Screening of Influent and Effluent Water in Sewage Treatment Plants

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Questions

- What slips through Sewage Treatment Plants (STPs)?
- Common structural features?
- Sources?
- Suitable Methodology for Digital Banking?

C-omics

At last, the mystery of the Mayan calendar revealed.

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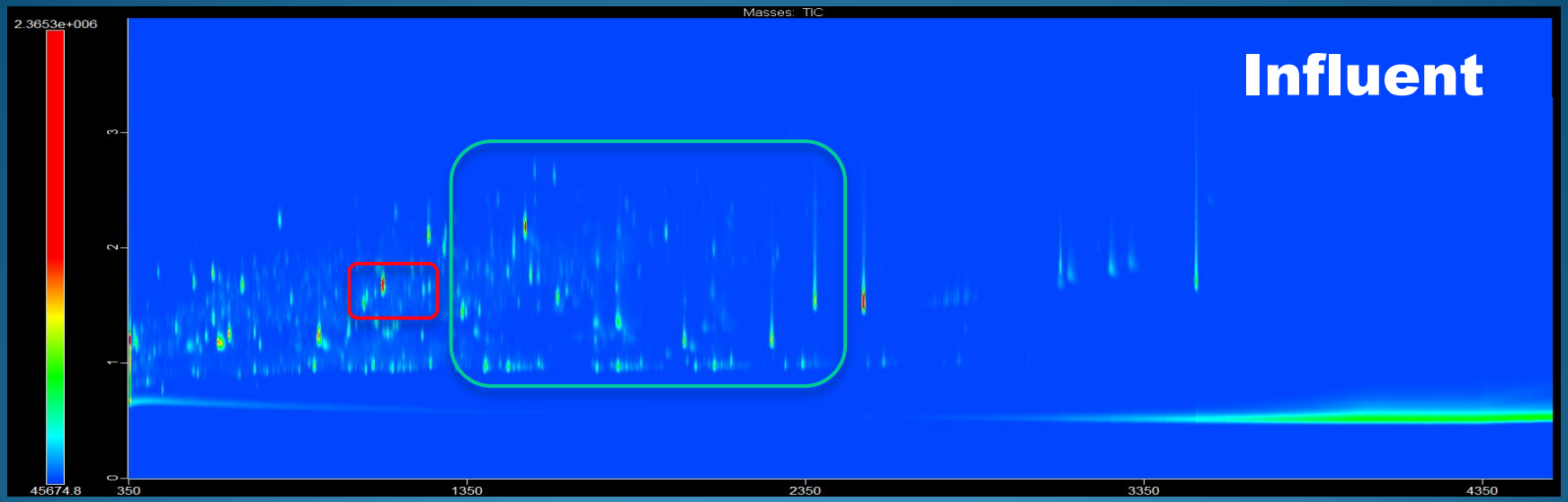
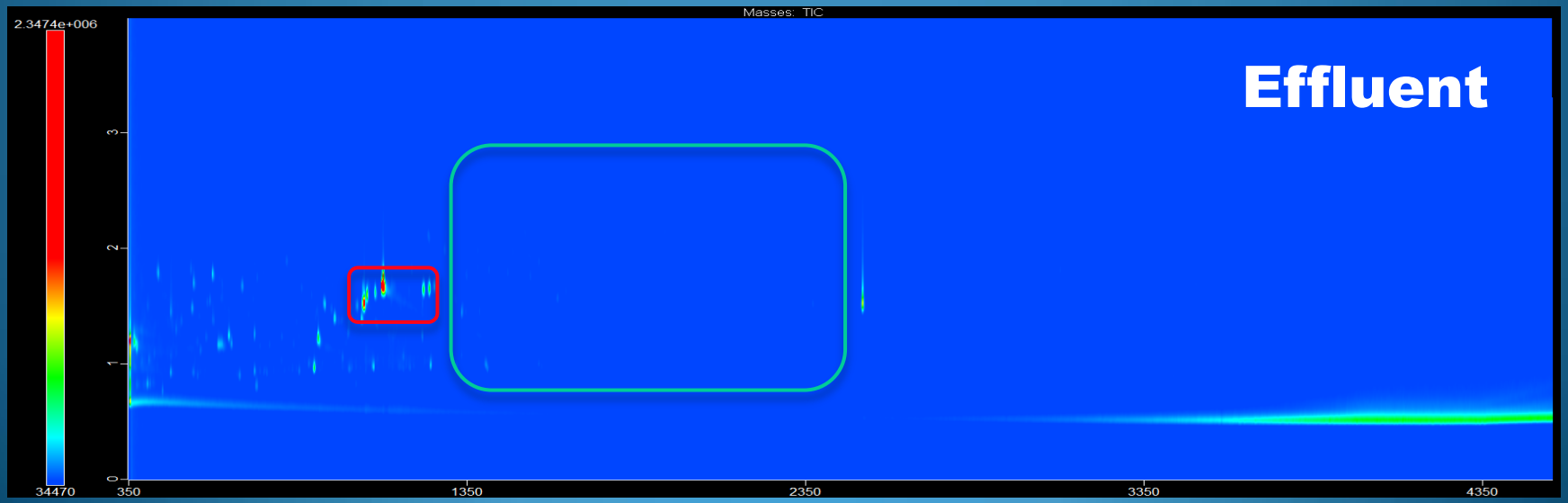
GC×GC-ToF-MS

- Primary separation based on volatility
- Secondary separation based on polarity, polarizability, H-bonding ability, shape, etc.
- Excellent peak capacity
- Good sensitivity
- GC×GC-ToF-MS
  - 3D data
  - Deconvolution of peaks and spectra
  - Exceptional separation power

