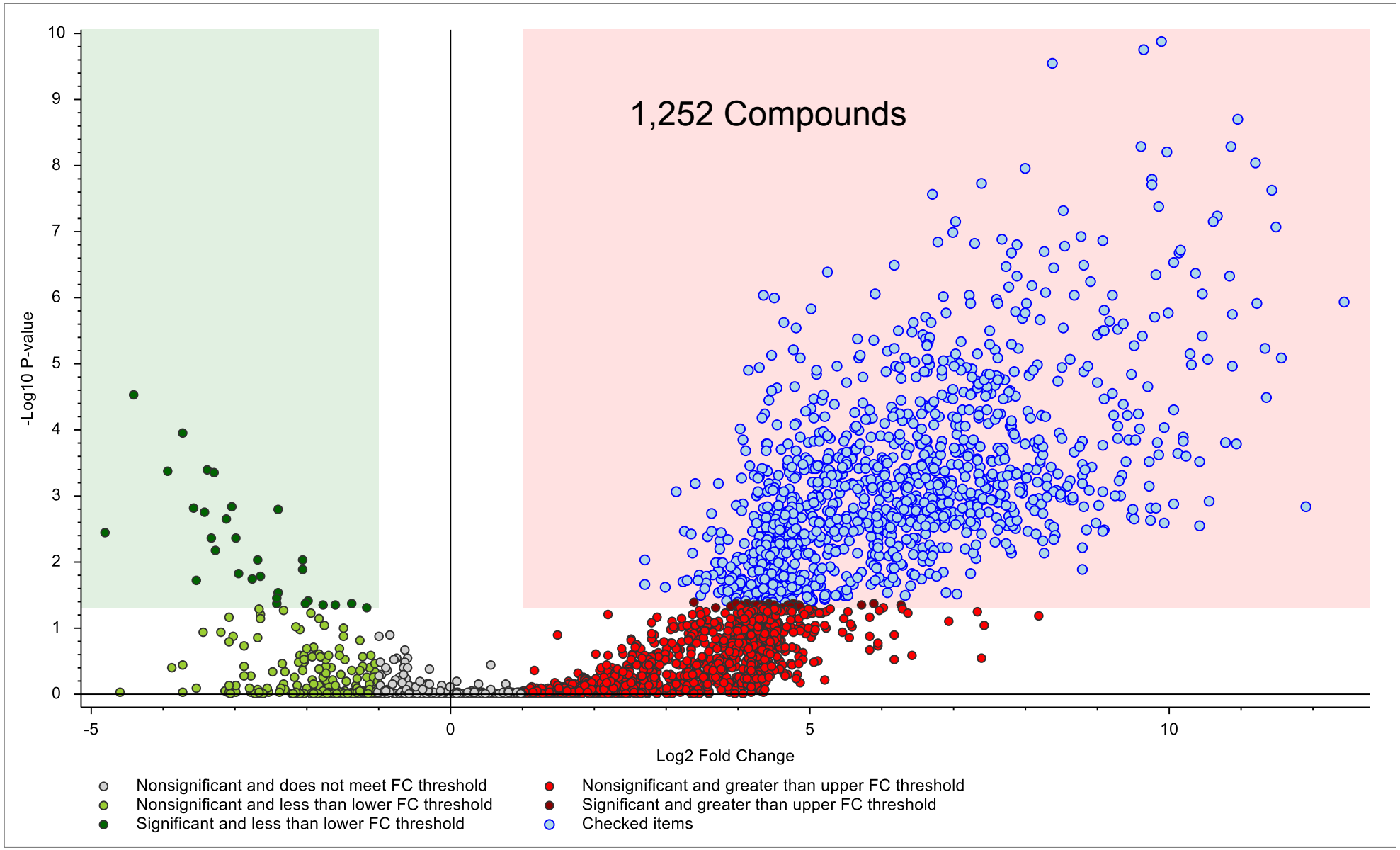
Deployment

Retrieval

POCIS

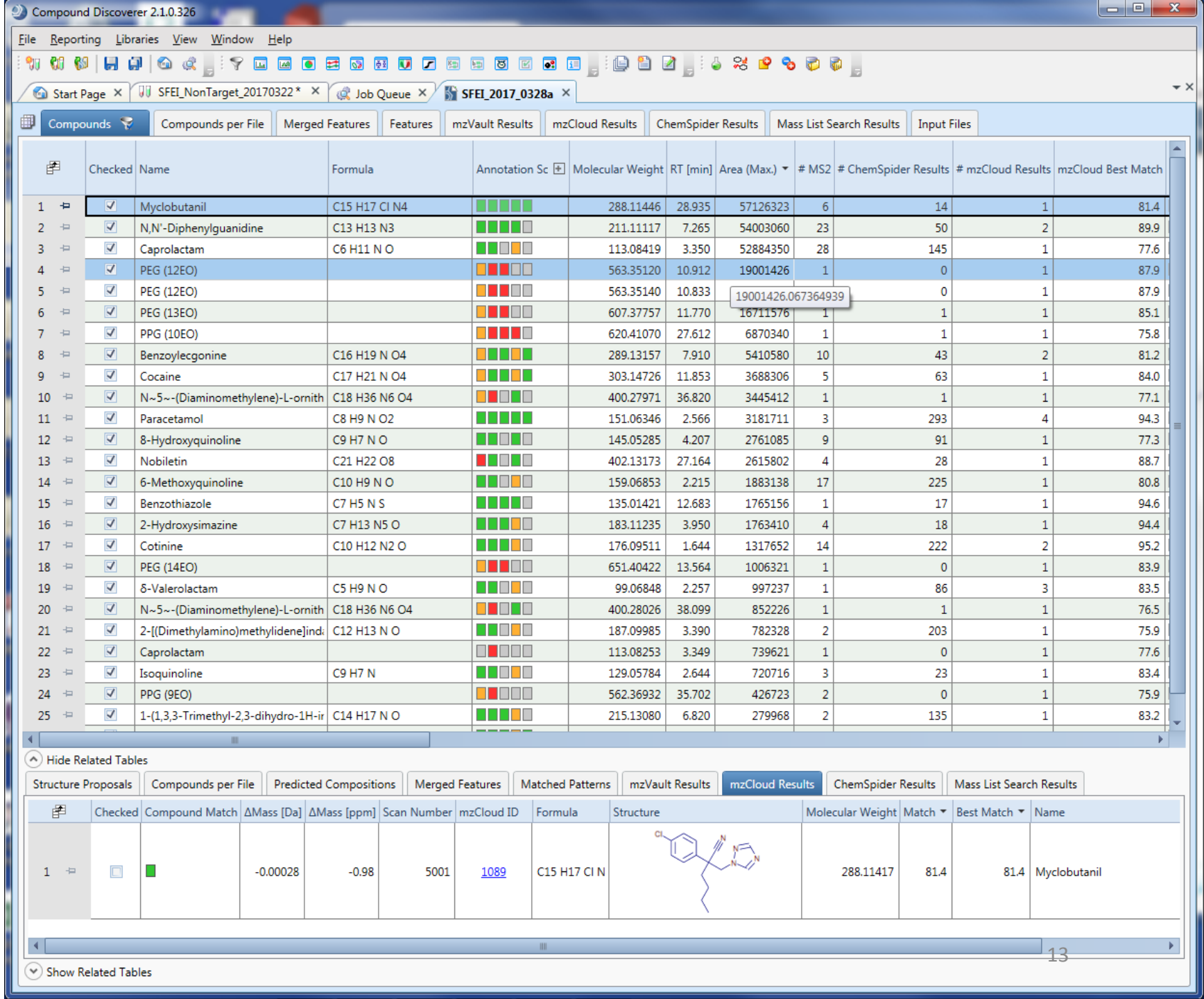


Differential analysis: Relative abundance of compounds in San Leandro Bay vs. WWTP Effluent (average)



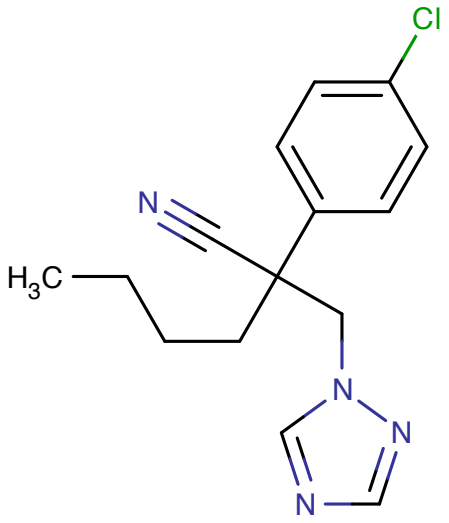
Identifying compounds in San Leandro Bay water:

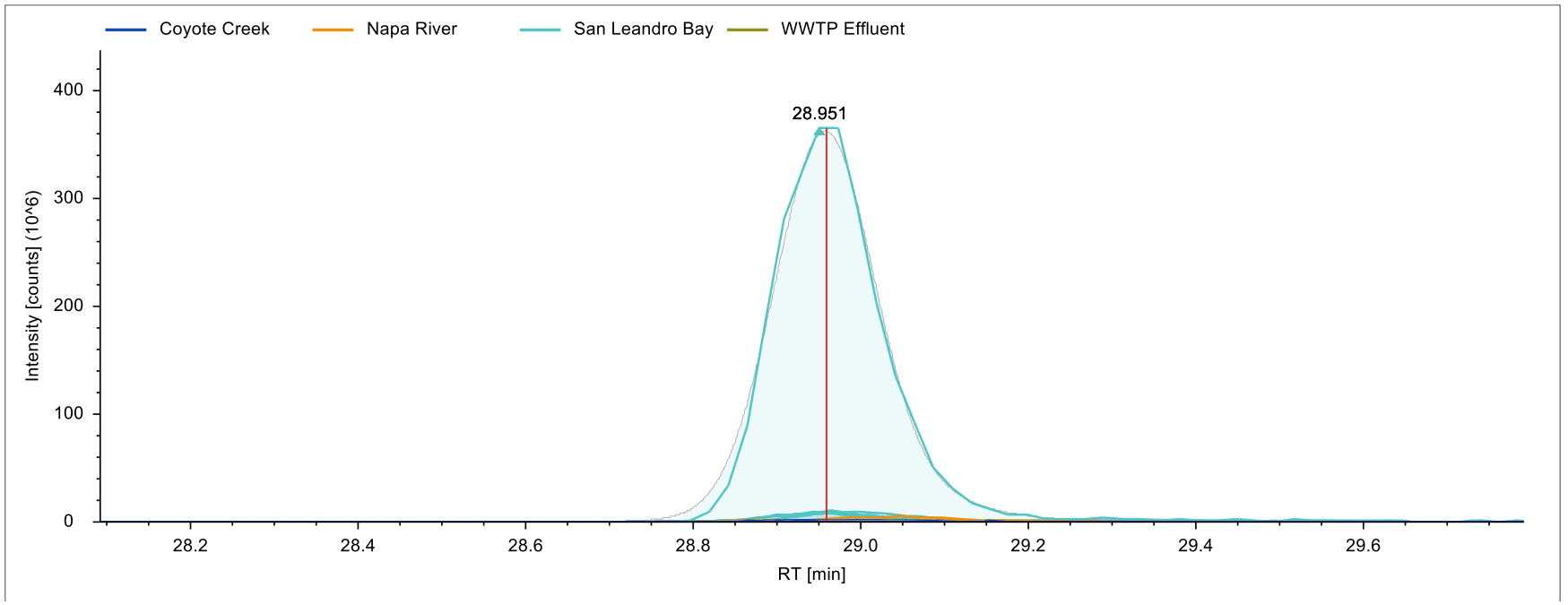
- Big picture: SLB is extremely complex: Higher pollutant burden than wastewater effluent!
- Large number (> 50) high confidence MS/MS library hits from mzCloud spectral library.
- Occurrence of many polyethoxylated compounds indicates untreated contaminant source.
- Highest abundance compounds identified are fungicide myclobutanil and several polymer/rubber additives.
- Pharmaceuticals and illicit drugs are also identified with high confidence.

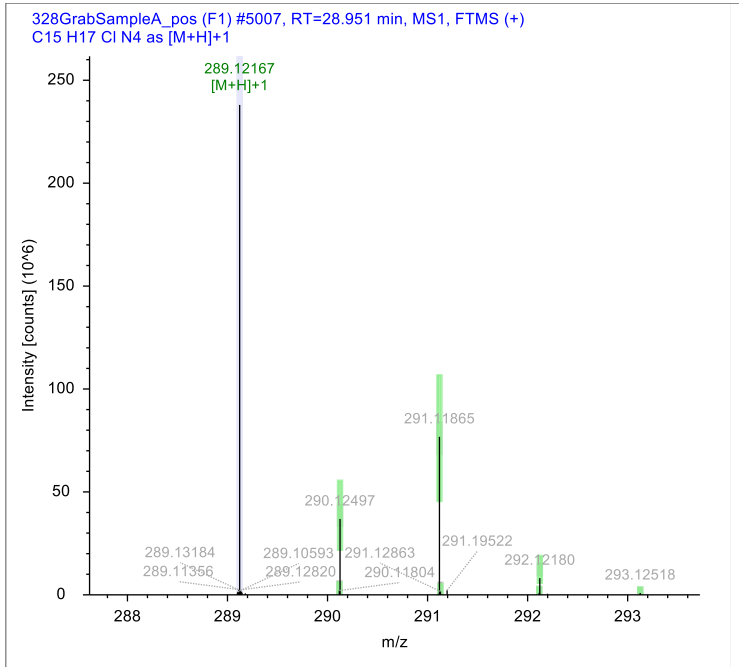


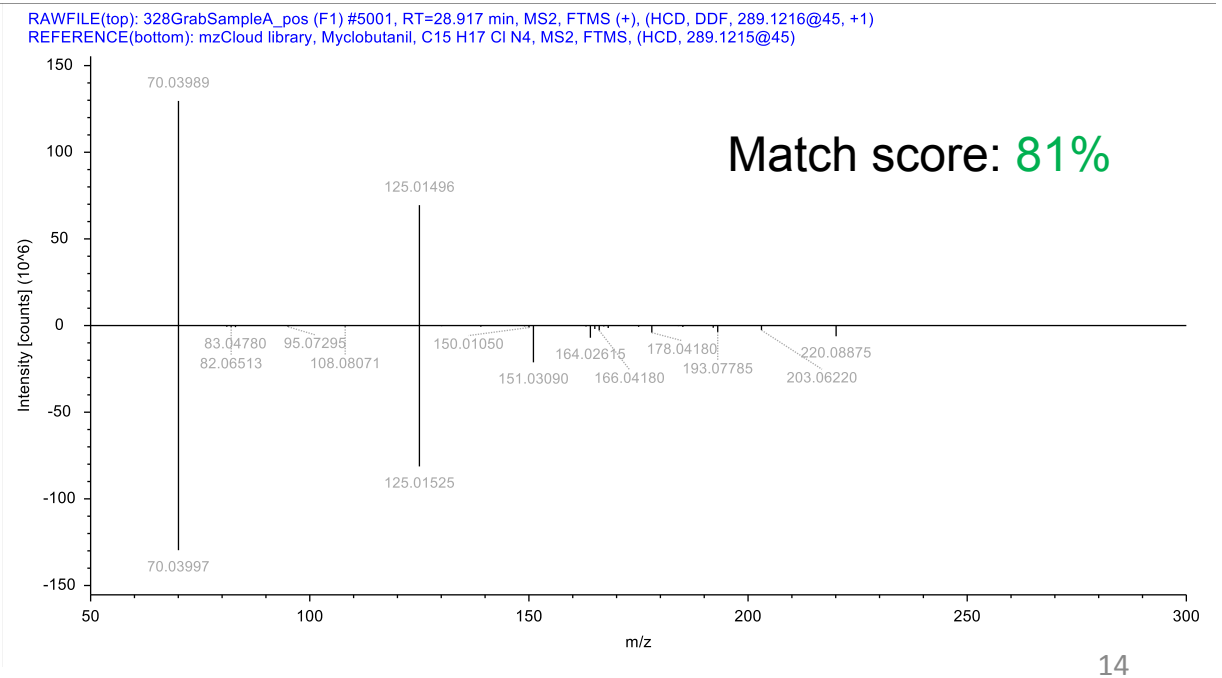
Myclobutanil: Conazole fungicide used to control fungal infections in table & wine grapes (primarily in California). Also used for cannabis cultivation.

