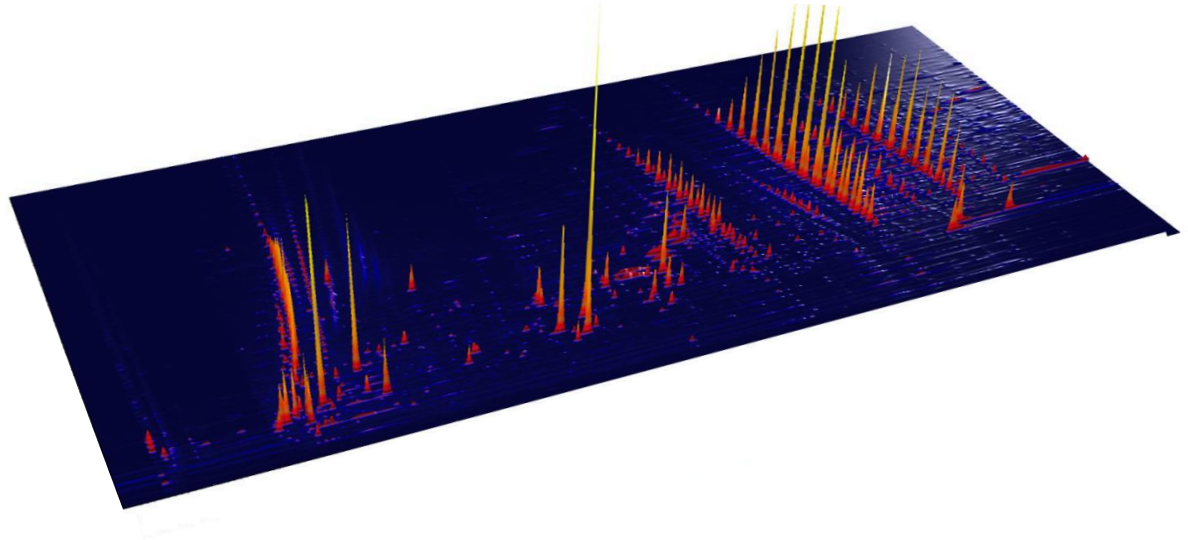
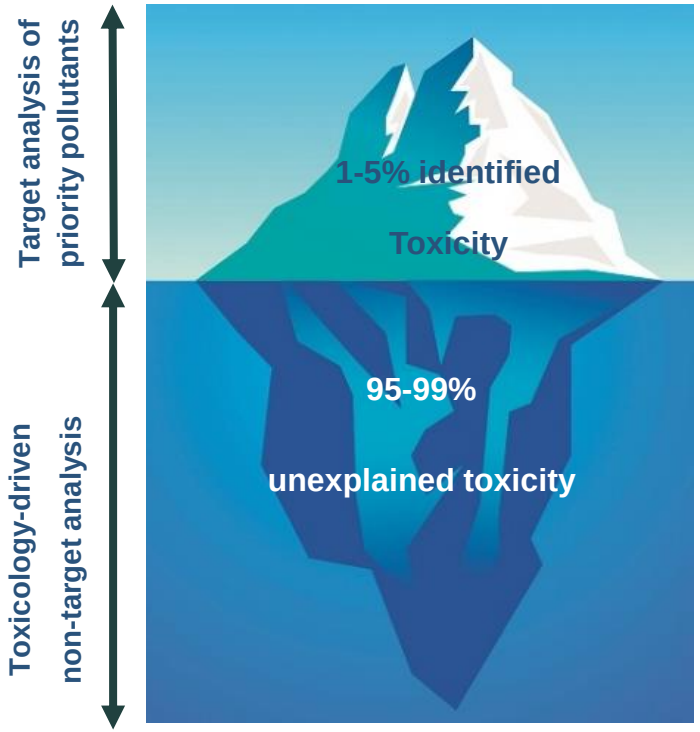


Selina Tisler

HOW NON-TARGET ANALYSIS CAN PROVIDE A FUNDAMENT FOR DECISIONS- VANDALF PROJECT

May 2022

VANDALF



Aim:

Identification of

high-risk Chemicals of Emerging Concern (CECs)

in wastewater effluent

How:

combination of non-targeted chemical

and toxicological fingerprinting

Public

Research | **Development** | **Implementation**

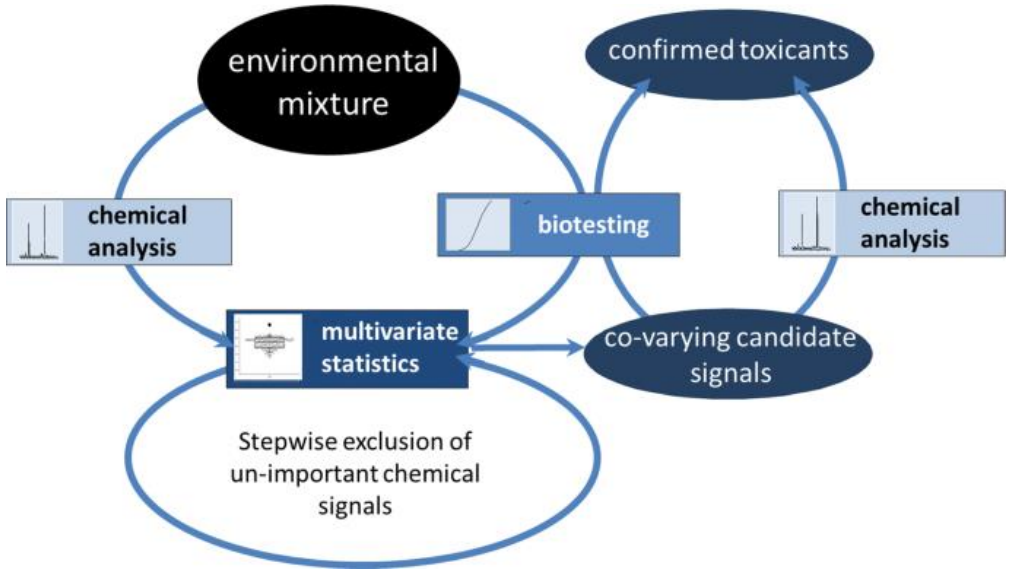
Industry

Virtual Effect-Directed analysis (VEDA)

- VEDA: reducing the complexity of mixture components via multivariate statistics

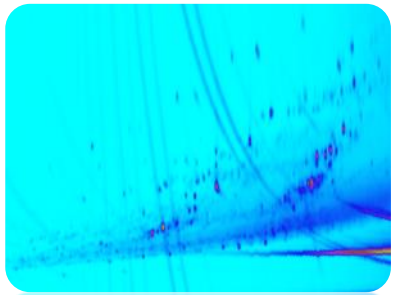
→ calculation of toxic units (TU) combined with non-target analysis

→ identify compounds that co-vary with biological effects



VEDA in the VANDALF concept

Representative sampling



Chemical fingerprinting

Toxicology tests

Data analysis

VEDA Approach

(Virtual Effect Directed Analysis)

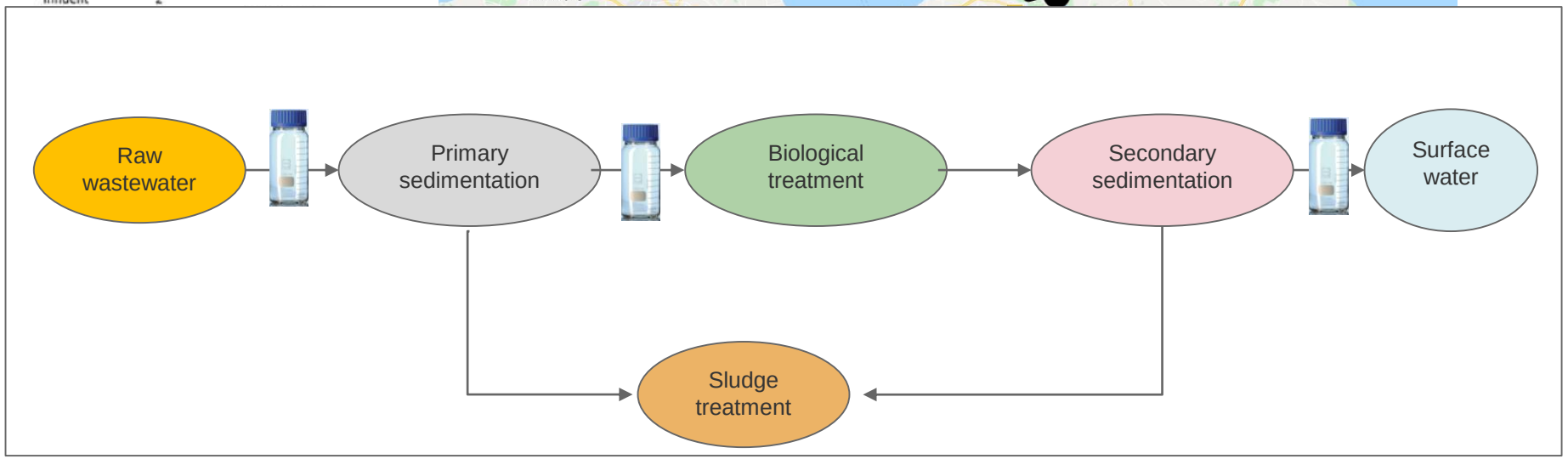
Key Chemical Hazards Ordered by Toxicity (AEGL-3, 30 min)