Sewage treatment plant water

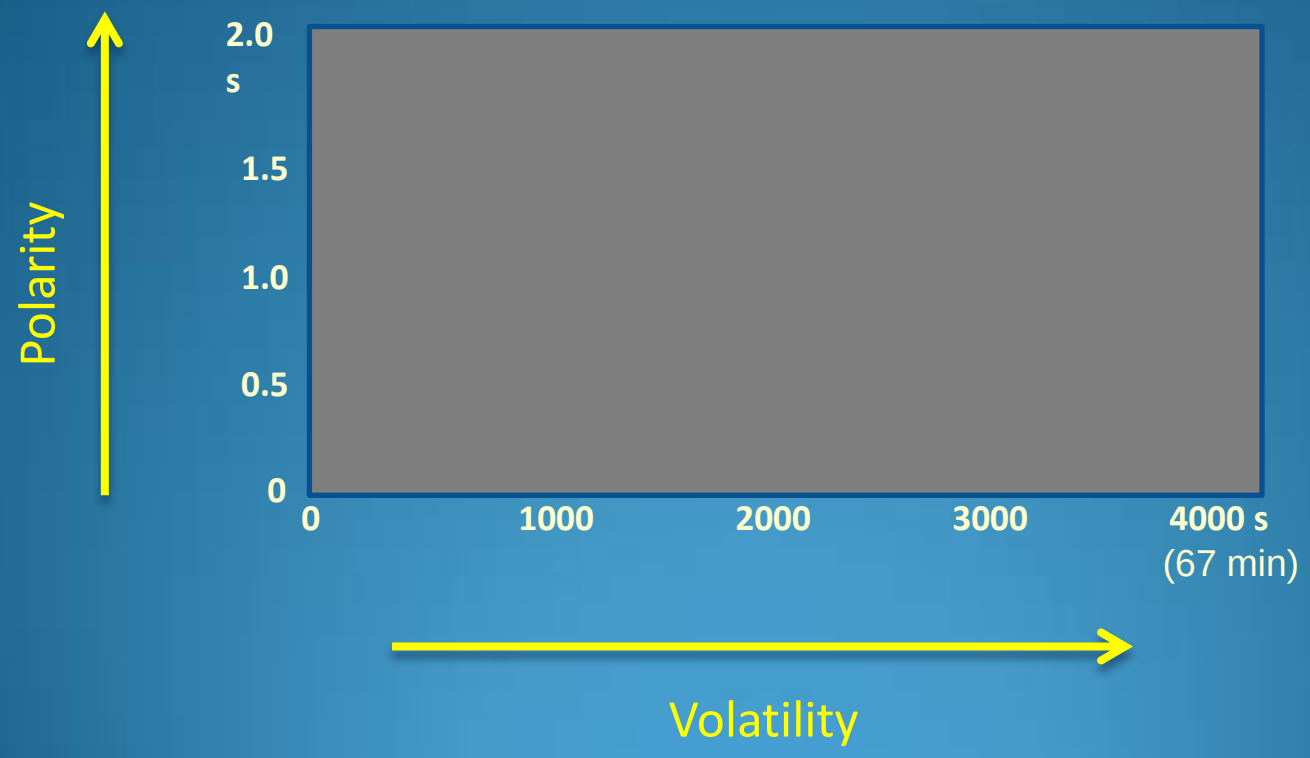




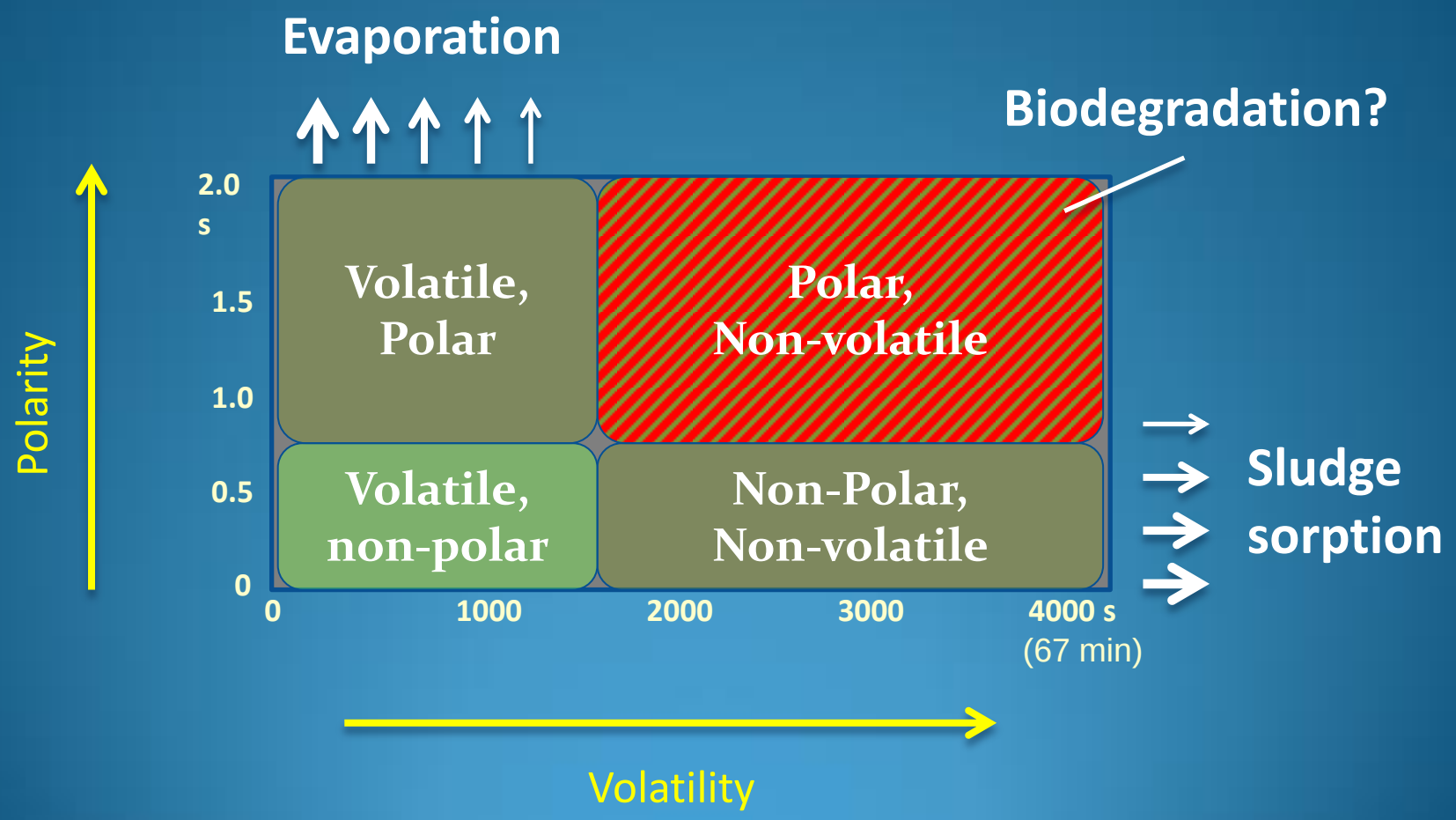
STP efficiency evaluation

- All peaks (compounds) are detected and integrated
- A composite influent water used as template to which all samples (effluent and influent) were compared.
  - Effluent/influent << 1, **treatment successful**
  - Effluent/influent ratio = 1, **treatment failed**
  - Effluent/influent > 1, **transformation product**
- Data evaluation: focus on POPs and Semi-POPs