http://www.toxipedia.org/display/toxipedia/Myclobutanil



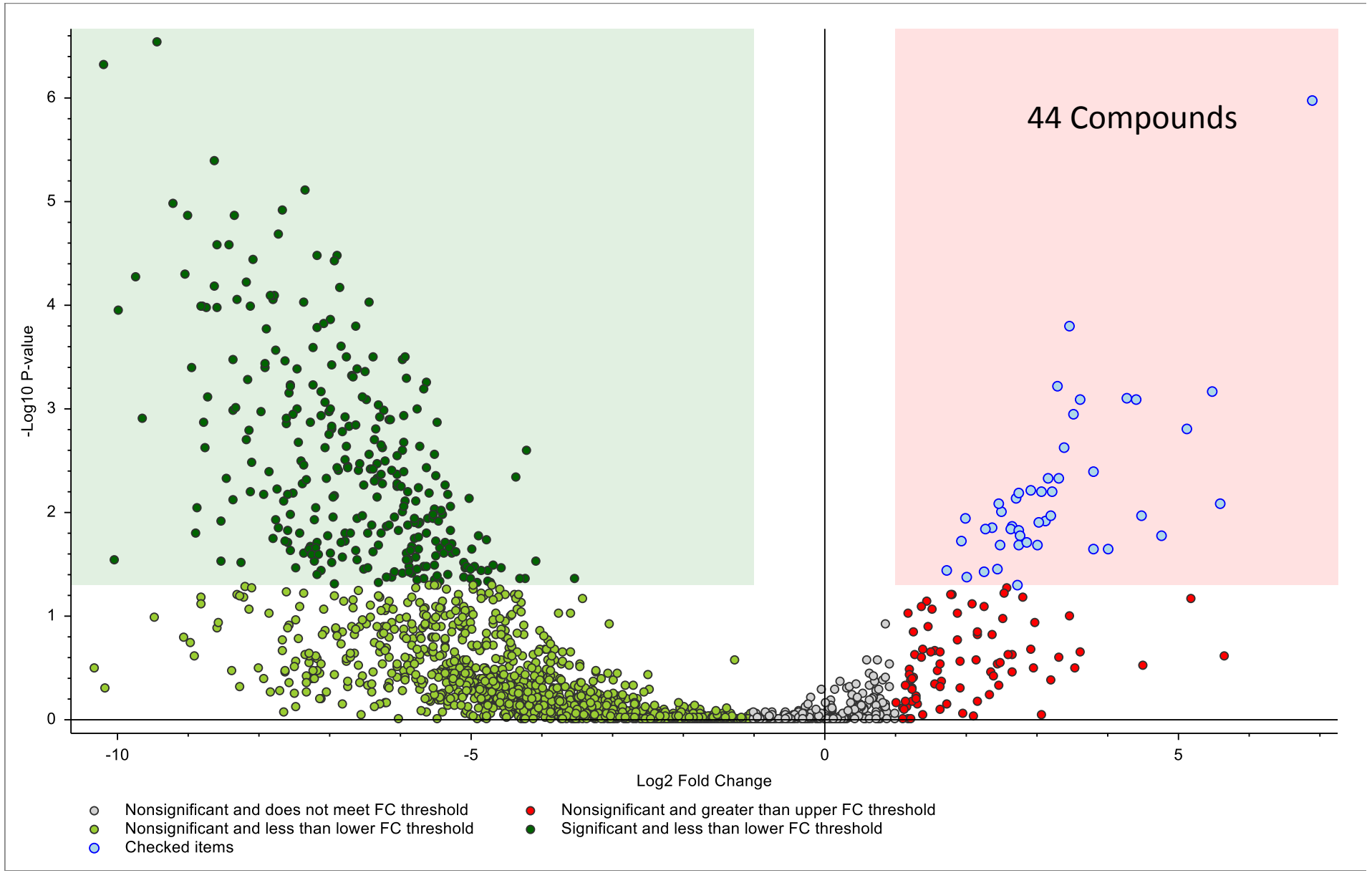






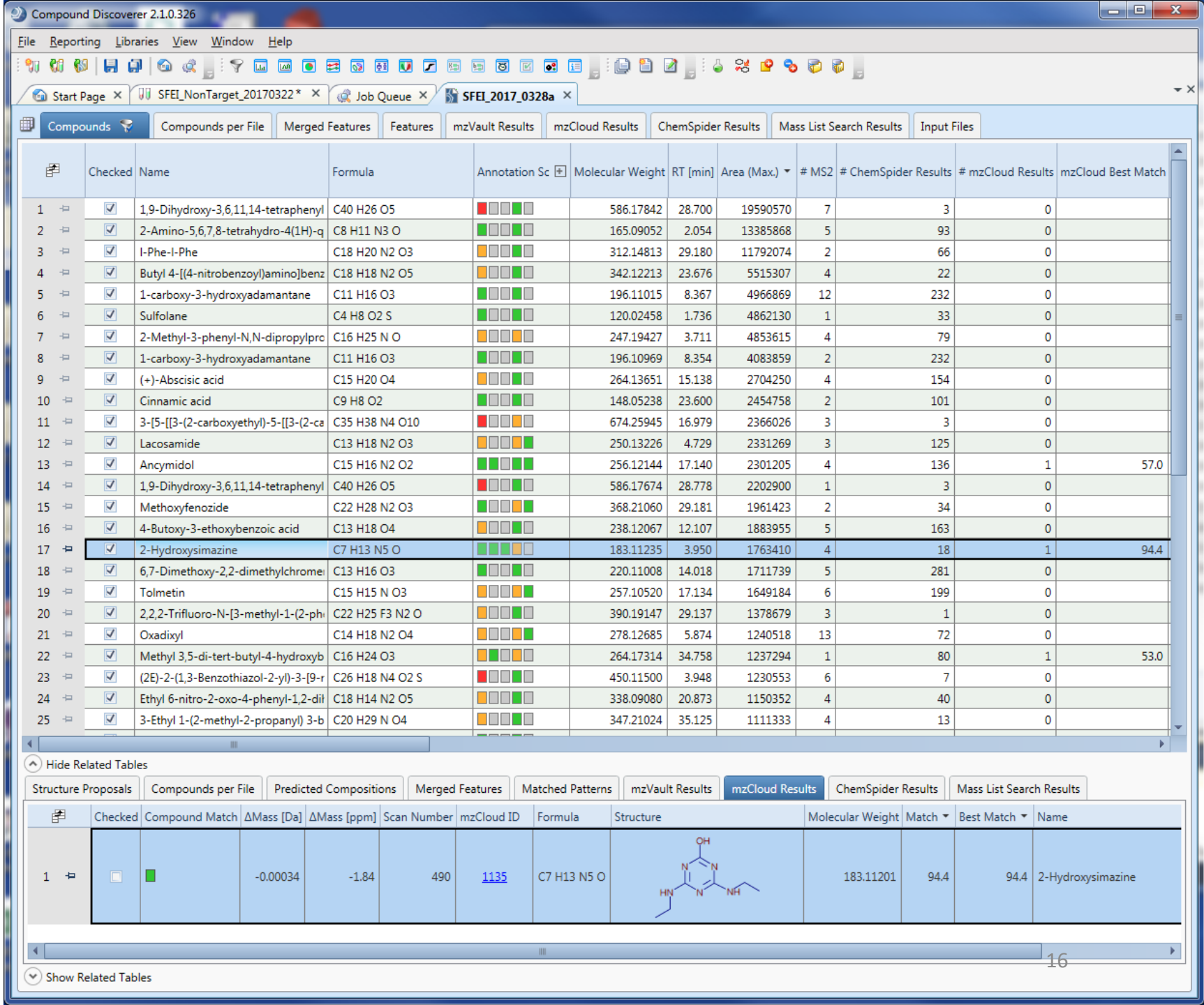
Match score: 81%

Differential analysis: Relative abundance of compounds in Napa River vs. WWTP Effluent (average)

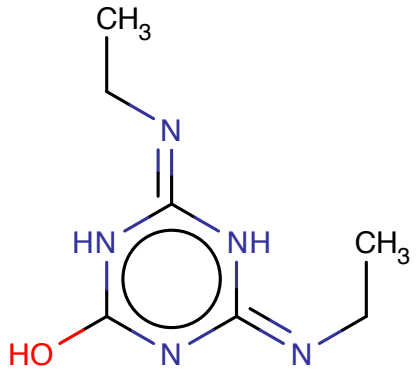


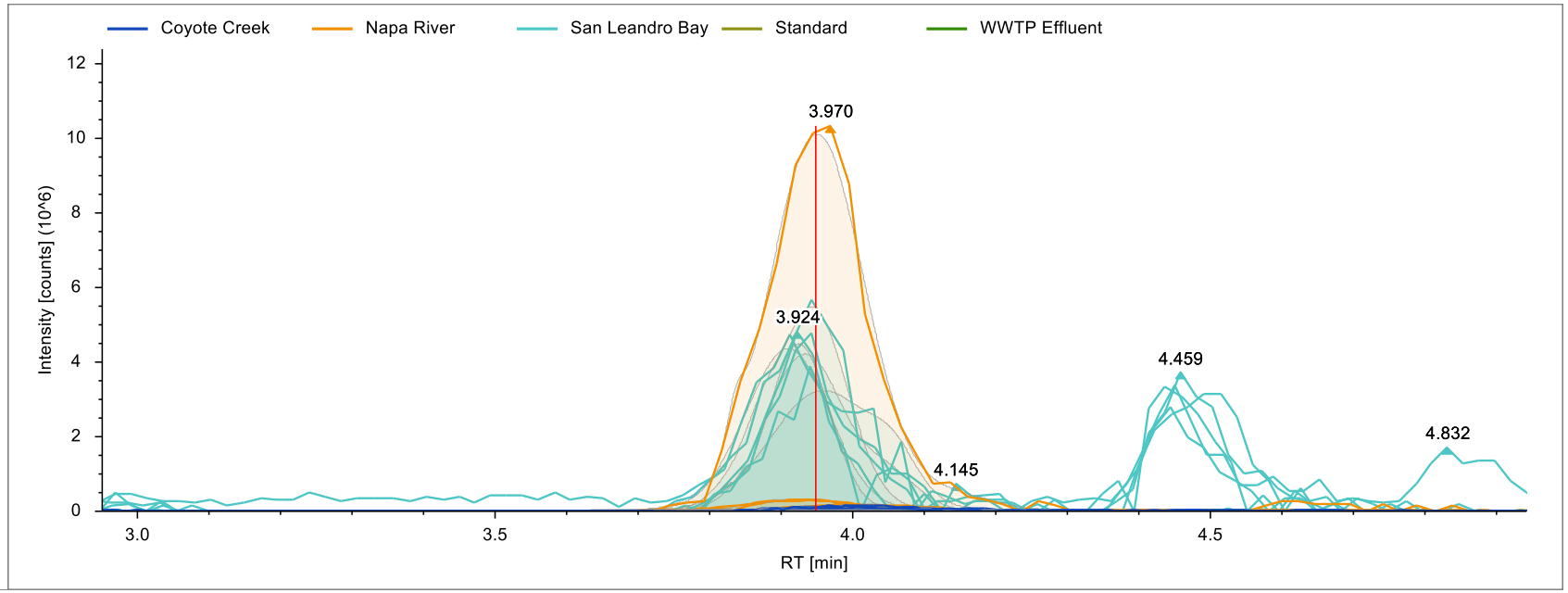
Identifying compounds in Napa River water:

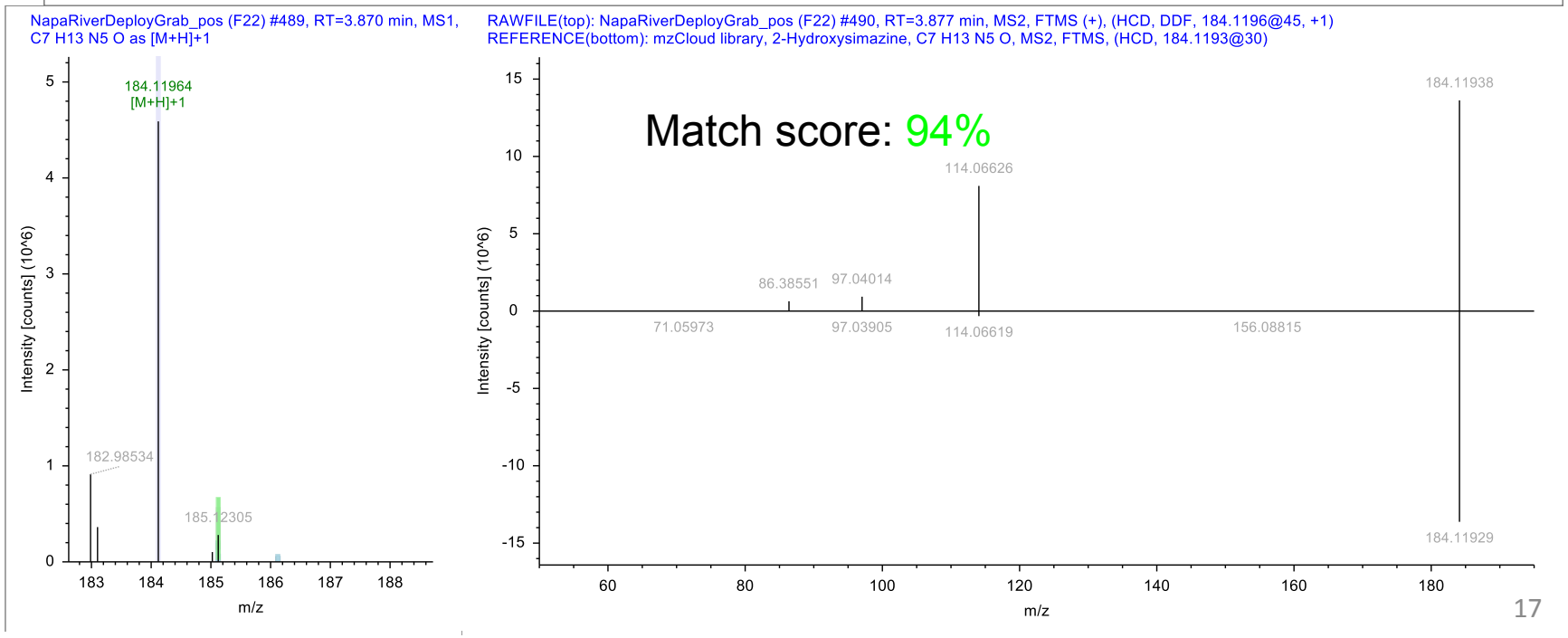
- Far fewer compounds had elevated levels in Napa River water relative to WWTP effluent.
- Only one compound (2-hydroxysimazine) matched with high confidence to library spectra.
- Highly uncertain (mass-only) tentative identifications of other compounds indicates many natural products.
- No indication of significant wastewater pollutant sources in the Napa River.
- Several candidates had MS/MS spectra consistent with agrochemicals and commercial chemical transformation products.