Chemical	CAS	Syndrome	AEGL-3, ppm	IDLH, ppm
Warfare agent - VX	50782-69-9	N	0.0014	0.002
Warfare agent - Sarin (GB)	107-44-8	N	0.032	0.017
Warfare agent - Sulfur Mustard (HD)	505-60-2	S/E	0.041	
Warfare agent - Tabun (GA)	77-81-6	N	0.057	
Warfare agent - Soman (GD)	96-64-0	N	0.25	0.008
Warfare agent - Cyclosarin (GF)	329-99-7	N	0.27	
Methyl Isocyanate	624-83-9	P	0.4	3
Parathion (AEGL-3 entry approx for rank purpose)	56-38-2	N	0.4	10 mg/m³
Arsine	7784-42-1	M	0.83	3
Phosphorous oxychloride (phosphoryl trichloride)	10025-87-3	P	1.1	
Warfare agent - Lewisite	541-25-3	S/E	1.4	
Phosgene (CG)	75-44-5	P	1.5	2
Acrolein	107-02-8	P	2.5	2
Cyanogen Chloride (CK) (AEGL-3 entry approx for r	506-77-4	M	2.5	
Hydrogen selenide	7783-07-5	P	3.1	1
Methyl hydrazine	60-34-4	N	3.5	20
Phosphorous trichloride	1207/7719	P	7	25
Phosphine	7803-51-2	P	7.2	
Chlorine	7782-50-5	P	7.3	15
Bromine	7726-95-6	N	12	3
Fluorine	7782-41-4	P	19	25
Hydrogen cyanide (HCN)	74-90-8	M	21	50
Nitrogen Dioxide	10102-44-0	P	25	20
Allyl Alcohol	107-18-6	P	25	20
Chlorine	7782-50-5	P	28	10
Sulfur dioxide	9/5/7446	P	32	100
Hydrazine	302-01-2	N	45	50
Hydrogen sulfide	7783-06-4	N	59	100
Hydrogen fluoride (HF)	7664-39-3	P	82	30
Formaldehyde	50-00-0	S/E	70	20
Methyl Mercaptan	74-93-1	P	85	150
Nitric acid	7697-37-2	P	120	25
Boron trifluoride	7/2/7637	P	140	25
Sulfur bioxide	1/5/7446	P	300	
Sulfuric acid	7664-93-9	P	200	15 mg/m³
Acrylonitrile (AEGL-3 entry approx for rank purpose)	107-13-1	M	200	85
Hydrogen chloride	7647-01-0	P	210	50
Hydrogen bromide	10035-10-6	P	250	30
Dimethylamine	124-40-3	P	309	500
Ethylene oxide	75-21-8	P	360	800
Methylamine	74-89-5	P	510	100
Carbon disulfide	75-15-0	N	800	500
Carbon monoxide	630-08-0	N	600	1200
Bromomethane (methyl bromide)	74-83-9	P	1300	250
Propylene oxide	75-56-9	P	1300	400
Ammonia	7664-41-7	P	1600	300
Color Key to primary associated syndromes				
PULMONARY				
NEUROTOXIC				
METABOLIC				
SKIN/EYE				