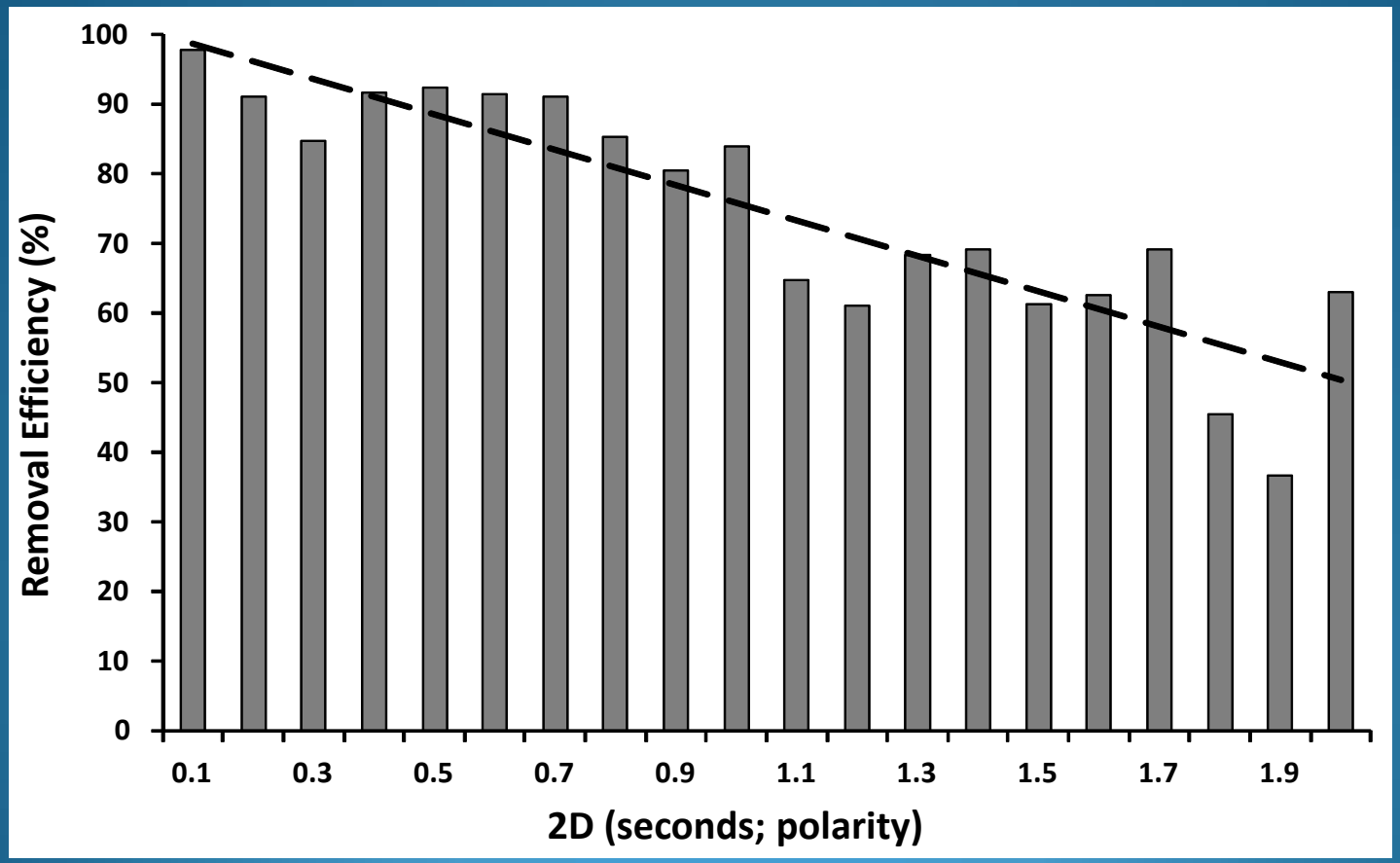
Expected STP Removal vs. RT



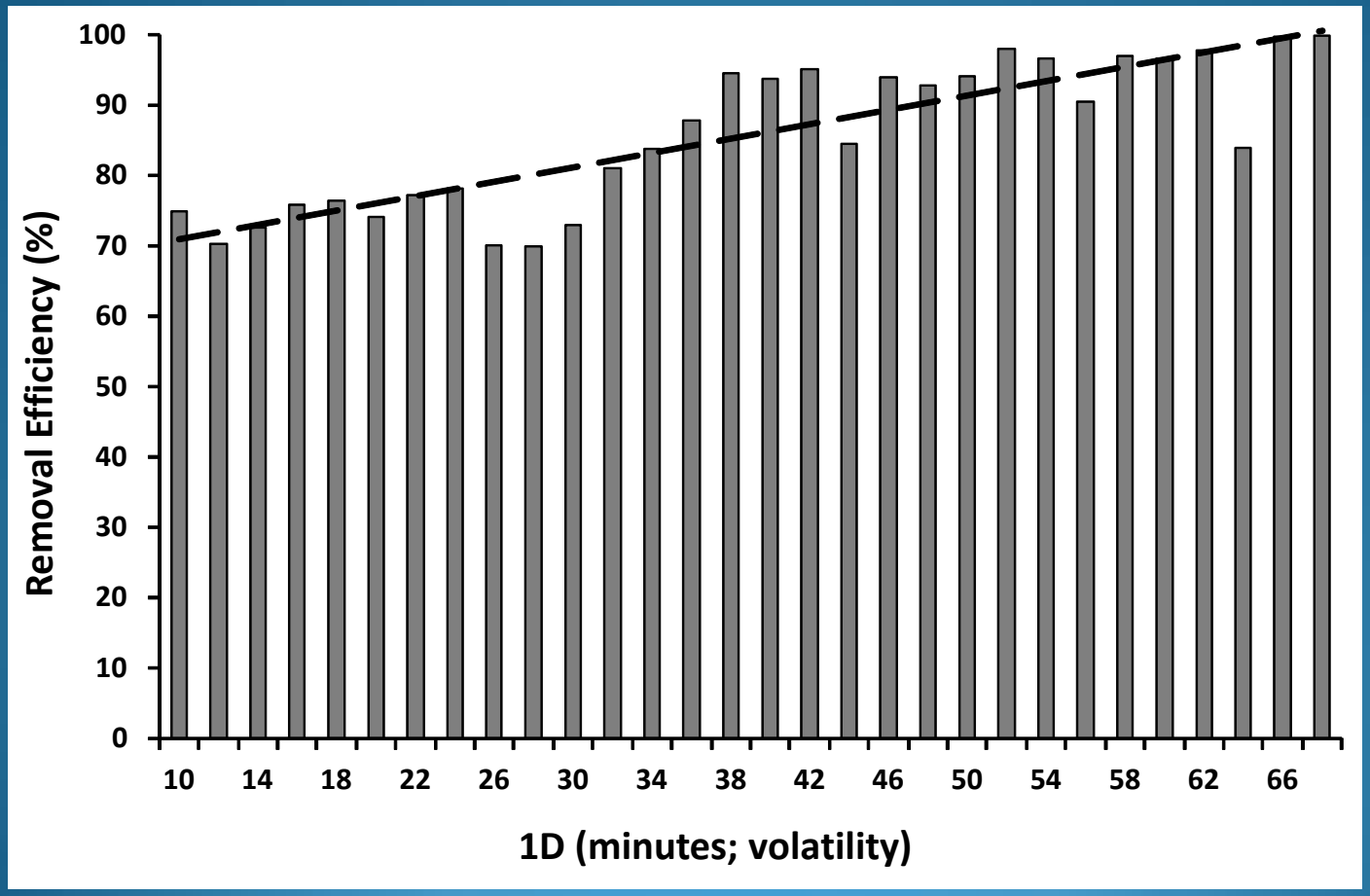
Expected STP Removal vs. RT



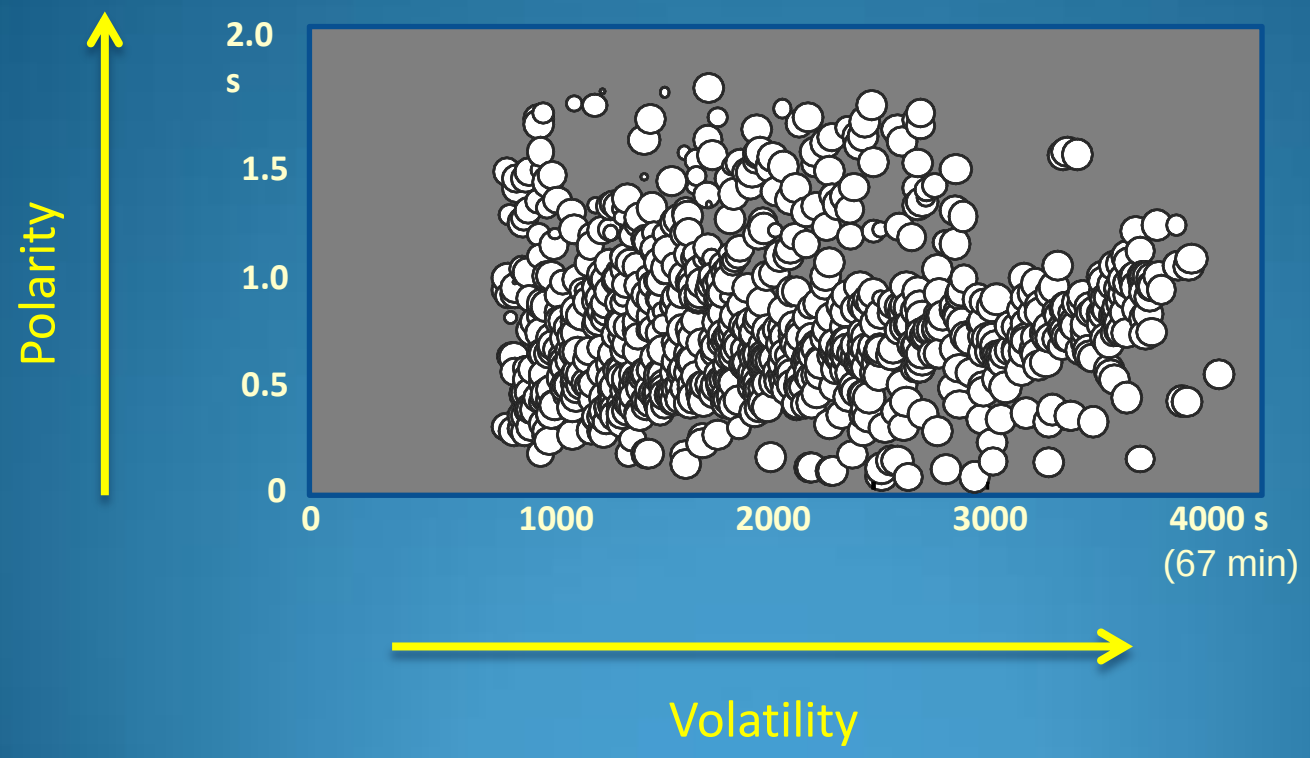
Removal vs. ^{2}D-retention



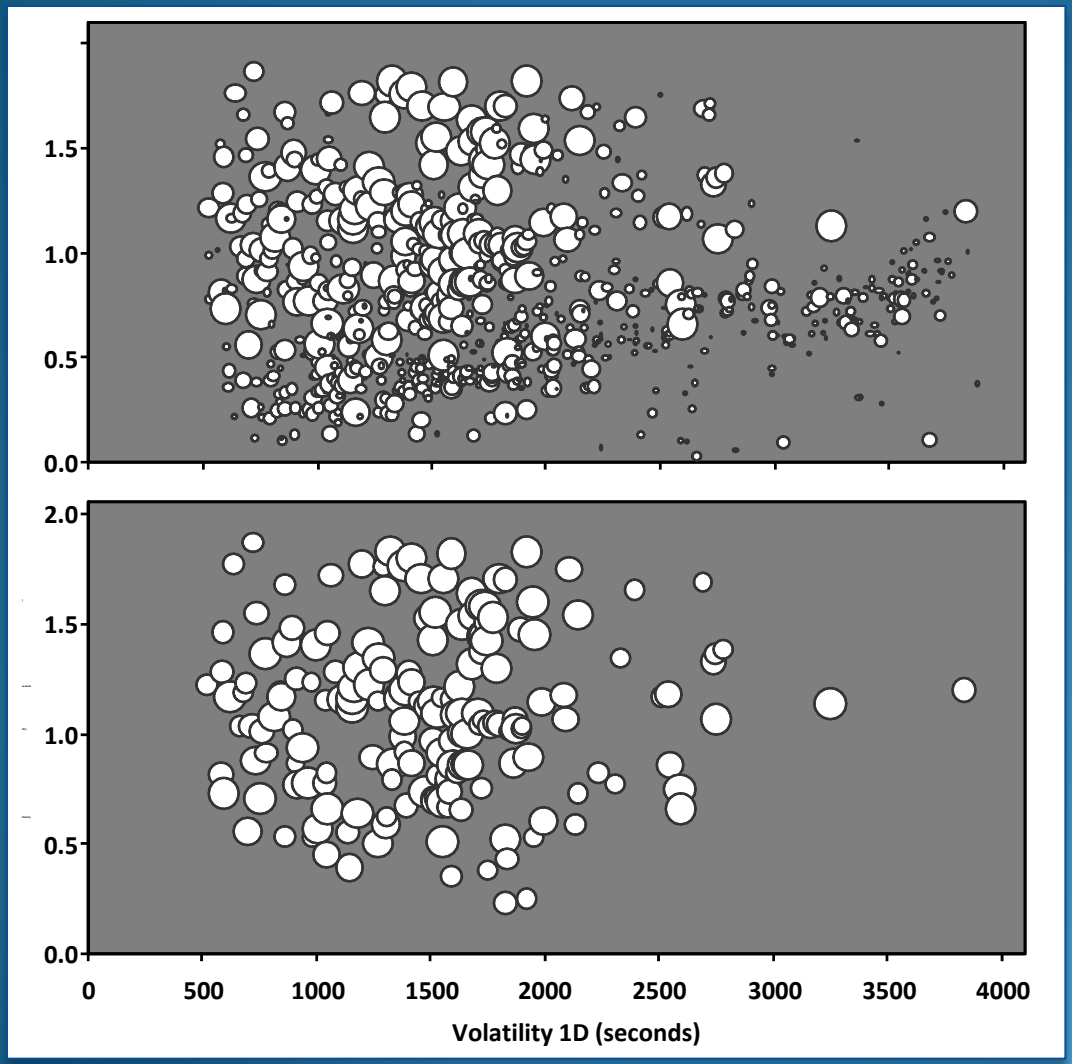
Removal vs. ^{1}D-retention



Bubble Plot of % STP Removal



STP Breakthrough %



> 35%

188 compounds

(1/3 or more is passing the STP)

Identification Workflow

1. NIST library search
2. Manual evaluation of peaks with "similarity" >75%
3. Semi-quantification *vs.* IS (D_{10}-Phenanthrene)
4. Verification using GCxGC-HR-ToF-MS