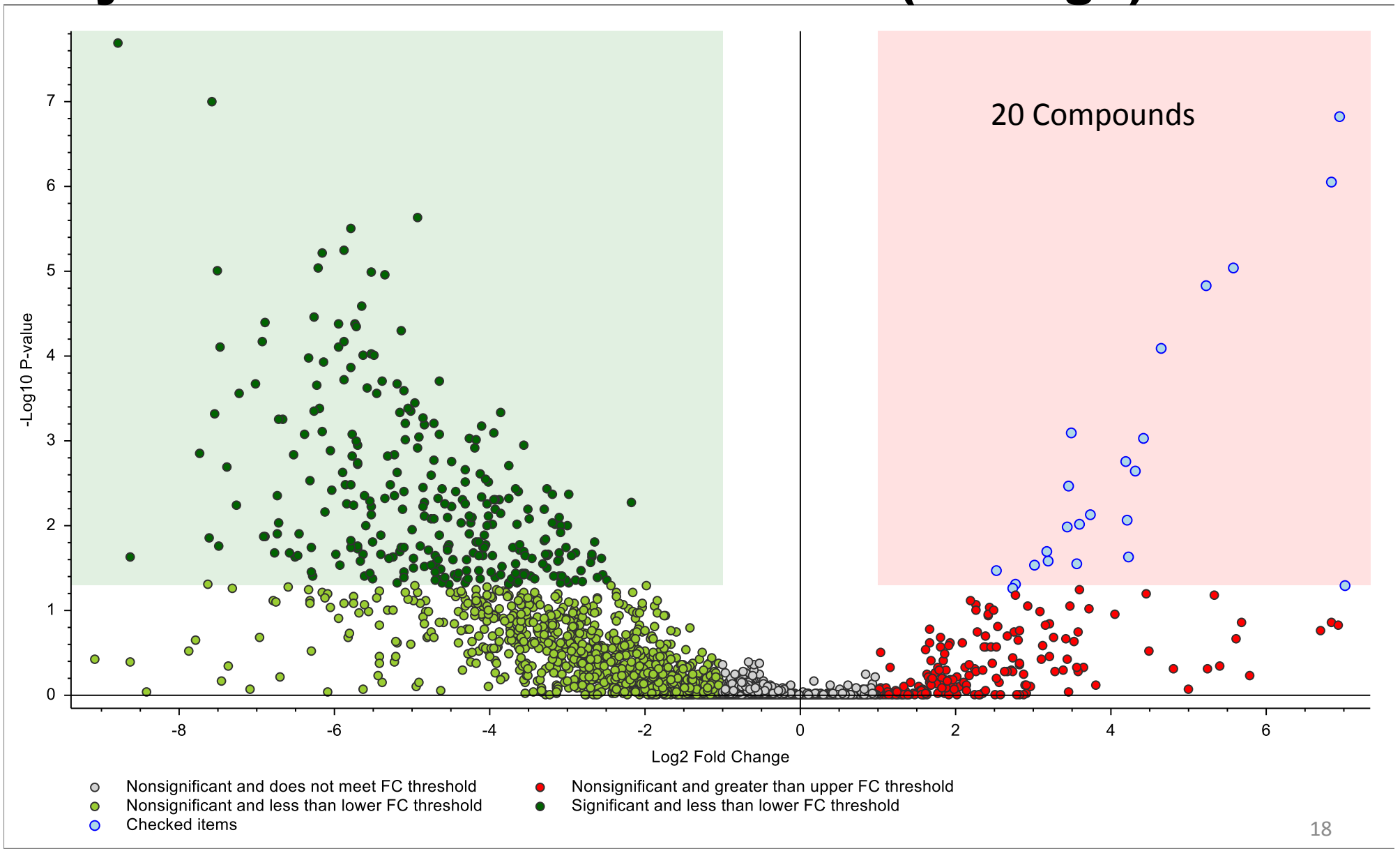
2-Hydroxysimazine:
Transformation product of the widely-used triazine herbicide simazine (broadleaf weed and grass killer).





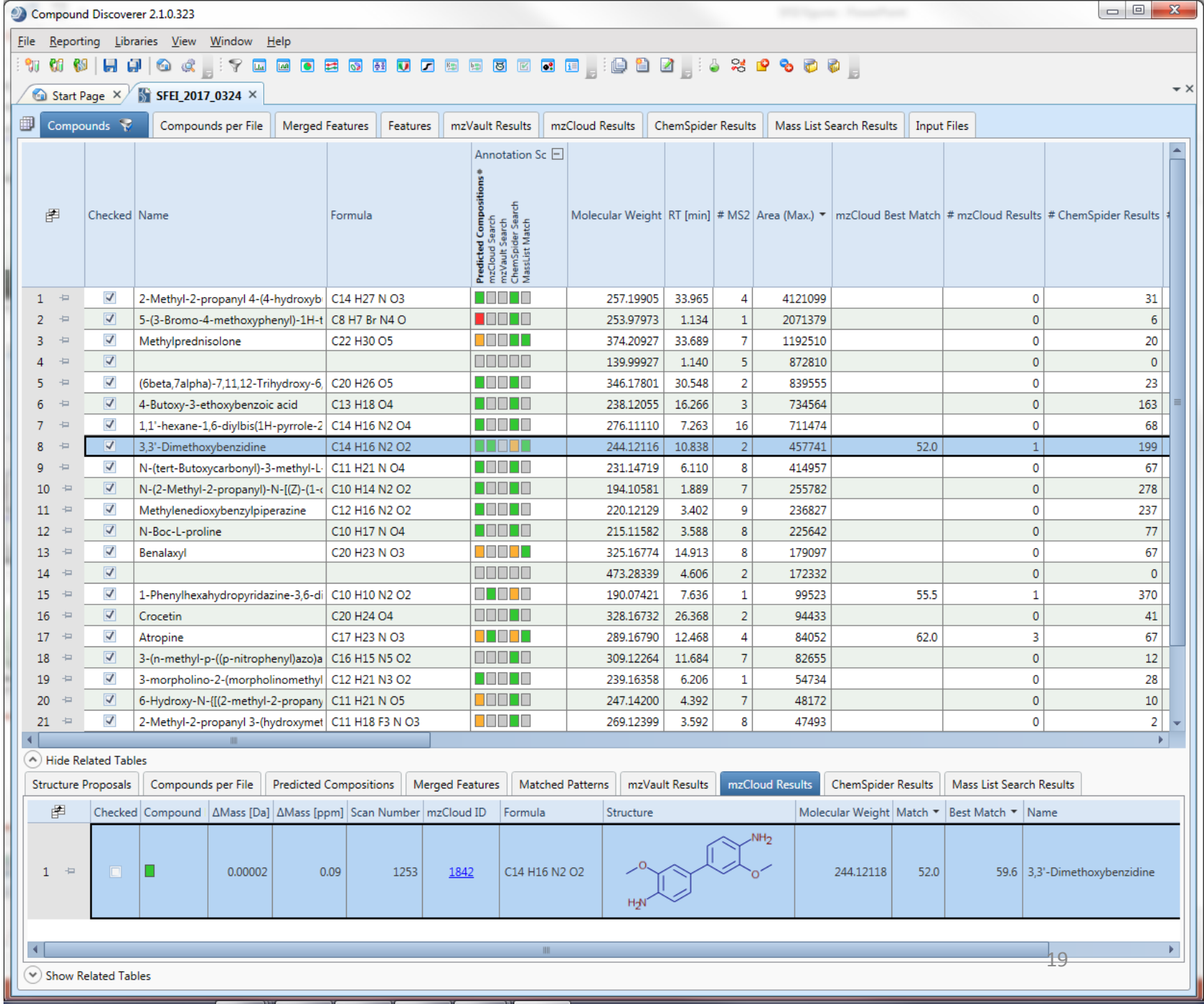


Differential analysis: Relative abundance of compounds in Coyote Creek vs. WWTP Effluent (average)

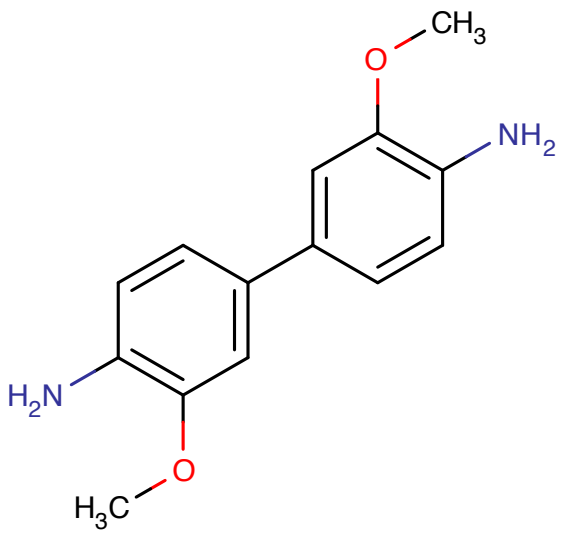


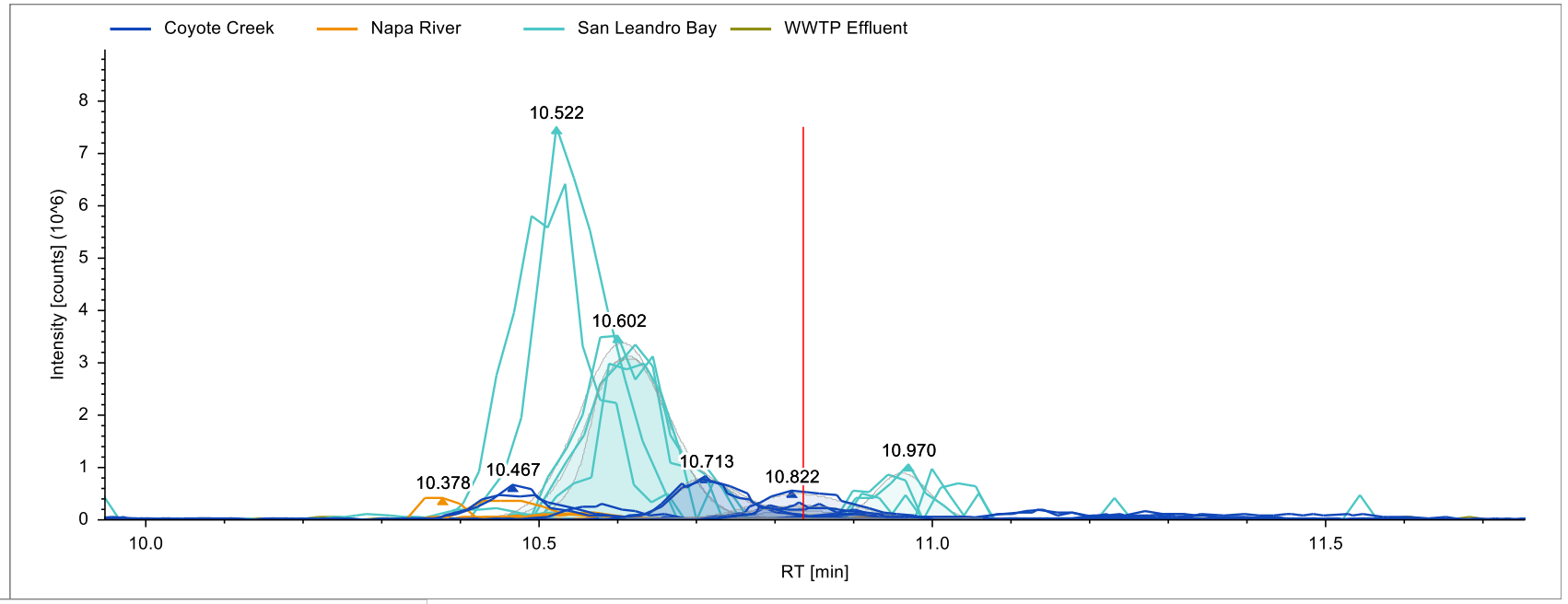
Identifying compounds in Coyote Creek water:

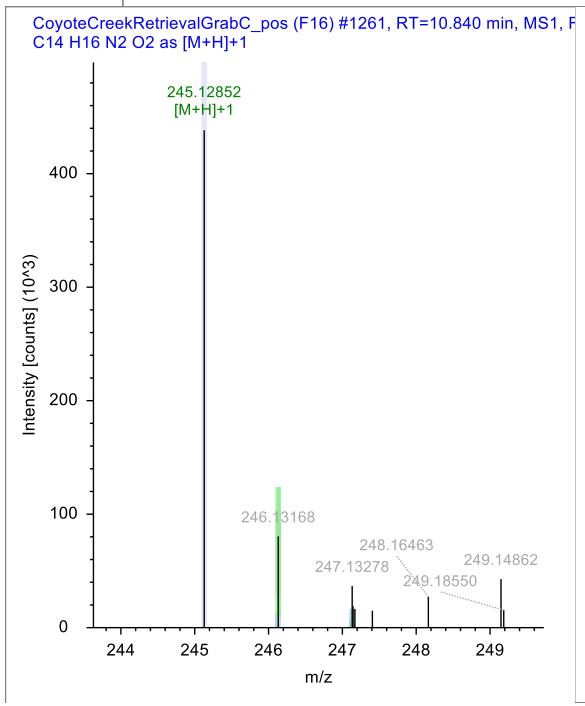
- Few unique compounds in Coyote Creek.
- Most detected compounds are also found in high abundance in WWTP effluent (Coyote Creek resembles diluted effluent).
- No high confidence identifications from Spectral library.
- Several low-confidence spectral library matches can be examined.

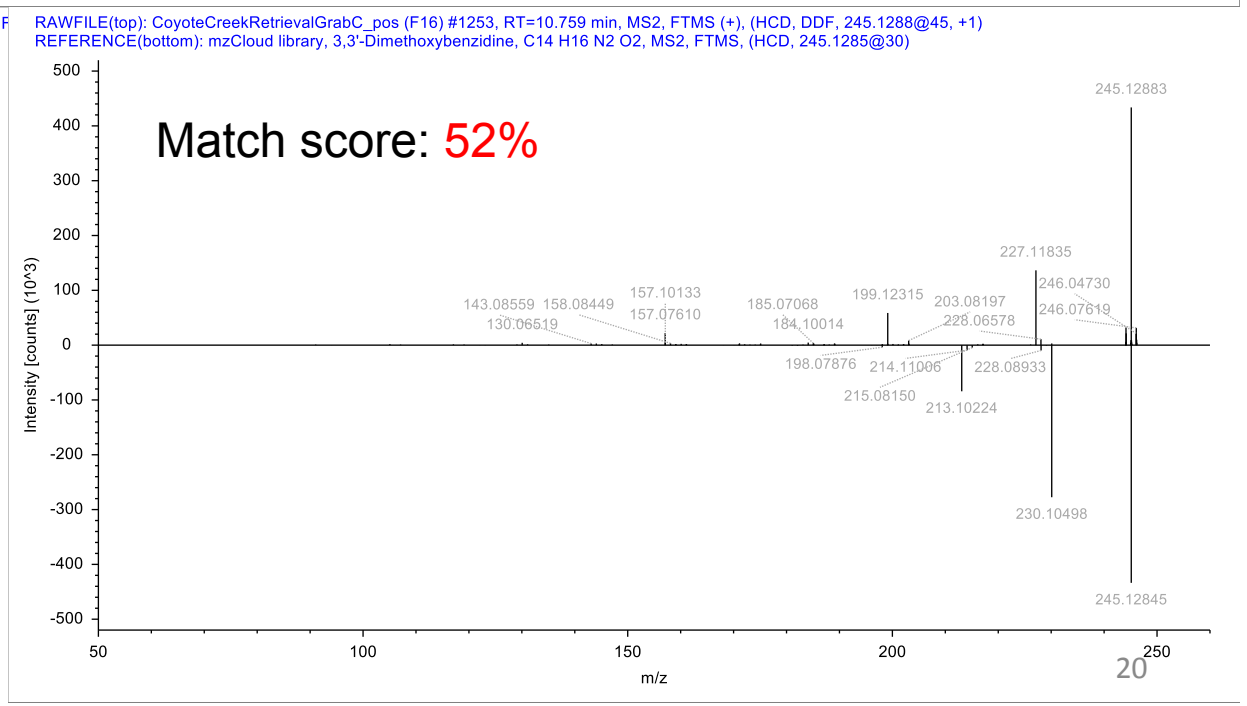


3,3’-Dimethoxybenzidine?: This could be a reductive transformation product of diazobenzene dyes, but the spectral match is relatively poor.









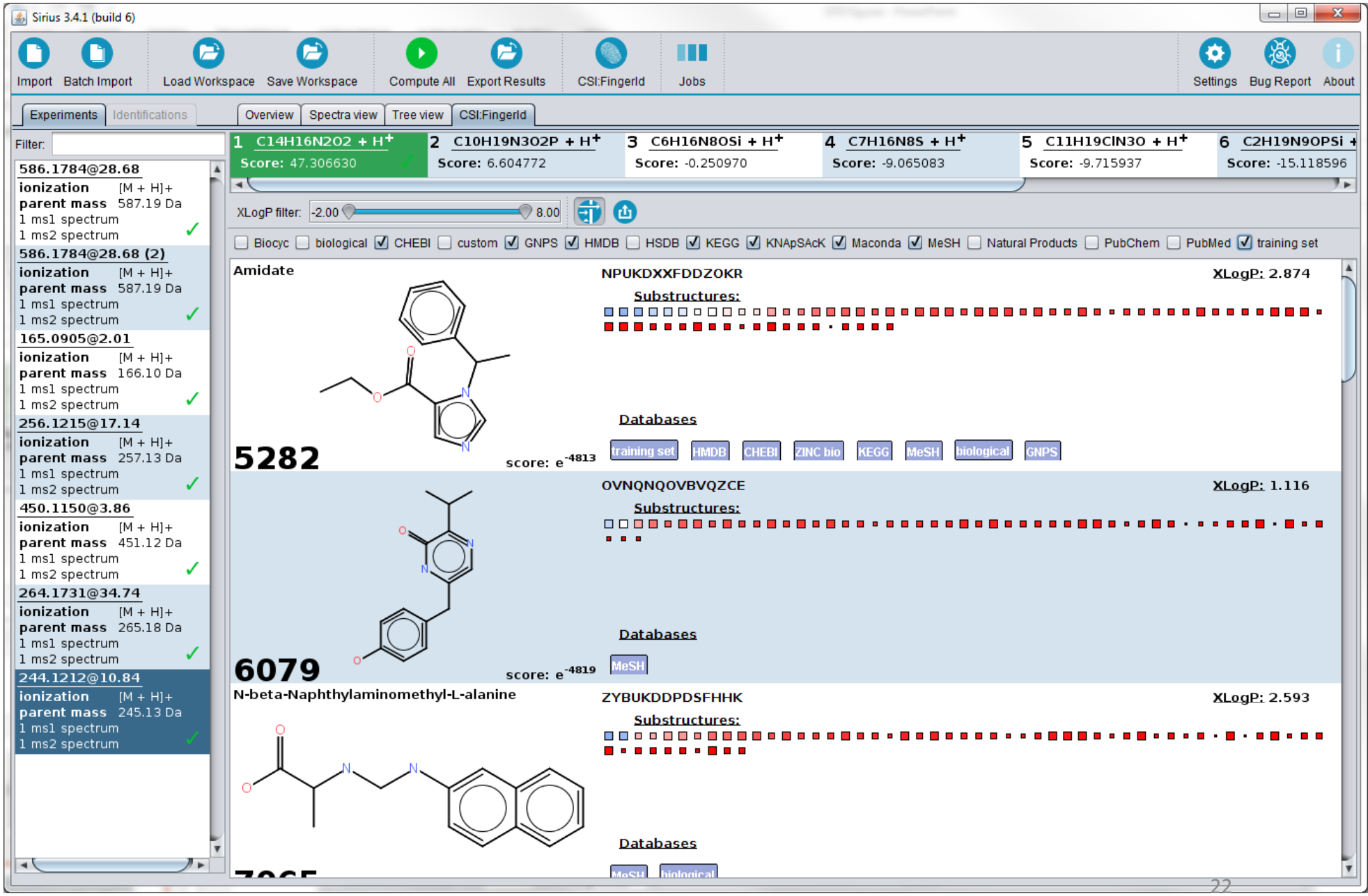
Can library match be verified by *in silico* fragmentation?

Computational fragment tree analysis by Sirius 3.4 supports the assignment of $C_{14}H_{16}N_2O_2$ as candidate molecular formula…

Can library match be verified by *in silico* fragmentation?

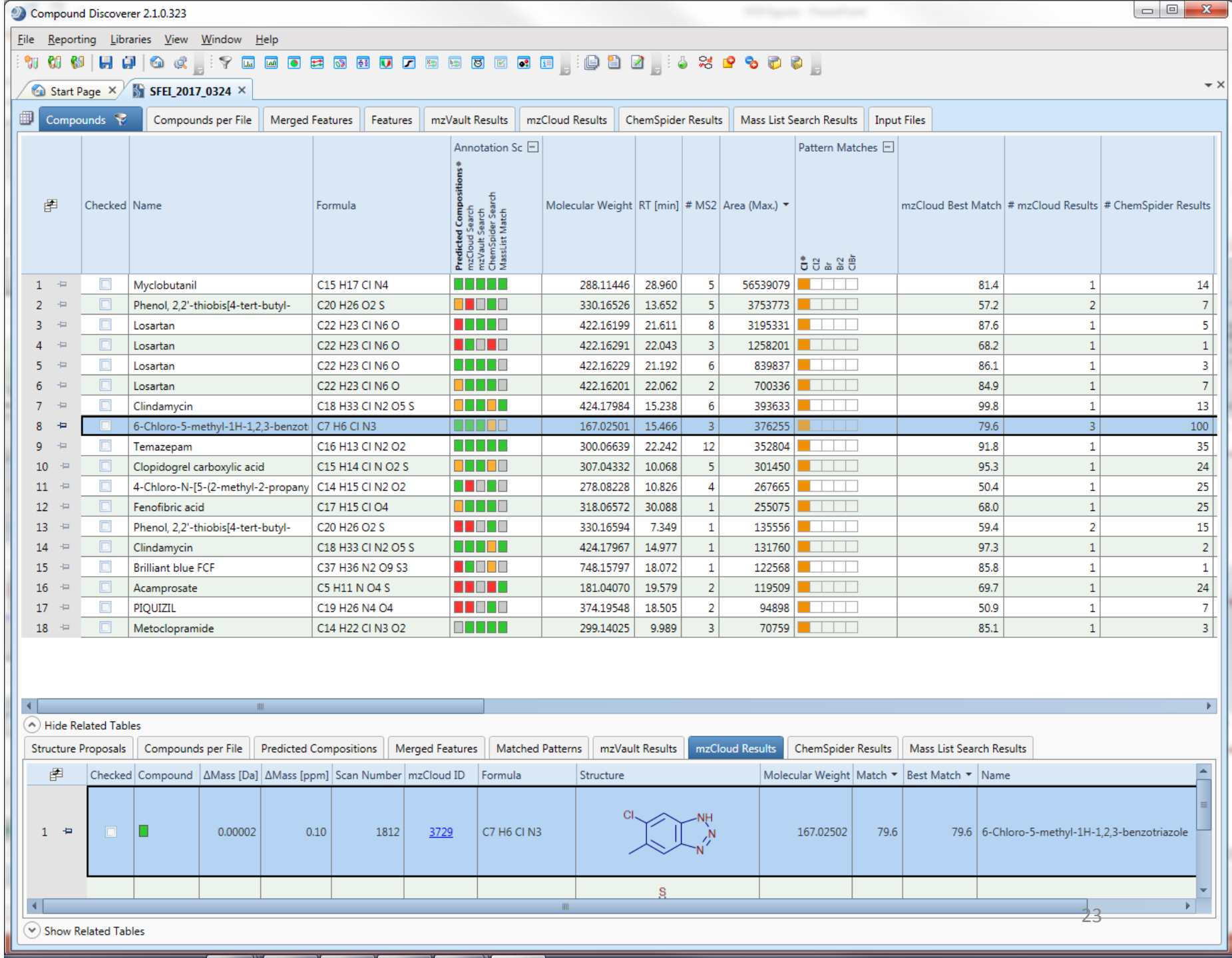
… however, structural fragment matching does not support identity of compound as 3,3'-dimethoxybenzidine.

An alternative identity may be Amidate (Etomidate), an anesthetic/hypnotic compound used in medical procedures. This must be considered a tentative identification.



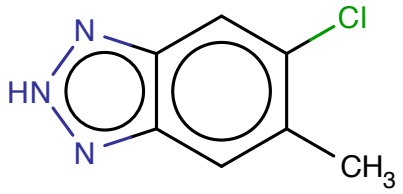
Alternative approaches for prioritizing compounds for identification:

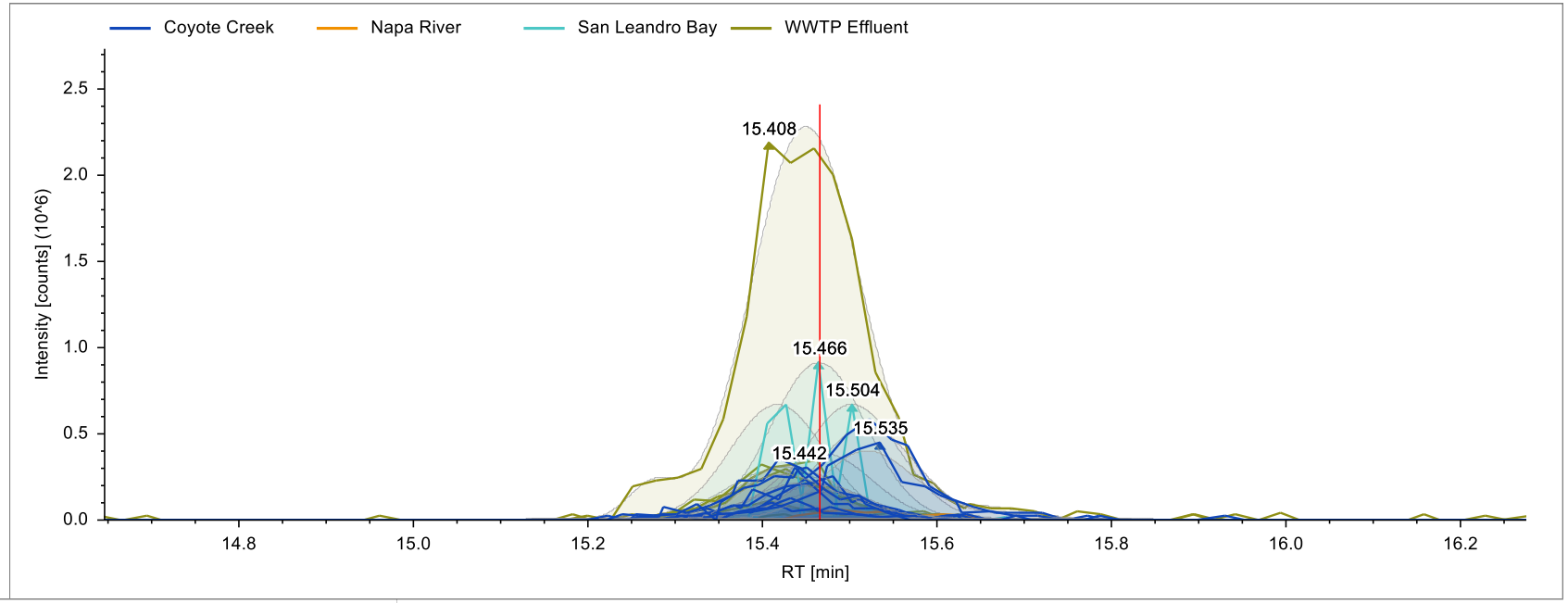
- Chlorine isotope matching on molecular ion clusters.
- This approach uses allows “identity-blind” focus on chlorine and/or bromine-containing compounds in samples.
- Spectral library matches were available for only 18 “Cl”-pattern matched compounds in the SF Bay sample set.
- Most of these compounds were pharmaceuticals and/or agrochemicals.