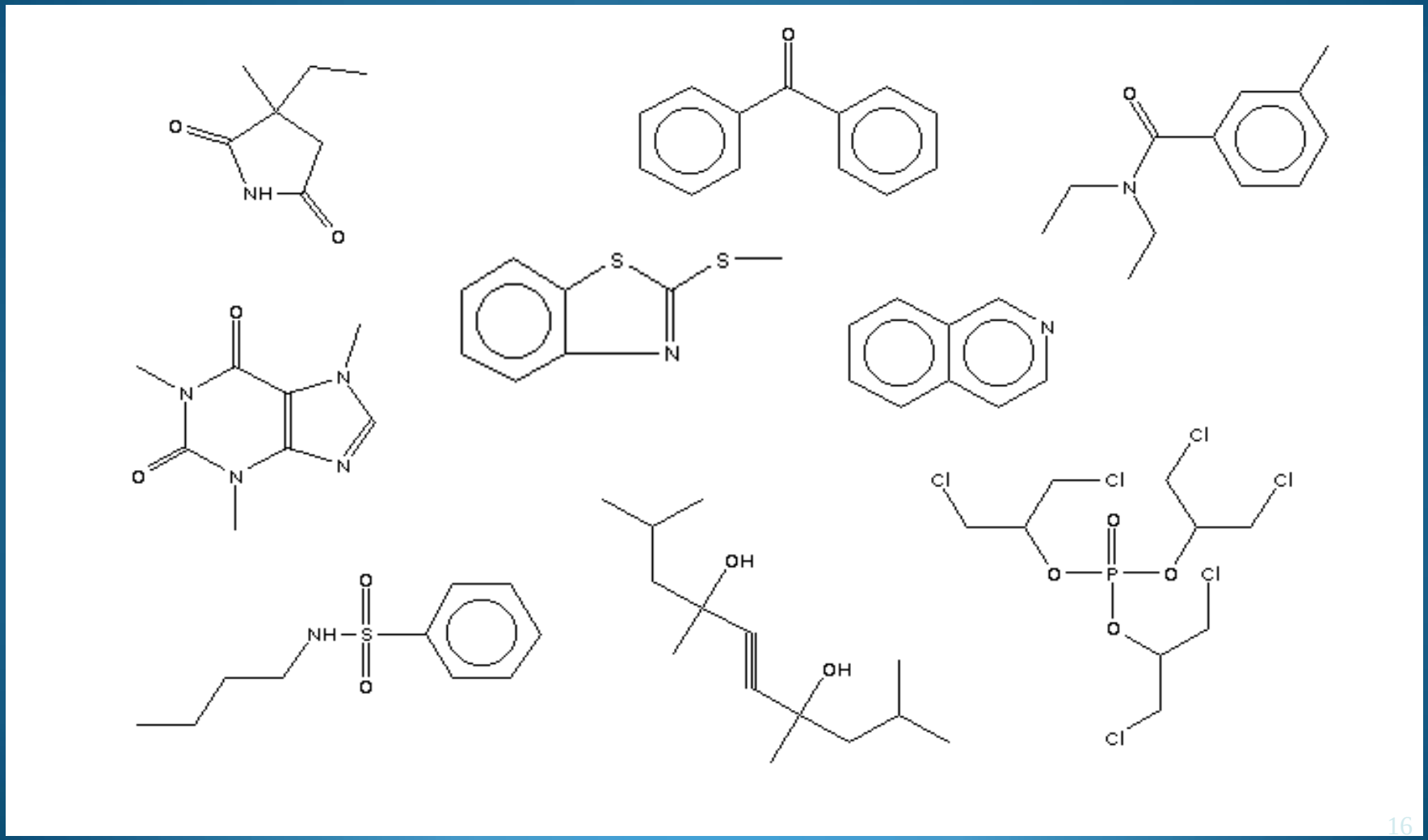
Tentatively Identified (n = 69/188)

Tentative name	Effluent (ng/L)	Retention time (s)		Break-through (%)	Origin
		^{1}D (s)	^{2}D (s)		
2,4,7,9-Tetramethyl-5-decyn-4,7-diol	12000	1042	0.46	73	Defoamer in paint
Benzenesulfonamide, N-butyl-	5500	1770	1.53	100	Plasticizer
Tris(butoxyethyl) phosphate	3600	2586	0.75	100	Floor polish
Benzothiazole, 2-(methylthio)-	2200	1454	1.70	100	Rubber industry
Tris(3-chloropropyl) phosphate (TCPP 1)	1500	1758	1.04	67	Flame retardant
Benzophenone	930	1494	1.53	100	UV initiator
Benzothiazole, 2-(methylthio) derivative?	650	1820	0.23	56	Rubber industry
Ethyl citrate	520	1506	0.97	71	Plasticizer, food additive
Caffeine	460	1916	1.82	100	Coffee, soft drinks
Tris(3-chloropropyl) phosphate (TCPP 2)	390	1780	1.05	63	Flame retardant
Tris(2-chloroethyl) phosphate	360	1726	1.44	100	Flame retardant
2,2,2-Trichloro-1-phenylethanol	320	1268	1.34	100	Flavor and fragrance
Oxybenzone	230	2144	1.54	100	Cosmetics, sunscreen
4-*tert*-butyl-cyclohexanone	220	750	0.71	100	Cosmetics, fragrance
Ethosuximide	150	812	1.08	98	Pharmaceutical
Tris(1,3-dichloroisopropyl) phosphate	150	2534	1.39	72	Flame retardant
Isoquinoline	140	770	1.18	100	Traffic
4-*tert*-octyl-phenol	140	1410	0.96	69	Surfactants; resins
Diethyltoluamide (DEET)	110	1386	1.20	100	Insect repellent
Benzenesulfonamide, N-ethyl-2-methyl-	100	1554	1.70	100	Plasticizer
2,3,6,7-Tetramethylquinoxaline	100	1586	1.16	56	Traffic