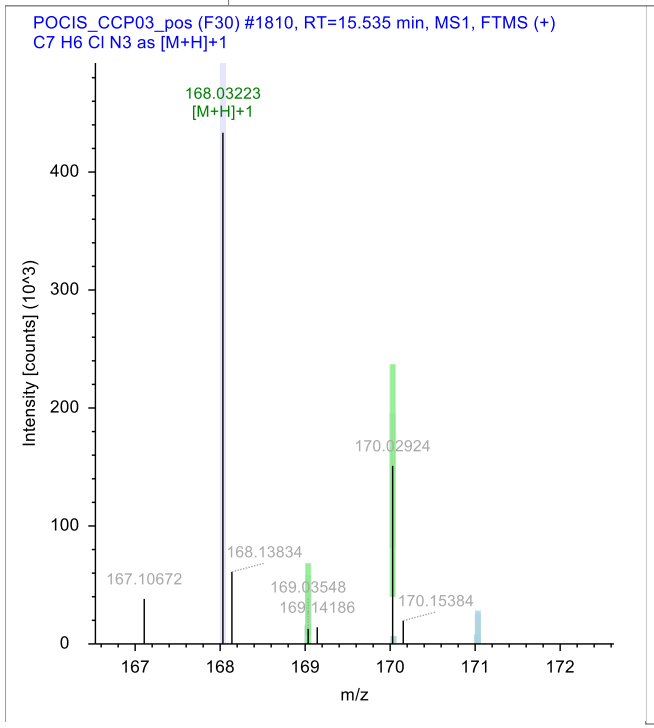


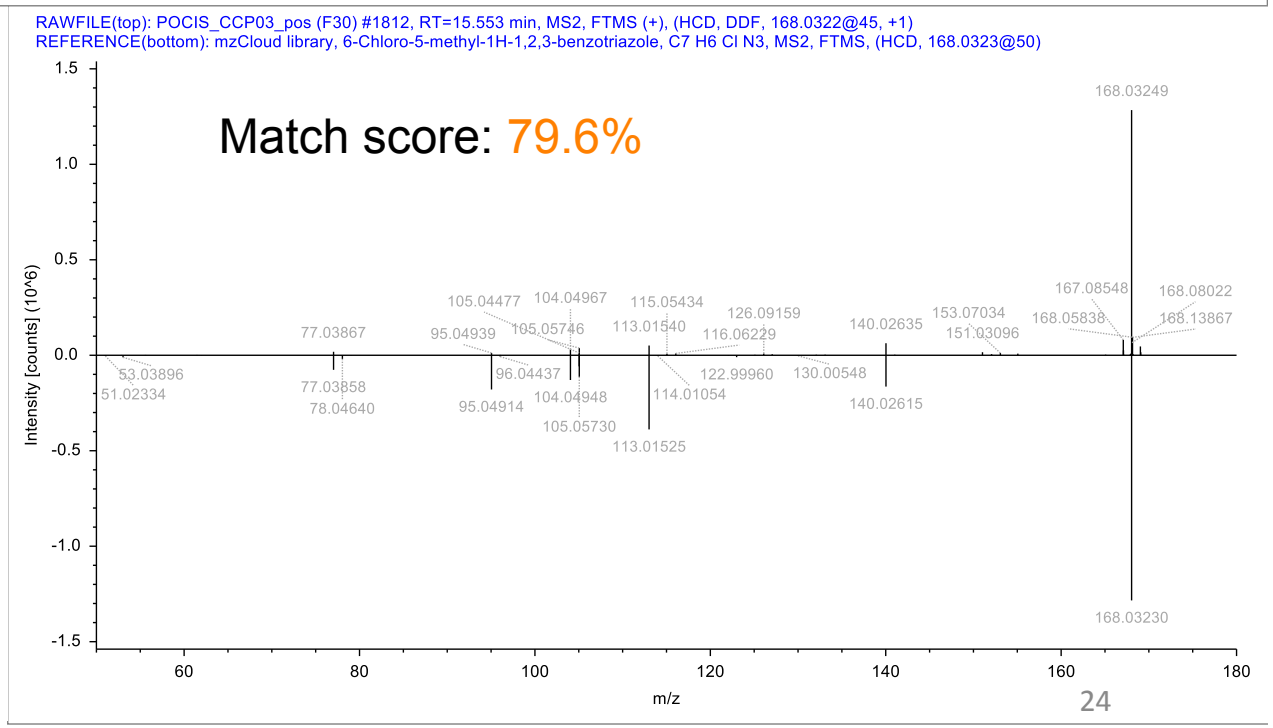
6-Chloro-5-methyl-1H-1,2,3-benzotriazole:

Chlorinated benzotriazoles are used in polymer additive UV inhibitors. This may be a precursor or transformation product of such polymer additives.





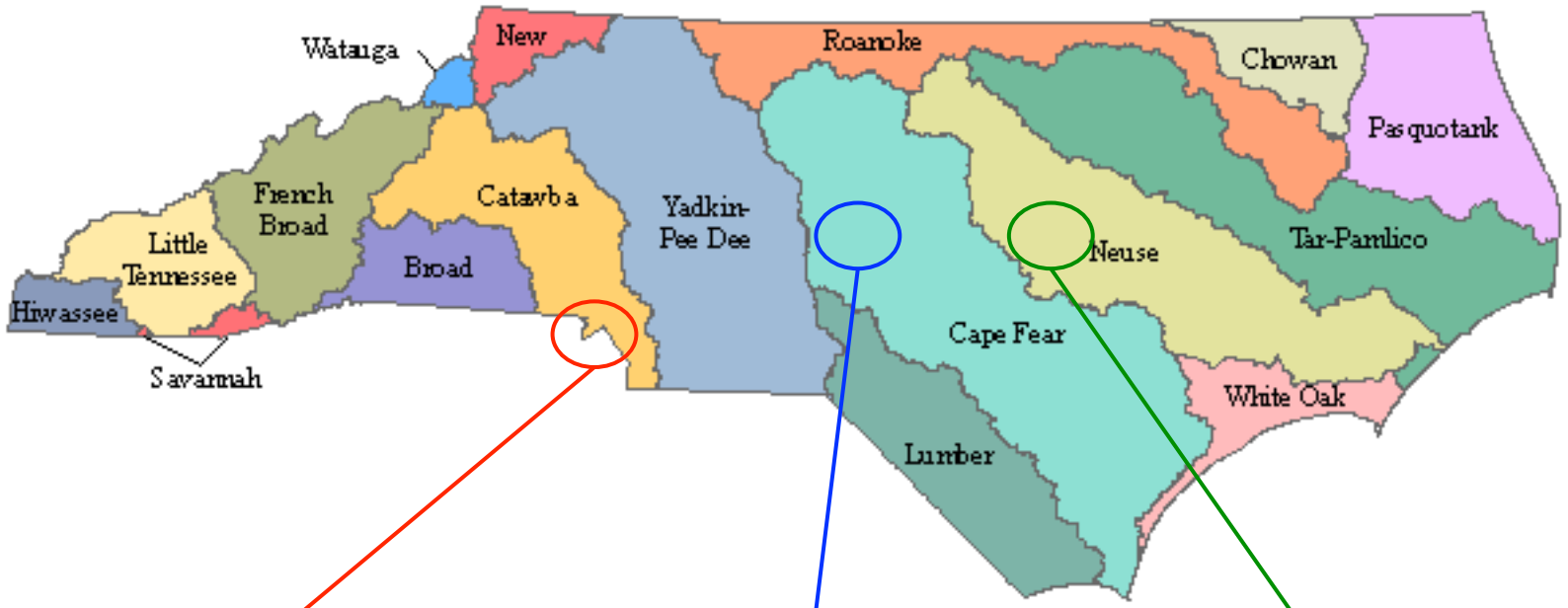




Conclusions: SF Bay

- Bay waters are impacted by a variety of organic pollutant sources.
- Stormwater seems to be an important contributor of organic organic pollutant burdens in some areas of the Bay, as illustrated by findings of abundant polyethoxylated compounds and additive chemicals in San Leandro Bay.
- Agrochemicals and natural products appear to be the organic compounds most specifically detected in the Napa River.
- Passive sampling and discrete grab-sampling are complementary approaches for non-targeted analysis of ambient waters.

Emerging pollutants in NC river water

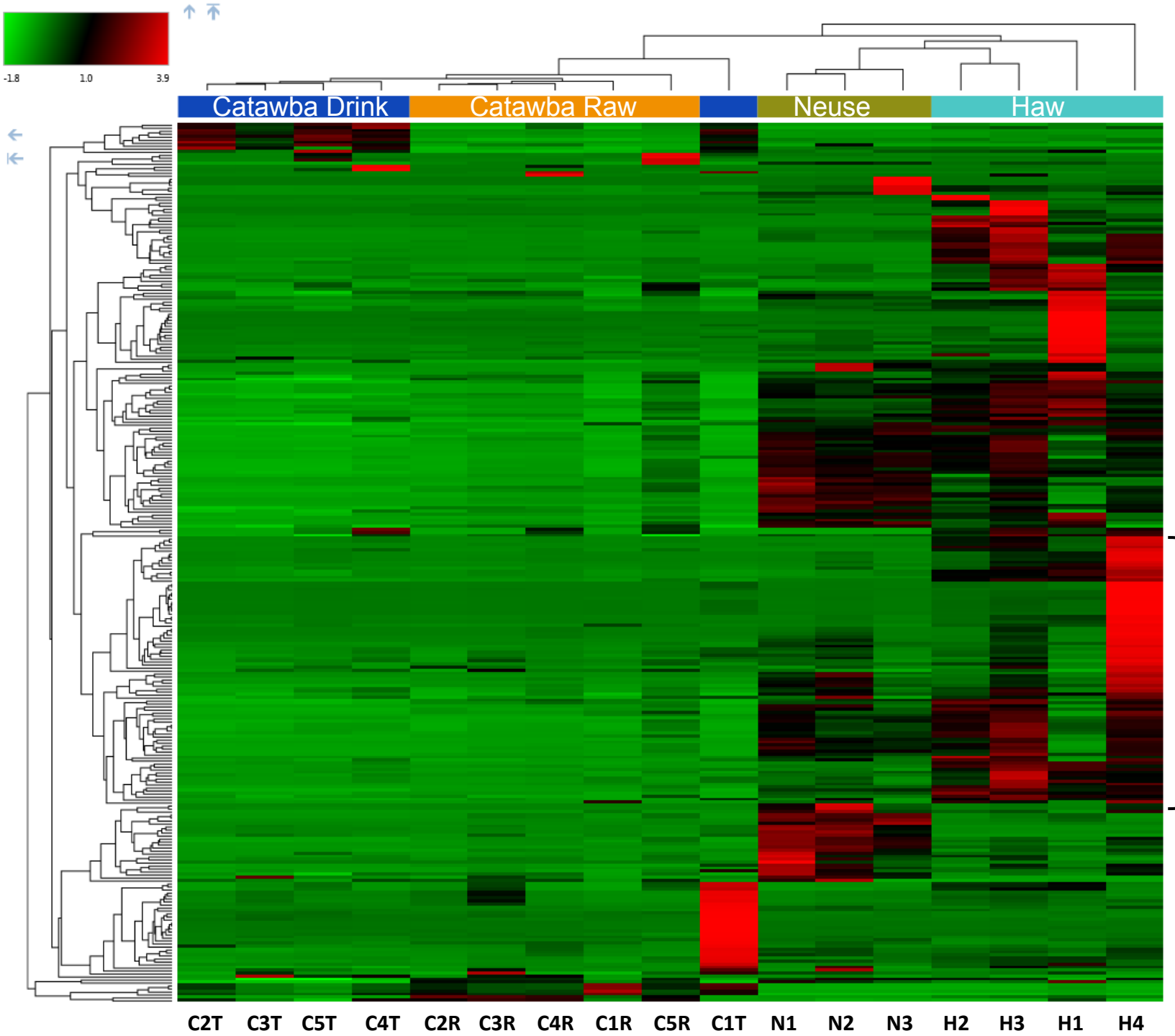


Catawba river: highly urbanized, significant wastewater inputs. Drinking water source for Charlotte, NC Metro area

Haw river: within the Cape Fear watershed. Industry and urbanization are likely pollution sources.

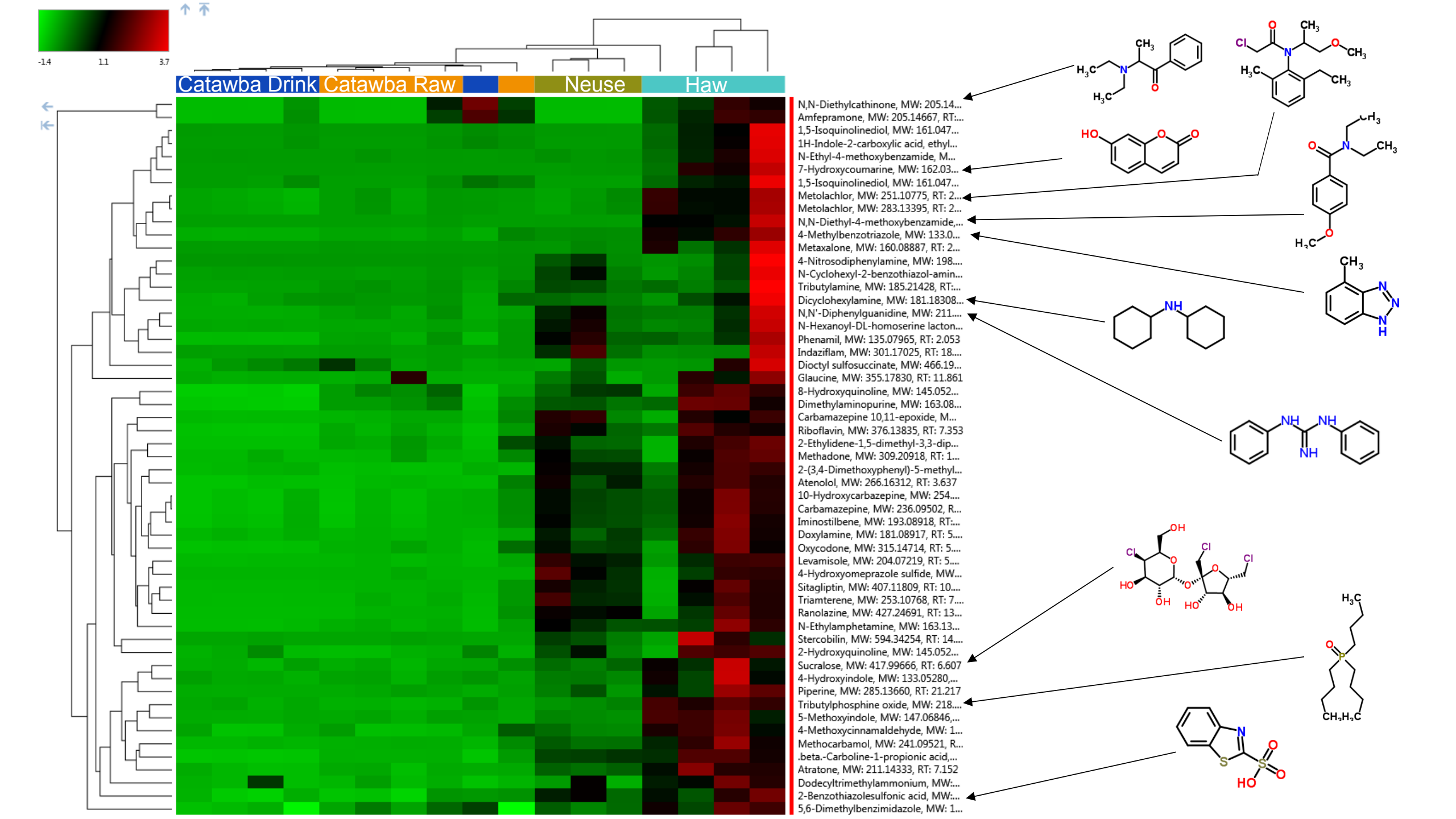
Neuse river: agriculture is the dominant land-use. Tobacco, corn, hog farms ubiquitous throughout watershed.

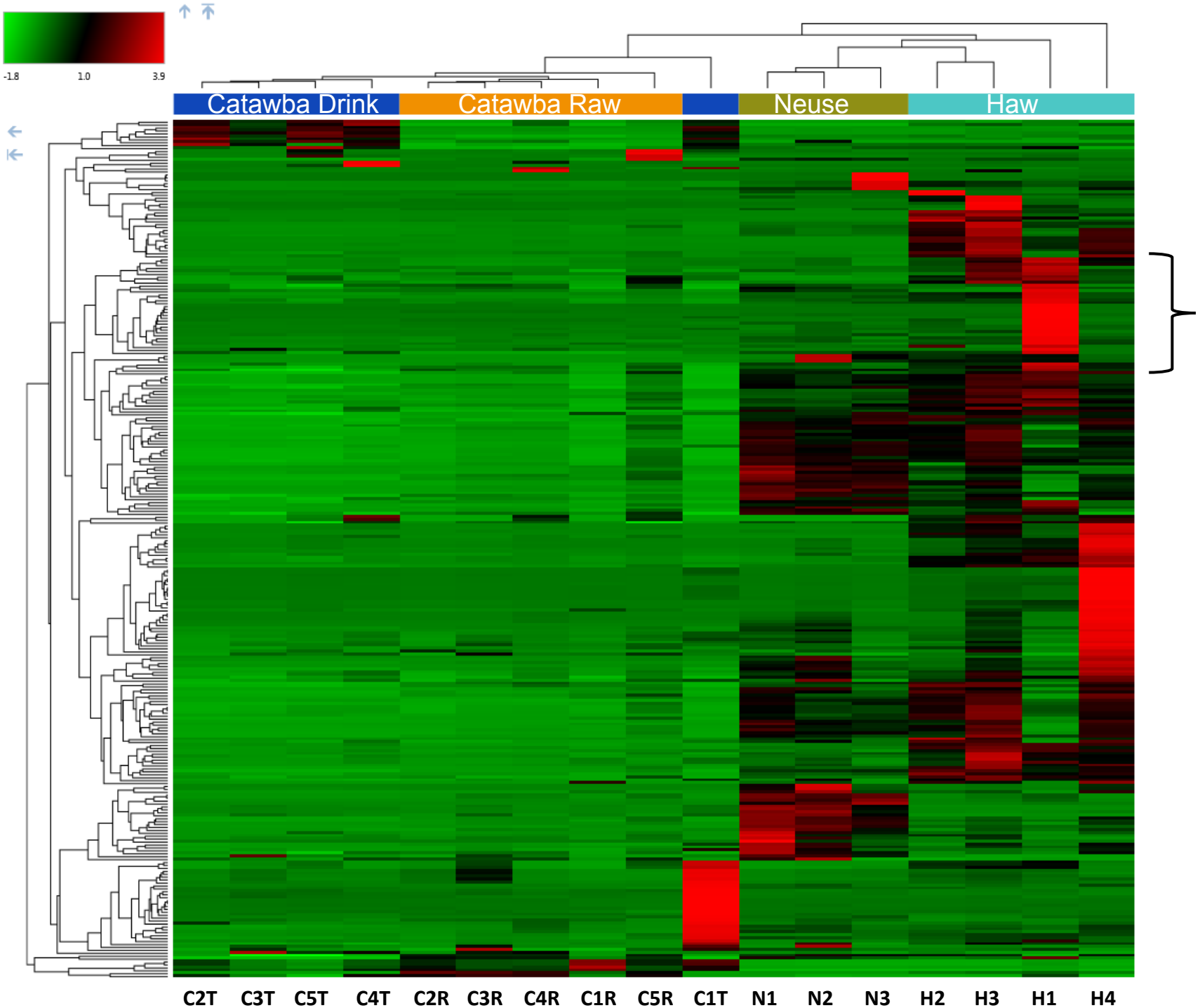
- Discovery of GenX (next-generation PFOA replacement chemical) at high levels in drinking water downstream of a manufacturer on the Cape Fear river has heightened awareness of emerging pollutants in NC waters.
- Collaboration with non-profit riverkeeper alliances and EPA NERL (RTP) established to perform emerging contaminant reconnaissance.
- Initial non-targeted analysis work has focused on source (raw) and treated (drinking) waters in three basins within NC.

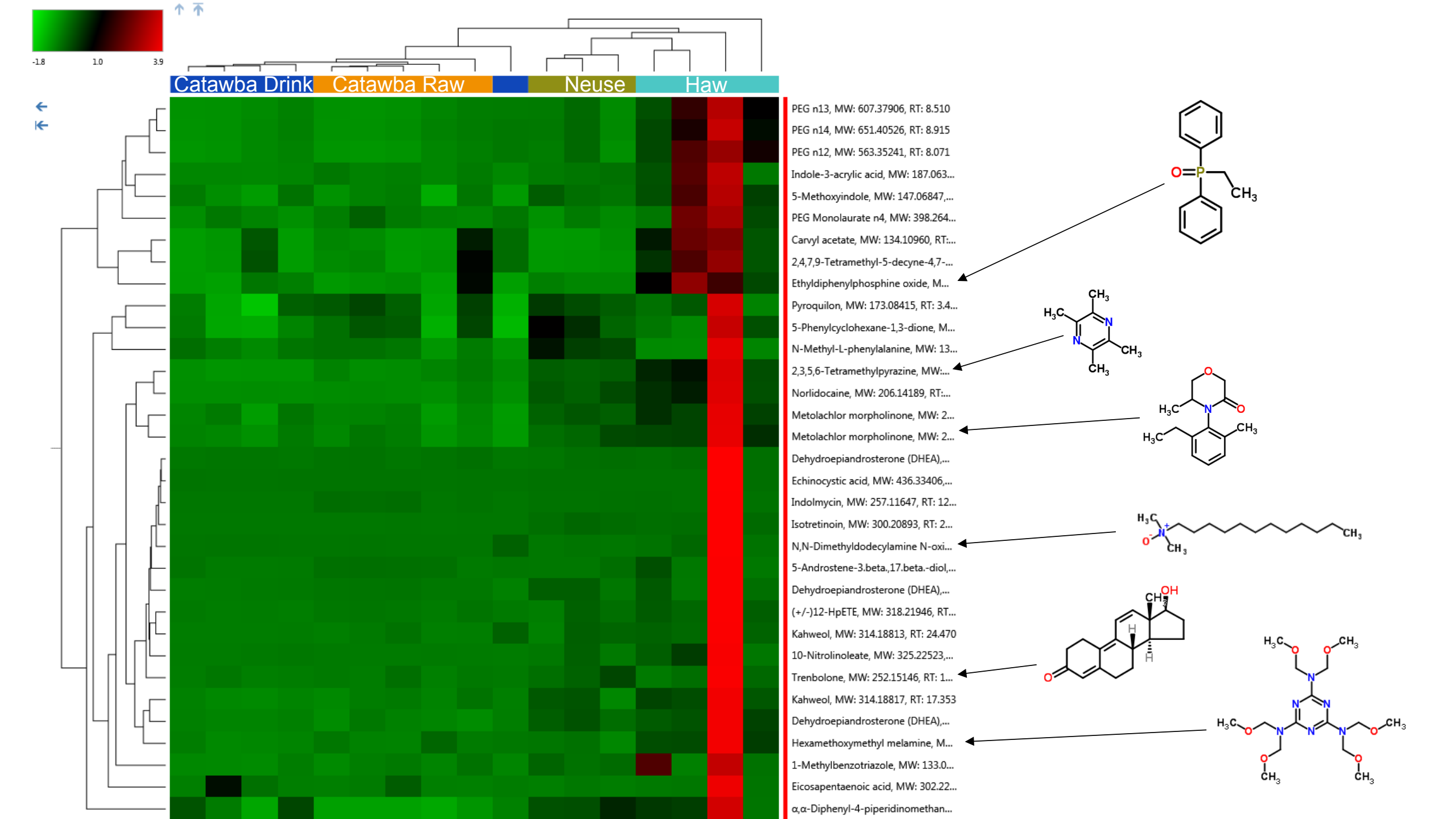


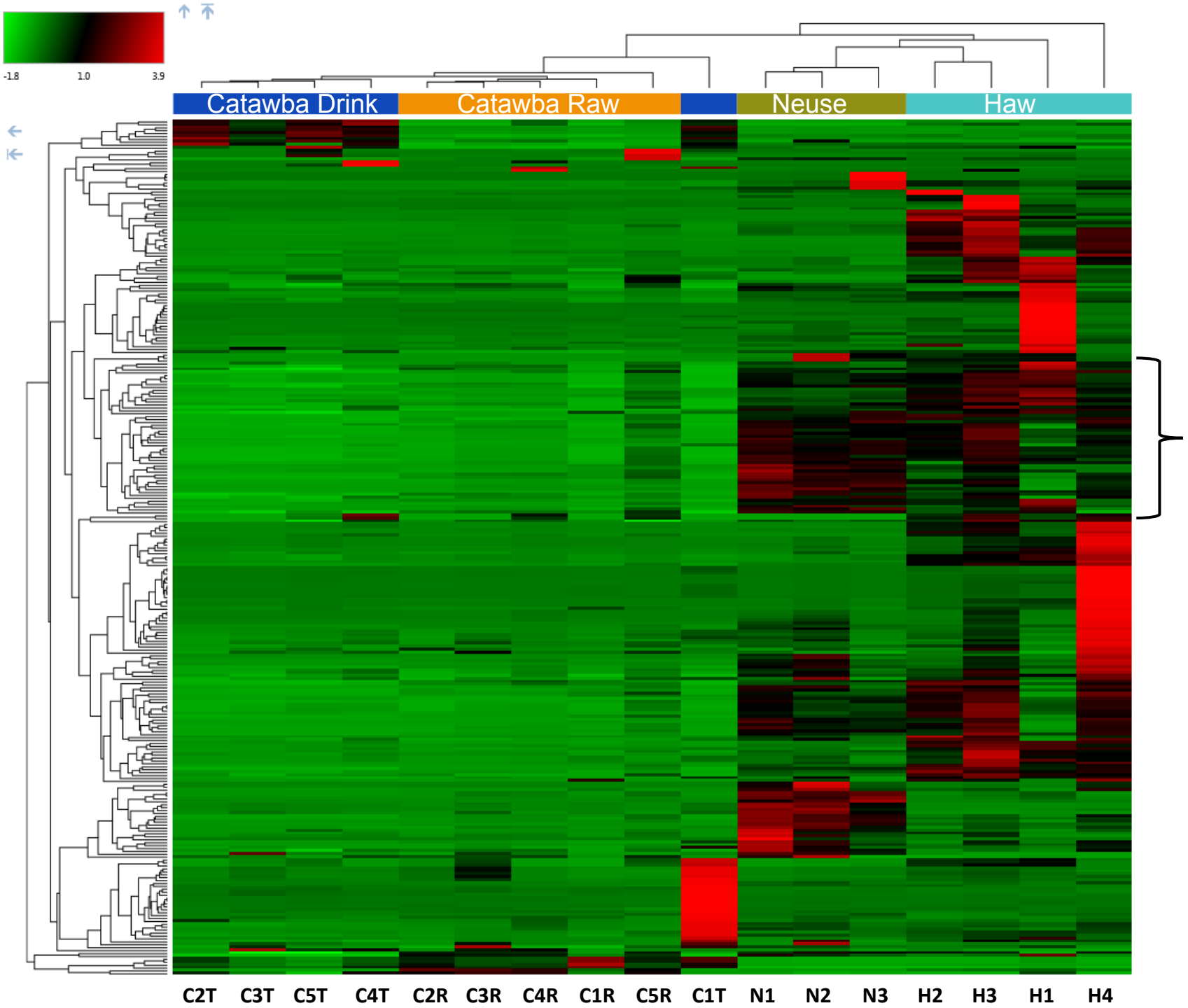
- Non-target analysis by LC-HRMS/MS (Orbitrap Fusion Lumos)
- Positive ion detection only
- Sampling dates:
  - Catawba: 1/24/2018
  - Haw: 3/14/2018
  - Neuse: 3/27/18
- 5,450 Compounds detected
- 293 Compounds with spectral library match > 75%

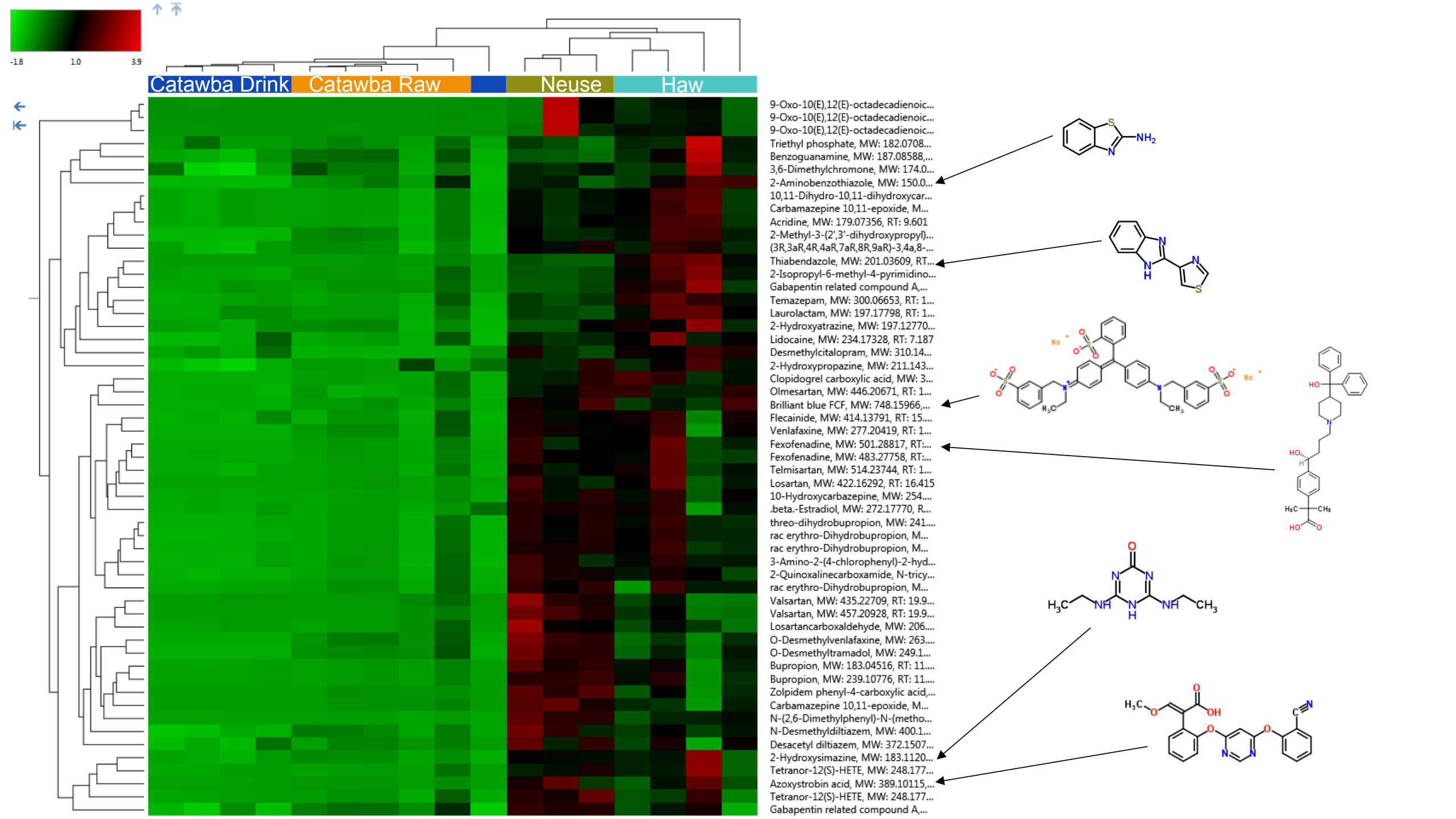
Cluster of compounds enriched within a specific Haw River sample