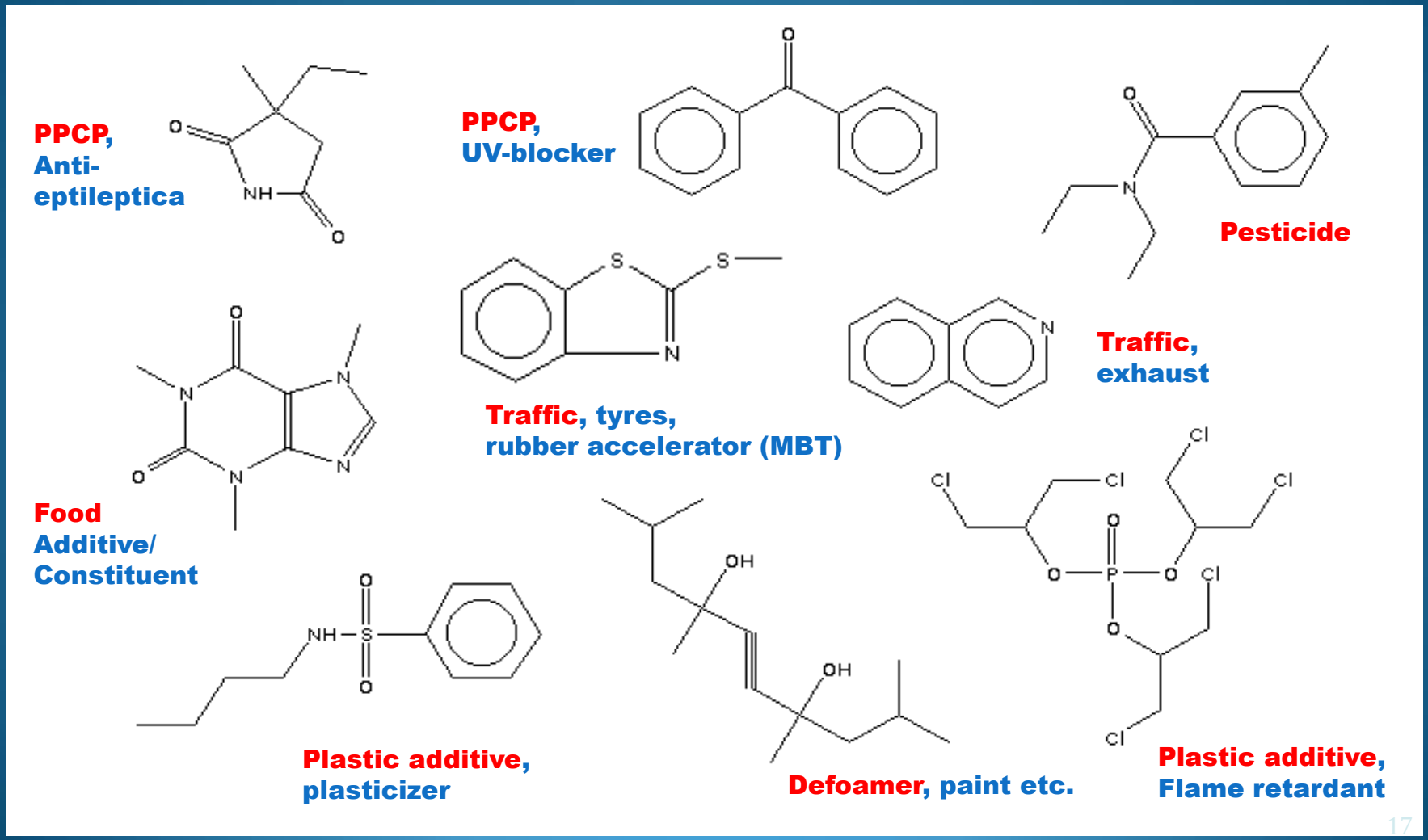
Results breakdown

- Expected Stuff…
- Stuff in Stuff…
- Stuff made from Stuff…

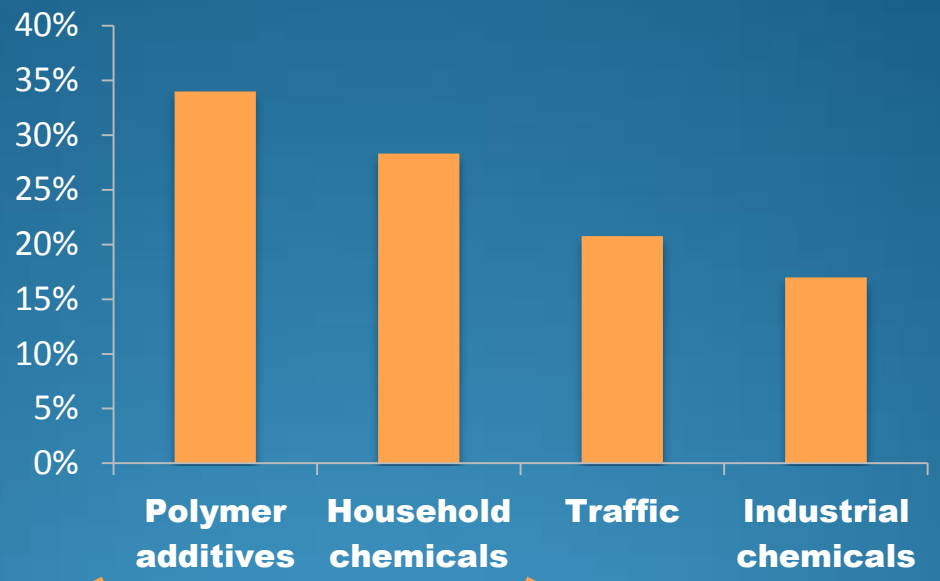
The Stuff…

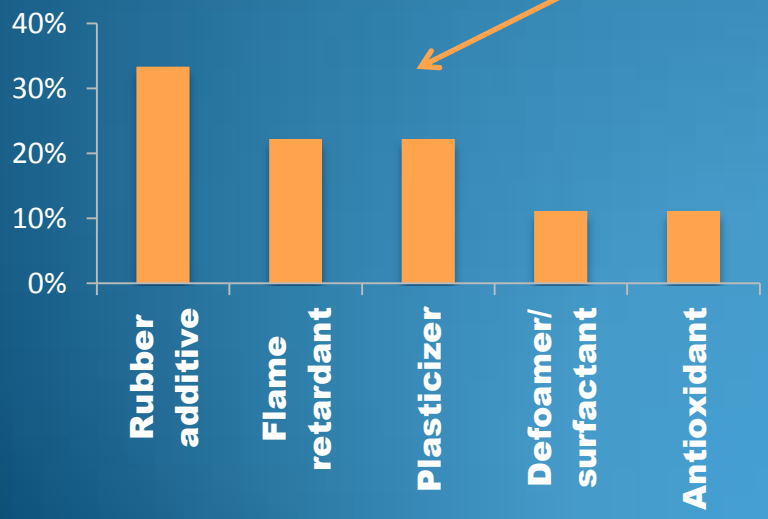


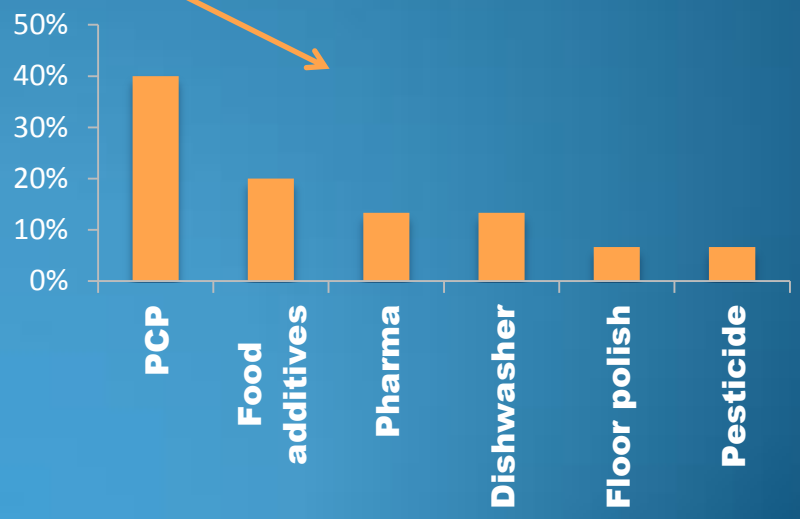
Sources


PPCP,
Anti-
eptileptica
PPCP,
UV-blocker
Pesticide
Traffic,
exhaust
Traffic, tyres,
rubber accelerator (MBT)
Food
Additive/
Constituent
Plastic additive,
plasticizer
Defoamer, paint etc.
Plastic additive,
Flame retardant

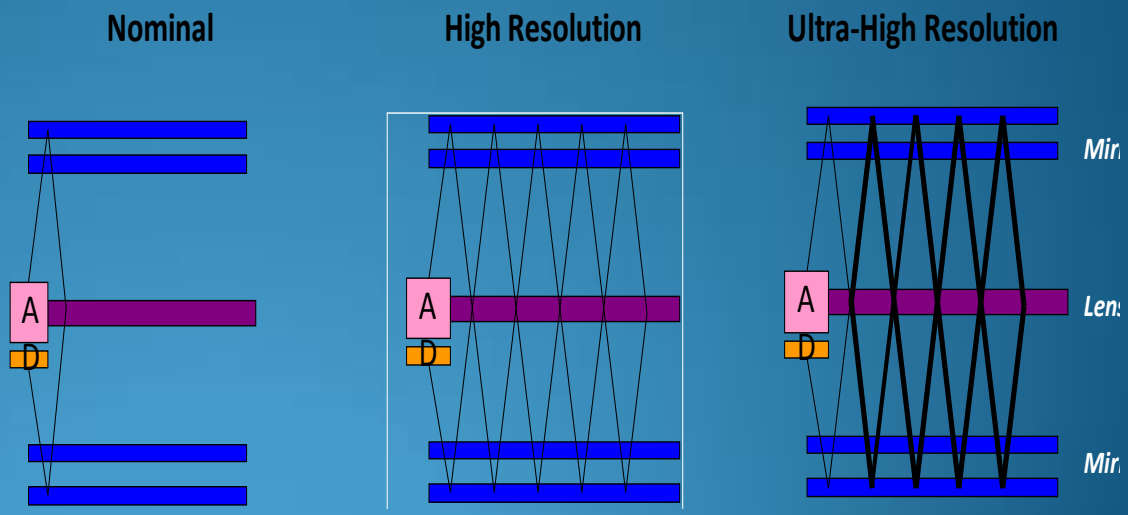
Origin


40%
35%
30%
25%
20%
15%
10%
5%
0%
Polymer additives
Household chemicals
Traffic
Industrial chemicals


40%
30%
20%
10%
0%
Rubber additive
Flame retardant
Plasticizer
Defoamer/ surfactant
Antioxidant


50%
40%
30%
20%
10%
0%
PCP
Food additives
Pharma
Dishwasher
Floor polish
Pesticide

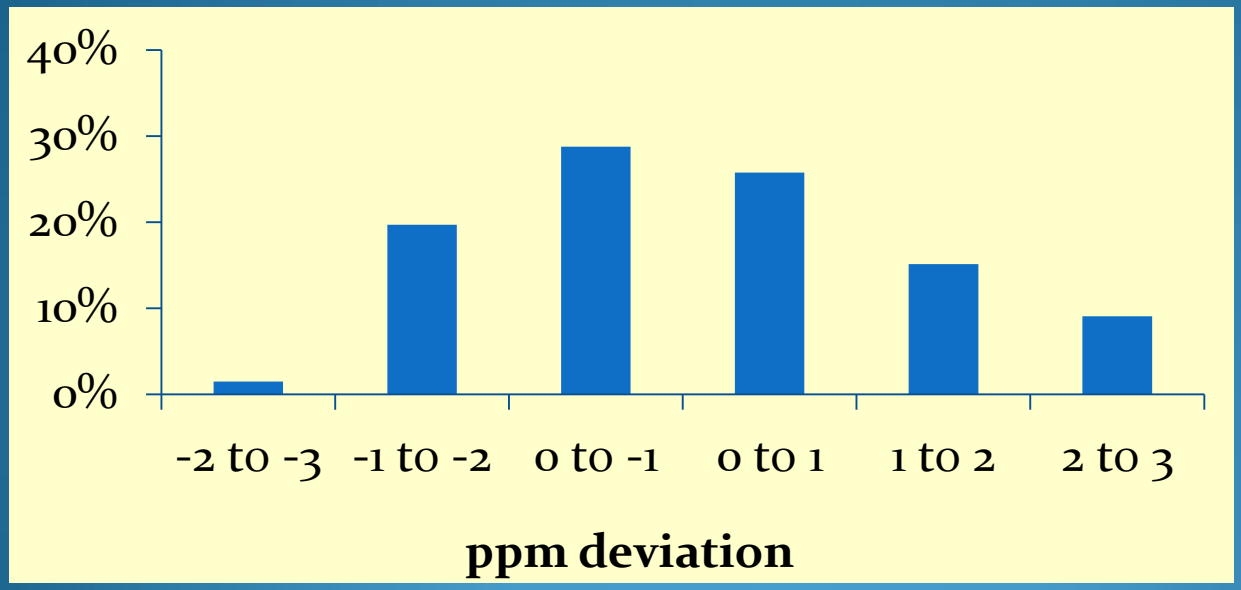
Validation by GCxGC-HR-ToF-MS



Nominal	High Resolution	Ultra-High Resolution
L = 2m	L = 20m	L = 40m
R = 1,800	R = 25,000	R = 50,000

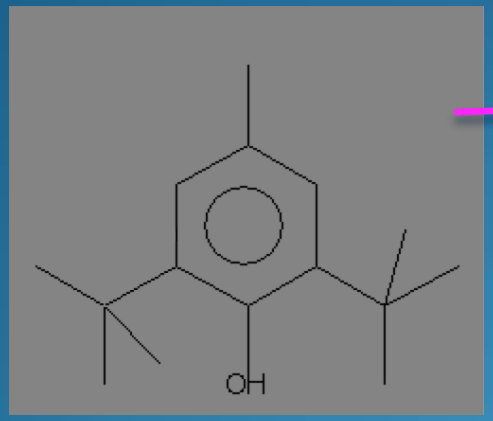
GCxGC-HRMS validation

Most compounds were in excellent agreement!