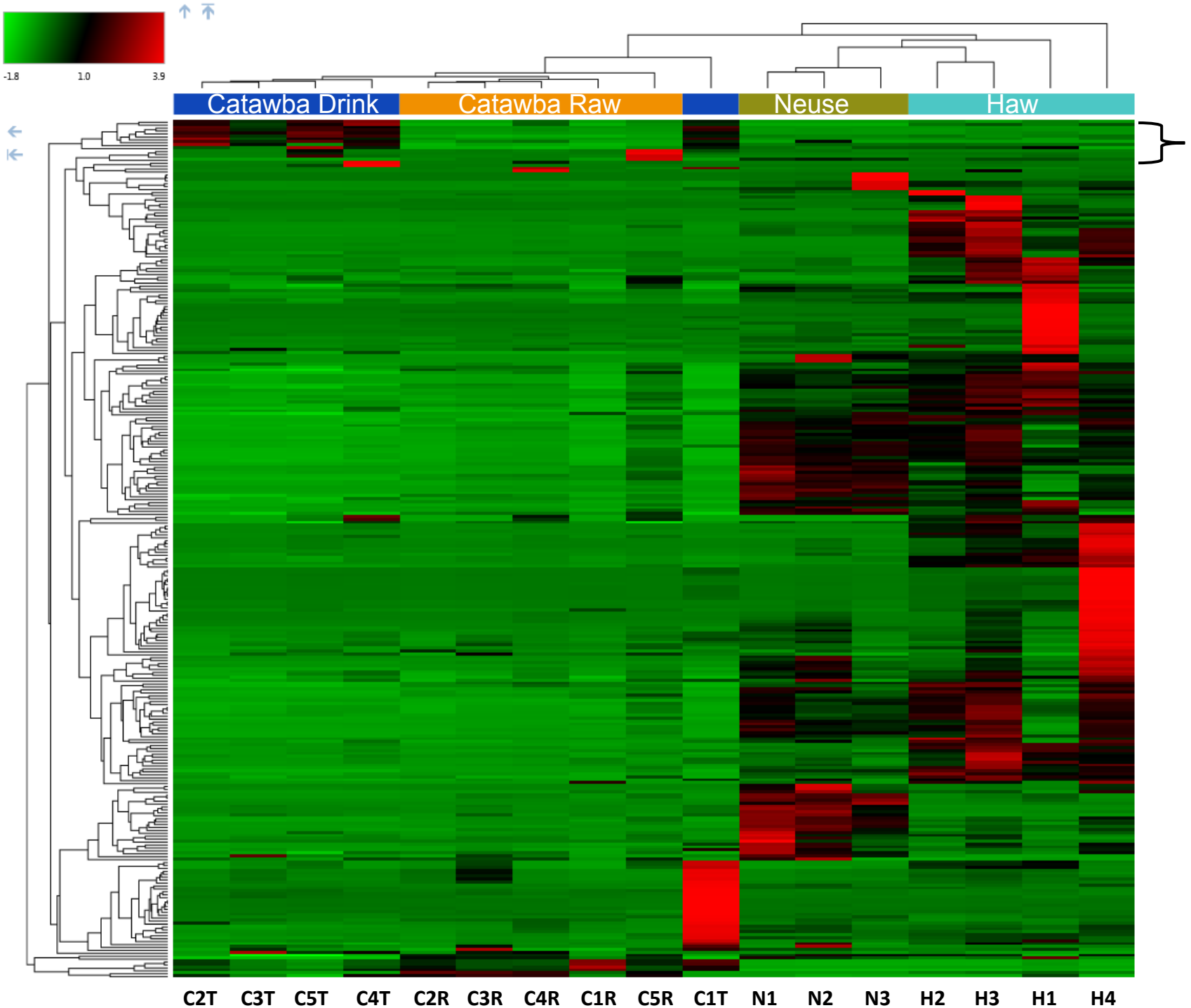

-1.4
1.1
3.7
Catawba Drink
Catawba Raw
Neuse
Haw
N,N-Diethylcathinone, MW: 205.14...
Amfepramone, MW: 205.14667, RT:...
1,5-Isoquinolinediol, MW: 161.047...
1H-Indole-2-carboxylic acid, ethyl...
N-Ethyl-4-methoxybenzamide, M...
7-Hydroxycoumarine, MW: 162.03...
1,5-Isoquinolinediol, MW: 161.047...
Metolachlor, MW: 251.10775, RT: 2...
Metolachlor, MW: 283.13395, RT: 2...
N,N-Diethyl-4-methoxybenzamide,...
4-Methylbenzotriazole, MW: 133.0...
Metaxalone, MW: 160.08887, RT: 2...
4-Nitrosodiphenylamine, MW: 198....
N-Cyclohexyl-2-benzothiazol-amin...
Tributylamine, MW: 185.21428, RT:...
Dicyclohexylamine, MW: 181.18308...
N,N'-Diphenylguanidine, MW: 211....
N-Hexanoyl-DL-homoserine lacton...
Phenamil, MW: 135.07965, RT: 2.053
Indaziflam, MW: 301.17025, RT: 18....
Dioctyl sulfosuccinate, MW: 466.19...
Glaucine, MW: 355.17830, RT: 11.861
8-Hydroxyquinoline, MW: 145.052...
Dimethylaminopurine, MW: 163.08...
Carbamazepine 10,11-epoxide, M...
Riboflavin, MW: 376.13835, RT: 7.353
2-Ethylidene-1,5-dimethyl-3,3-dip...
Methadone, MW: 309.20918, RT: 1...
2-(3,4-Dimethoxyphenyl)-5-methyl...
Atenolol, MW: 266.16312, RT: 3.637
10-Hydroxycarbazepine, MW: 254....
Carbamazepine, MW: 236.09502, R...
Iminostilbene, MW: 193.08918, RT:...
Doxylamine, MW: 181.08917, RT: 5....
Oxycodone, MW: 315.14714, RT: 5....
Levamisole, MW: 204.07219, RT: 5....
4-Hydroxyomeprazole sulfide, MW...
Sitagliptin, MW: 407.11809, RT: 10....
Triamterene, MW: 253.10768, RT: 7....
Ranolazine, MW: 427.24691, RT: 13...
N-Ethylamphetamine, MW: 163.13...
Stercobilin, MW: 594.34254, RT: 14....
2-Hydroxyquinoline, MW: 145.052...
Sucralose, MW: 417.99666, RT: 6.607
4-Hydroxyindole, MW: 133.05280,...
Piperine, MW: 285.13660, RT: 21.217
Tributylphosphine oxide, MW: 218....
5-Methoxyindole, MW: 147.06846,...
4-Methoxycinnamaldehyde, MW: 1...
Methocarbamol, MW: 241.09521, R...
.beta.-Carboline-1-propionic acid,...
Atratone, MW: 211.14333, RT: 7.152
Dodecyltrimethylammonium, MW:...
2-Benzothiazolesulfonic acid, MW:...
5,6-Dimethylbenzimidazole, MW: 1...

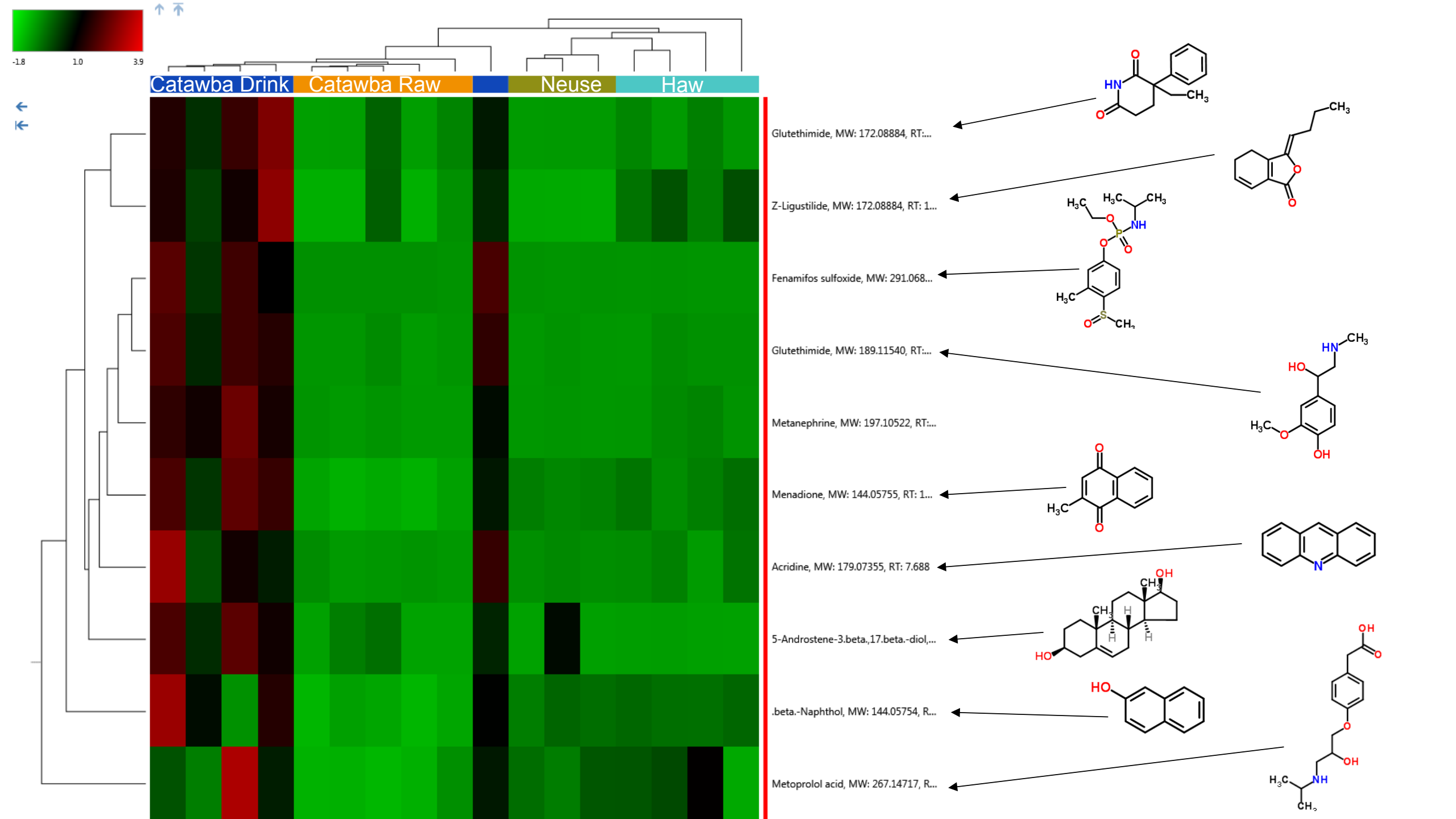

-1.8
1.0
3.9
Catawba Drink
Catawba Raw
Neuse
Haw
C2T
C3T
C5T
C4T
C2R
C3R
C4R
C1R
C5R
C1T
N1
N2
N3
H2
H3
H1
H4