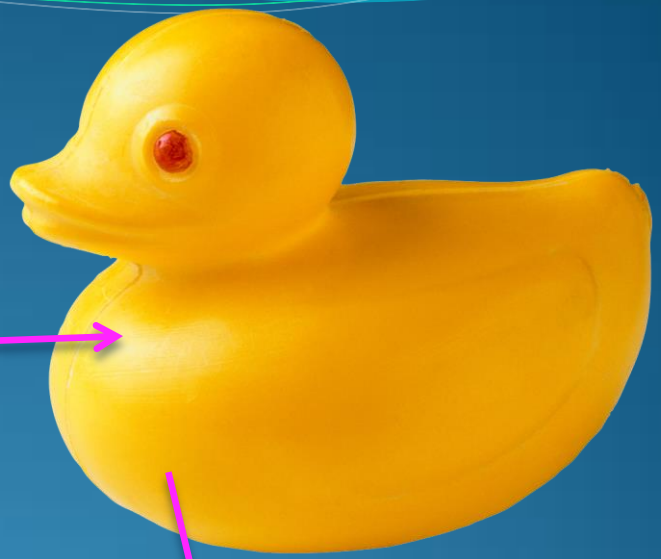


One false positive detected

Stuff in Stuff…

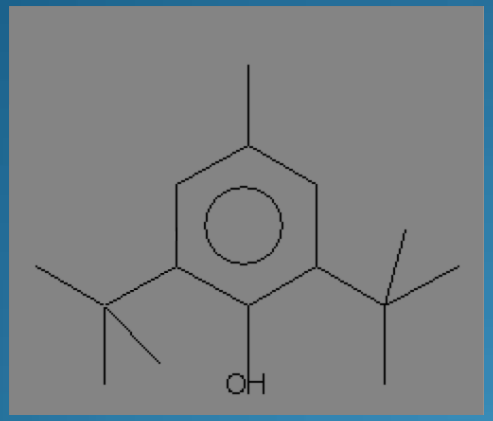


Expected

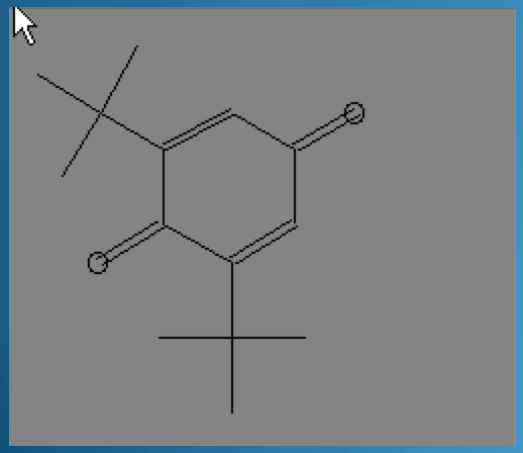


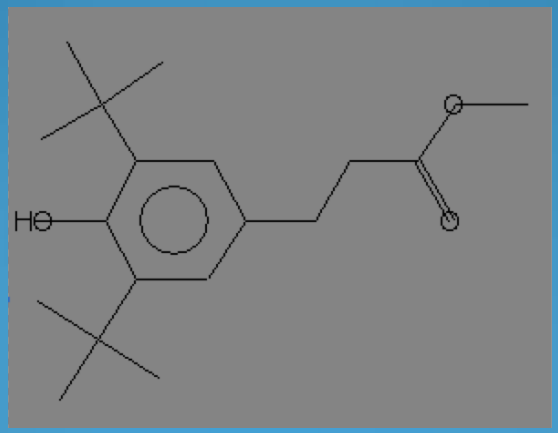
STP

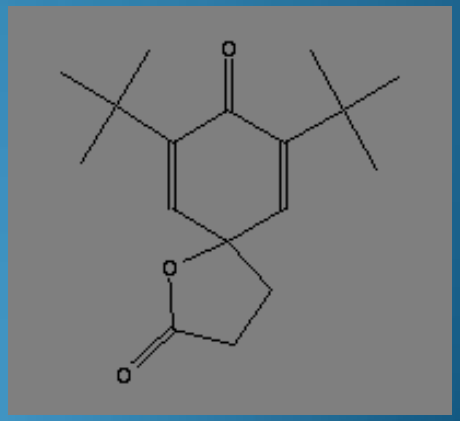
Stuff in Stuff…



Also found in sample







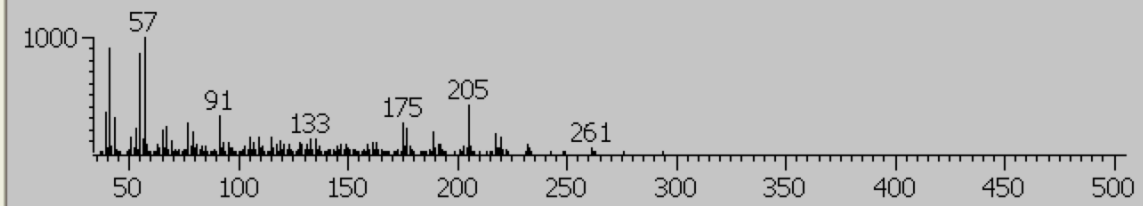
Stuff in Stuff…

Hit Table

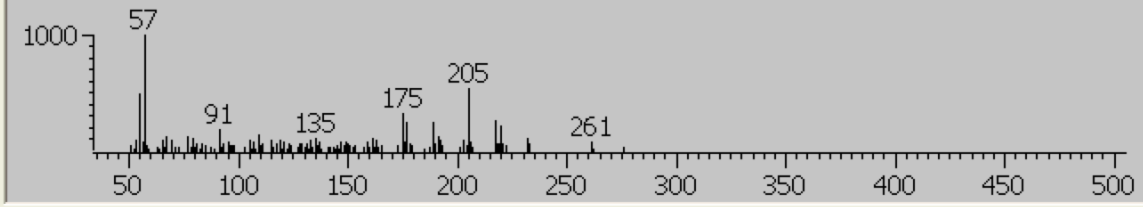
Hit	Name	Similarity	Reverse	Probabilit	CAS	Library	Id	Formula	Weight	Contributo
1*	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-	881	938	8890	82304-66-	mainlib	24148	C17H24O3	276	V.Lopez-A
2	4,6-di-tert-Butyl-m-cresol	716	748	213	497-39-2	mainlib	147772	C15H24O	220	Japan AIS
3	9-Isopropyl-1-methyl-2-methylene-5-oxa	698	737	110	0-00-0	mainlib	52066	C15H24O	220	Chemical C
4	Bicyclo[5.1.0]octan-2-one, 4,6-diisoprop	695	724	97	0-00-0	mainlib	2668	C16H24O	232	Chemical C
5	11,14-Octadecadiynoic acid, methyl est	681	738	60	56554-58-	mainlib	10561	C19H30O2	290	R.T.HOLM
6	Trichothec-9-en-8-one, 12,13-epoxy-3,	678	783	53	23282-20-	mainlib	148047	C15H20O7	312	MYCOTOX
7	Benzo[e]isobenzofuran-1,4-dione,1,3,4,	677	684	51	0-00-0	mainlib	54351	C15H20O3	248	Chemical C
8	2,5,5,8a-Tetramethyl-3-oxo-3,4,4a,5,6,	676	685	49	0-00-0	mainlib	98269	C16H24O3	264	Chemical C
9	Pent-4-enamine, 2-allyl-2-(2,3-dimethox	674	678	45	339244-81	mainlib	1564	C16H23NO2	261	A.A.Kutin,
10	Benzo[b]dihydropyran, 6-hydroxy-4,4,5,	670	701	38	50442-70-	mainlib	154701	C14H20O2	220	LAC, NIDD

- "NILU 14 influent:2"

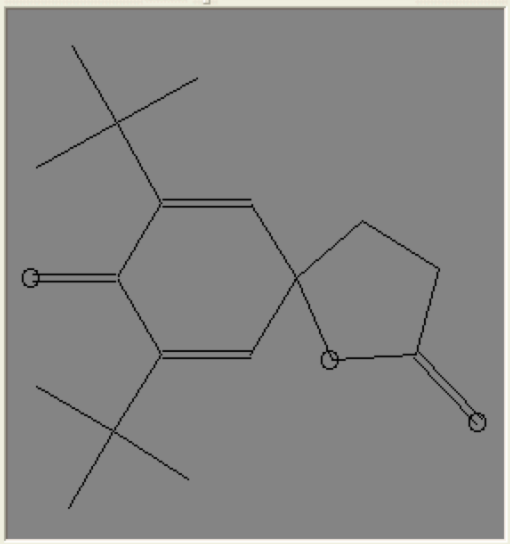
Peak True - sample "NILU 14 influent:2", peak 1744, at 2004 , 1.270 sec , sec



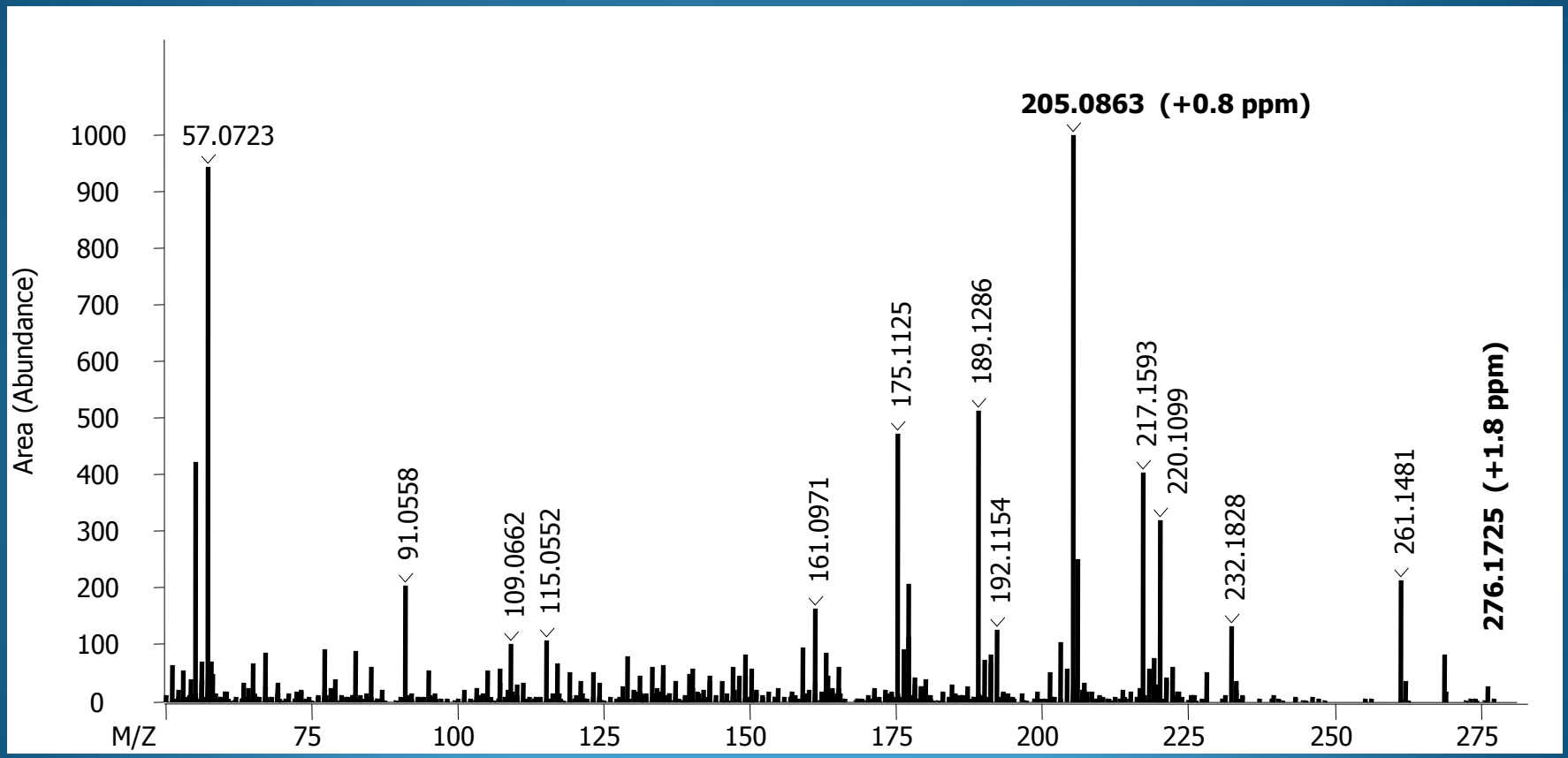
Library Hit - similarity 881, "7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione"



"7,9-Di-tert-b



GCxGC-HRMS Verification



Transformation products?

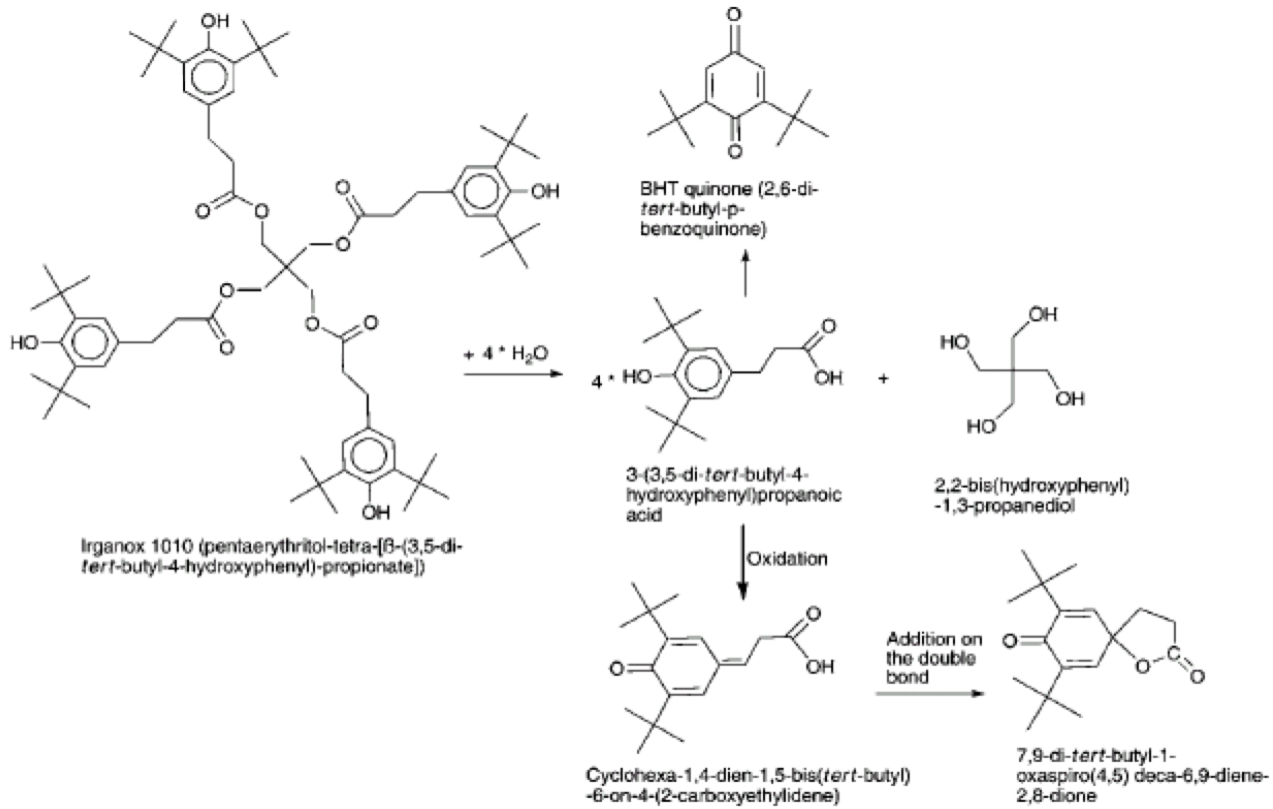


Fig. 7 Proposed degradation of antioxidant type 1010.