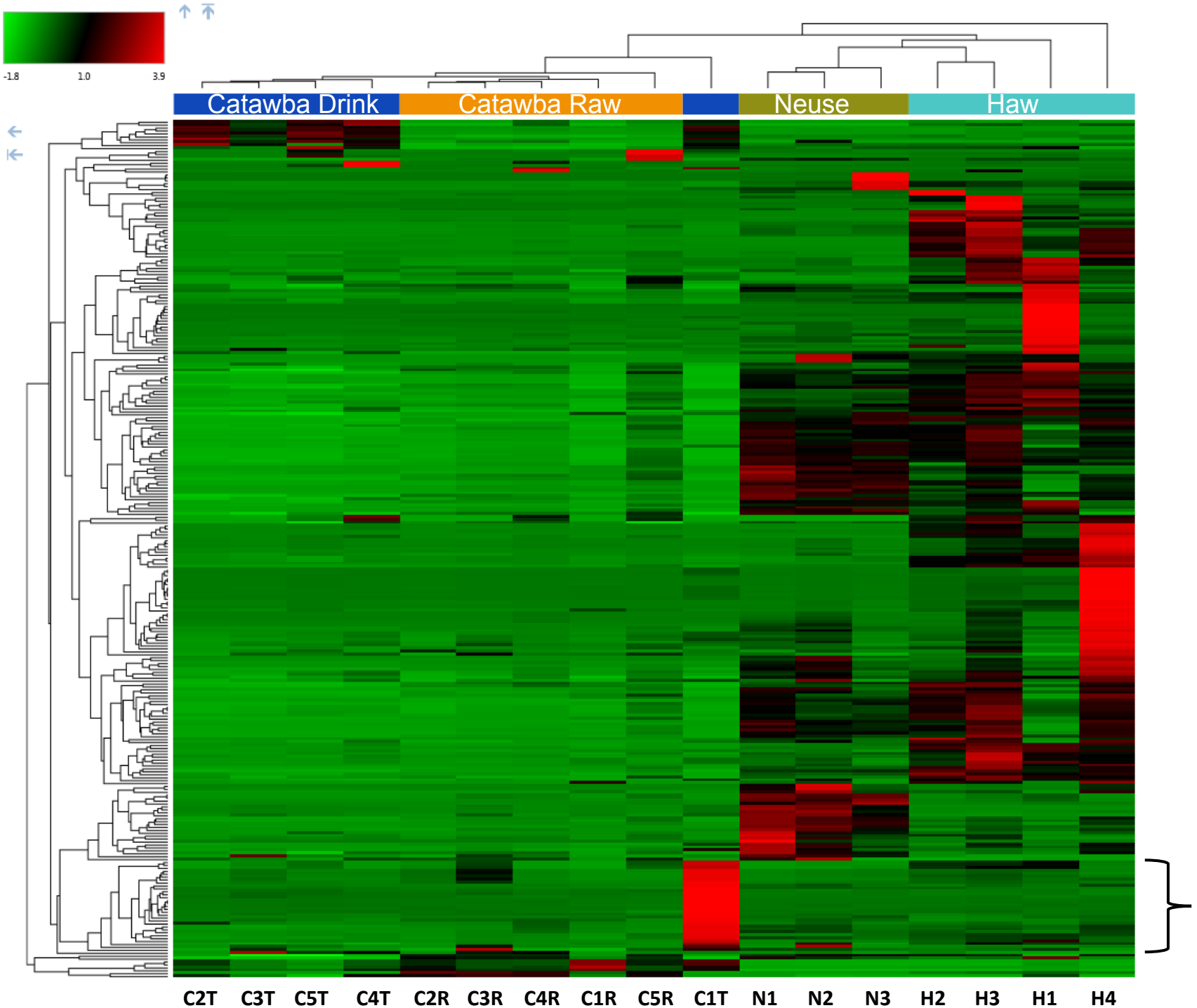

-1.8
1.0
3.9
Catawba Drink
Catawba Raw
Neuse
Haw
PEG n13, MW: 607.37906, RT: 8.510
PEG n14, MW: 651.40526, RT: 8.915
PEG n12, MW: 563.35241, RT: 8.071
Indole-3-acrylic acid, MW: 187.063...
5-Methoxyindole, MW: 147.06847,...
PEG Monolaurate n4, MW: 398.264...
Carvyl acetate, MW: 134.10960, RT:...
2,4,7,9-Tetramethyl-5-decyne-4,7-...
Ethyldiphenylphosphine oxide, M...
Pyroquilon, MW: 173.08415, RT: 3.4...
5-Phenylcyclohexane-1,3-dione, M...
N-Methyl-L-phenylalanine, MW: 13...
2,3,5,6-Tetramethylpyrazine, MW:...
Norlidocaine, MW: 206.14189, RT:...
Metolachlor morpholinone, MW: 2...
Metolachlor morpholinone, MW: 2...
Dehydroepiandrosterone (DHEA),...
Echinocystic acid, MW: 436.33406,...
Indolmycin, MW: 257.11647, RT: 12...
Isotretinoin, MW: 300.20893, RT: 2...
N,N-Dimethyldodecylamine N-oxi...
5-Androstene-3.beta.,17.beta.-diol,...
Dehydroepiandrosterone (DHEA),...
(+/-)12-HpETE, MW: 318.21946, RT...
Kahweol, MW: 314.18813, RT: 24.470
10-Nitrolinoleate, MW: 325.22523,...
Trenbolone, MW: 252.15146, RT: 1...
Kahweol, MW: 314.18817, RT: 17.353
Dehydroepiandrosterone (DHEA),...
Hexamethoxymethyl melamine, M...
1-Methylbenzotriazole, MW: 133.0...
Eicosapentaenoic acid, MW: 302.22...
α,α-Diphenyl-4-piperidinomethan...

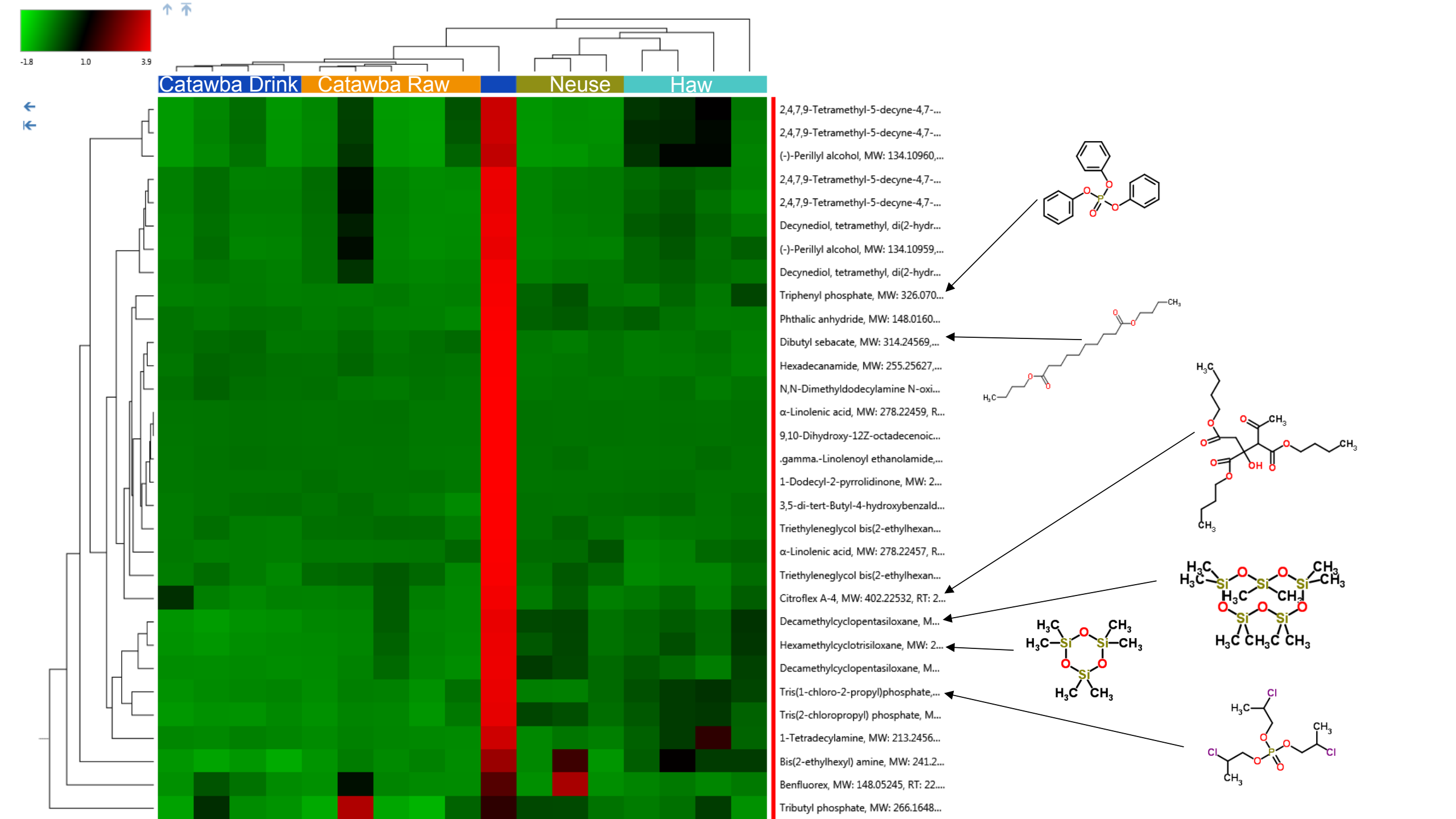

-1.8
1.0
3.9
Catawba Drink
Catawba Raw
Neuse
Haw
C2T
C3T
C5T
C4T
C2R
C3R
C4R
C1R
C5R
C1T
N1
N2
N3
H2
H3
H1
H4


-1.8
1.0
3.9
Catawba Drink
Catawba Raw
Neuse
Haw
9-Oxo-10(E),12(E)-octadecadienoic...
9-Oxo-10(E),12(E)-octadecadienoic...
9-Oxo-10(E),12(E)-octadecadienoic...
Triethyl phosphate, MW: 182.0708...
Benzoguanamine, MW: 187.08588,...
3,6-Dimethylchromone, MW: 174.0...
2-Aminobenzothiazole, MW: 150.0...
10,11-Dihydro-10,11-dihydroxycar...
Carbamazepine 10,11-epoxide, M...
Acridine, MW: 179.07356, RT: 9.601
2-Methyl-3-(2',3'-dihydroxypropyl)...
(3R,3aR,4R,4aR,7aR,8R,9aR)-3,4a,8-...
Thiabendazole, MW: 201.03609, RT...
2-Isopropyl-6-methyl-4-pyrimidino...
Gabapentin related compound A,...
Temazepam, MW: 300.06653, RT: 1...
Laurolactam, MW: 197.17798, RT: 1...
2-Hydroxyatrazine, MW: 197.12770...
Lidocaine, MW: 234.17328, RT: 7.187
Desmethylcitalopram, MW: 310.14...
2-Hydroxypropazine, MW: 211.143...
Clopidogrel carboxylic acid, MW: 3...
Olmesartan, MW: 446.20671, RT: 1...
Brilliant blue FCF, MW: 748.15966,...
Flecainide, MW: 414.13791, RT: 15....
Venlafaxine, MW: 277.20419, RT: 1...
Fexofenadine, MW: 501.28817, RT:...
Fexofenadine, MW: 483.27758, RT:...
Telmisartan, MW: 514.23744, RT: 1...
Losartan, MW: 422.16292, RT: 16.415
10-Hydroxycarbazepine, MW: 254....
.beta.-Estradiol, MW: 272.17770, R...
threo-dihydrobupropion, MW: 241....
rac erythro-Dihydrobupropion, M...
rac erythro-Dihydrobupropion, M...
3-Amino-2-(4-chlorophenyl)-2-hyd...
2-Quinoxalinecarboxamide, N-tricy...
rac erythro-Dihydrobupropion, M...
Valsartan, MW: 435.22709, RT: 19.9...
Valsartan, MW: 457.20928, RT: 19.9...
Losartancarboxaldehyde, MW: 206....
O-Desmethylvenlafaxine, MW: 263....
O-Desmethyltramadol, MW: 249.1...
Bupropion, MW: 183.04516, RT: 11....
Bupropion, MW: 239.10776, RT: 11....
Zolpidem phenyl-4-carboxylic acid,...
Carbamazepine 10,11-epoxide, M...
N-(2,6-Dimethylphenyl)-N-(metho...
N-Desmethyldiltiazem, MW: 400.1...
Desacetyl diltiazem, MW: 372.1507...
2-Hydroxysimazine, MW: 183.1120...
Tetranor-12(S)-HETE, MW: 248.177...
Azoxystrobin acid, MW: 389.10115,...
Tetranor-12(S)-HETE, MW: 248.177...
Gabapentin related compound A,...


-1.8
1.0
3.9
Catawba Drink
Catawba Raw
Neuse
Haw
C2T
C3T
C5T
C4T
C2R
C3R
C4R
C1R
C5R
C1T
N1
N2
N3
H2
H3
H1
H4


-1.8
1.0
3.9
Catawba Drink
Catawba Raw
Neuse
Haw
Glutethimide, MW: 172.08884, RT:...
Z-Ligustilide, MW: 172.08884, RT: 1...
Fenamifos sulfoxide, MW: 291.068...
Glutethimide, MW: 189.11540, RT:...
Metanephrine, MW: 197.10522, RT:...
Menadione, MW: 144.05755, RT: 1...
Acridine, MW: 179.07355, RT: 7.688
5-Androstene-3.beta.,17.beta.-diol,...
.beta.-Naphthol, MW: 144.05754, R...
Metoprolol acid, MW: 267.14717, R...


-1.8
1.0
3.9
Catawba Drink
Catawba Raw
Neuse
Haw
C2T
C3T
C5T
C4T
C2R
C3R
C4R
C1R
C5R
C1T
N1
N2
N3
H2
H3
H1
H4


-1.8
1.0
3.9
Catawba Drink
Catawba Raw
Neuse
Haw
2,4,7,9-Tetramethyl-5-decyne-4,7-...
2,4,7,9-Tetramethyl-5-decyne-4,7-...
(-)-Perillyl alcohol, MW: 134.10960,...
2,4,7,9-Tetramethyl-5-decyne-4,7-...
2,4,7,9-Tetramethyl-5-decyne-4,7-...
Decynediol, tetramethyl, di(2-hydr...
(-)-Perillyl alcohol, MW: 134.10959,...
Decynediol, tetramethyl, di(2-hydr...
Triphenyl phosphate, MW: 326.070...
Phthalic anhydride, MW: 148.0160...
Dibutyl sebacate, MW: 314.24569,...
Hexadecanamide, MW: 255.25627,...
N,N-Dimethyldodecylamine N-oxi...
α-Linolenic acid, MW: 278.22459, R...
9,10-Dihydroxy-12Z-octadecenoic...
.gamma.-Linolenoyl ethanolamide,...
1-Dodecyl-2-pyrrolidinone, MW: 2...
3,5-di-tert-Butyl-4-hydroxybenzald...
Triethyleneglycol bis(2-ethylhexan...
α-Linolenic acid, MW: 278.22457, R...
Triethyleneglycol bis(2-ethylhexan...
Citroflex A-4, MW: 402.22532, RT: 2...
Decamethylcyclopentasiloxane, M...
Hexamethylcyclotrisiloxane, MW: 2...
Decamethylcyclopentasiloxane, M...
Tris(1-chloro-2-propyl)phosphate,...
Tris(2-chloropropyl) phosphate, M...
1-Tetradecylamine, MW: 213.2456...
Bis(2-ethylhexyl) amine, MW: 241.2...
Benfluorex, MW: 148.05245, RT: 22....
Tributyl phosphate, MW: 266.1648...

Conclusions: NC River monitoring

- A wide range of unregulated emerging contaminants were detectable in river waters across the state of North Carolina.
- Abundant compounds in the Haw River watershed included markers of urban stormwater, including tire-related chemicals and polymer additives.
- The Neuse river showed evidence of agrochemical contamination, consistent with land-use practices in the watershed.
- Non-targeted analysis of paired raw/drinking water revealed disinfection byproducts and suspected piping-derived polymer additive chemicals in finished drinking waters.

Future directions

- Statistically-sound, comprehensive identification of organic pollutants in water using a harmonized workflow: *in silico* MS/MS and evidence-based prioritization (moving beyond library matching).
- Application of computational transformation product prediction from identified “leads” for drilling-down into possible pollutant TP identifications.
- Enhanced prioritization of compound identification using pairwise differential analysis among spatial and temporal samples.
- Annotation of compound identifications by molecular ontology, functional use, and toxicity data/predictions using open-source tools including EPA CompTox Dashboard.

Acknowledgements

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- Richard Jack

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- Staff of the Regional Monitoring Program
- Participating wastewater treatment plants

Ferguson Lab Group

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- Tara Sabo Attwood (U. Florida)
- Mark Strynar (US EPA)

NC Riverkeepers Alliance
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- Sam Perkins (Catawba River)
- Matthew Starr (Neuse River)