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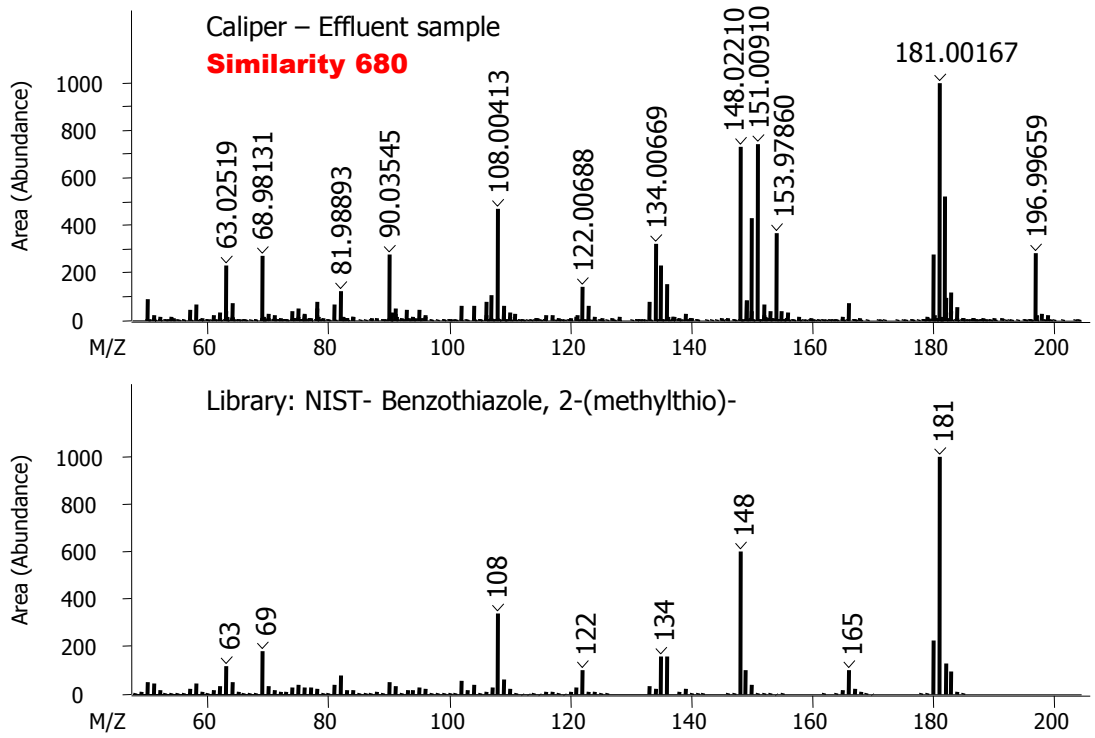
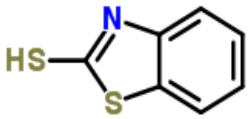
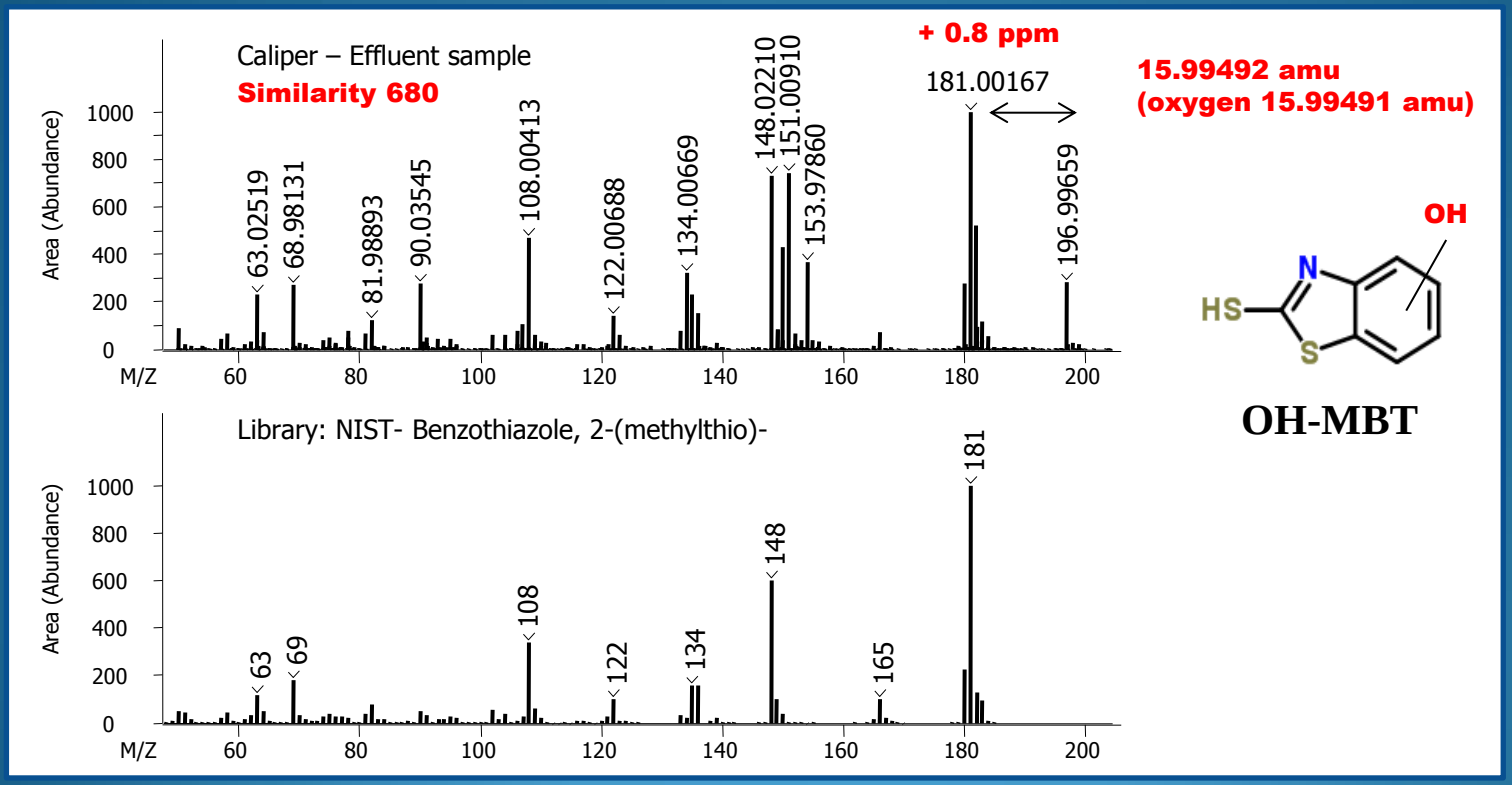
Stuff made from Stuff…



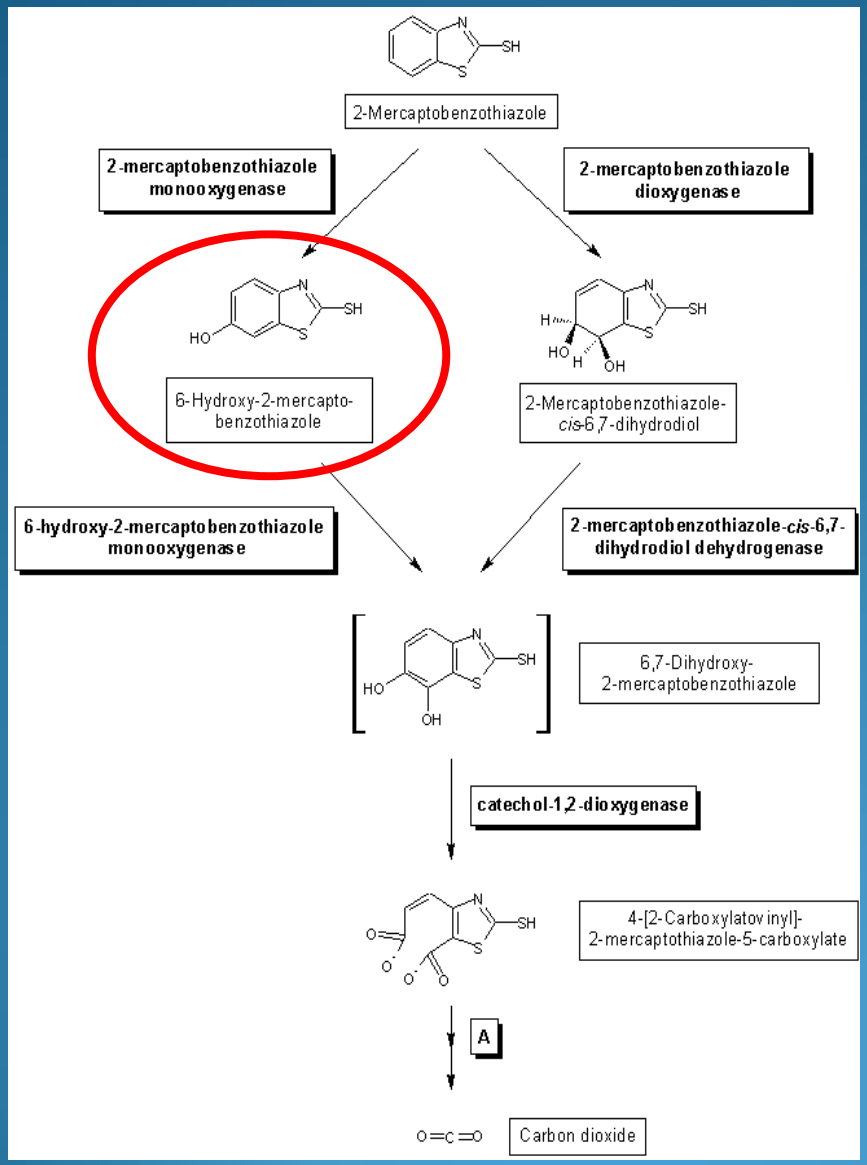


MBT
(Mercapto-Benzo-Thiazole)

Identification, formula



MBT bacterial degradation



Conclusions

The unsupervised process lead to the discovery of several compounds that are known to be difficult to remove

= The methodology seems to work

Most of the poorly removed compounds were aromatic and all had polar functional groups or moieties

Some of the emerging contaminants were sparsely described in the scientific literature, and some were present at relatively high levels

The HRMS accurate mass information was very valuable

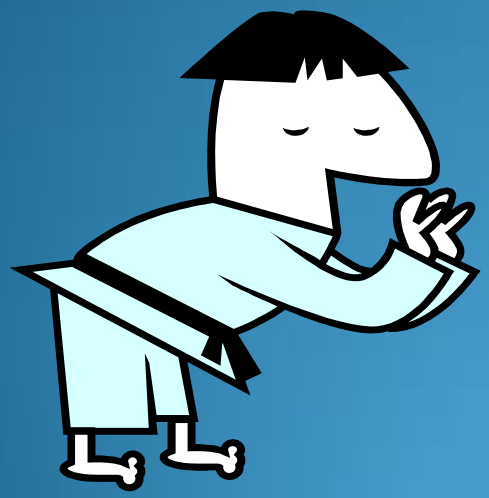
Future

1. **HRMS data will be used to identify additional compounds**

1. Swedish EPA fund a PhD student in the area

GCxGC-soft ionization-HRMS
Chemical ionization available
GCxGC-HRMS at prototype stage

Standardized protocols for extraction, clean up and analysis

3. NORMAN network intercalibration and harmonization activities

Thank you for your attention