Prioritization list of most toxic compounds

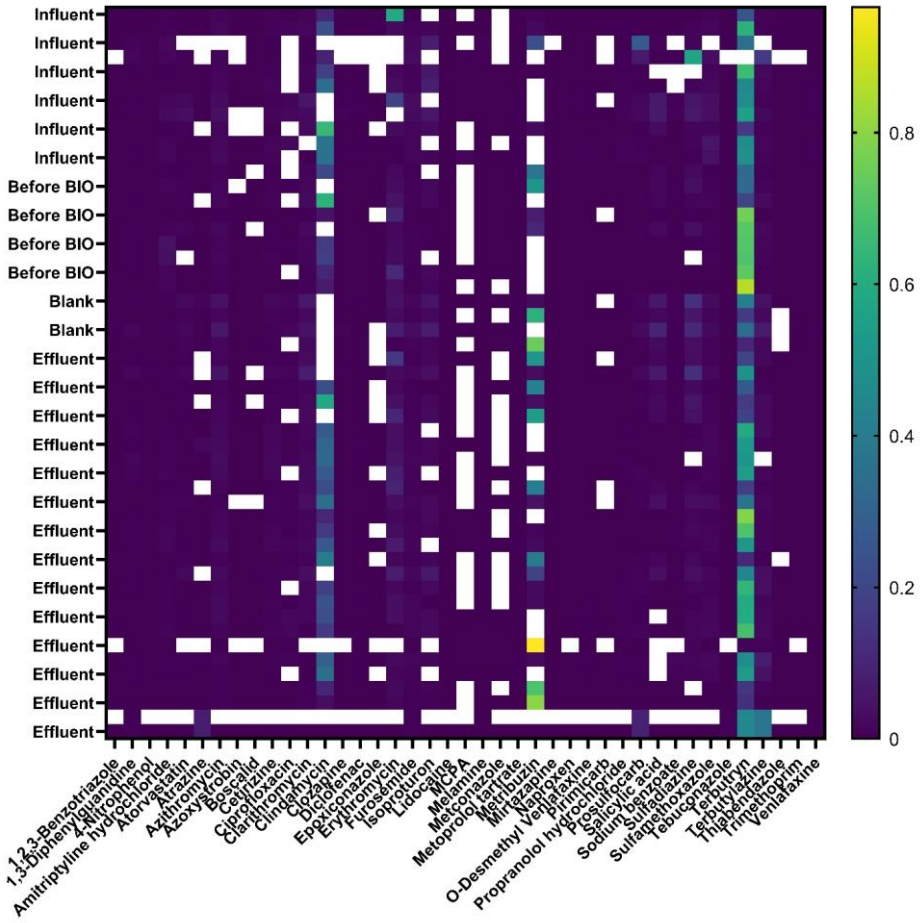
Case study: Wastewater samples in Denmark

Sample type	No. of samples	Sampling period (2020)
Avedøre		
Influent	1	
Before biology	1	22/06 – 02/07
Effluent	4	
Lynetten		
Influent	4	
Before biology	3	22/06 – 02/07
Effluent	4	
Damhusåen		
Influent	2	
Before biology	3	
Effluent	4	22/06 – 02/07
Blank	3	
Ejby Mølle		
Influent	2	
Before biology	2	07/07 – 22/07
Effluent	4	
Blank	2	
Nordøst		
Influent	2	



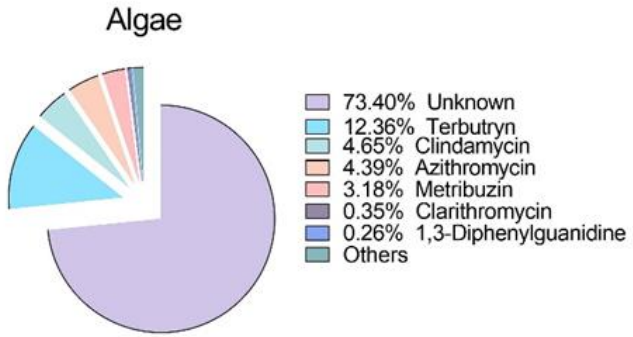
Toxicology tests- target data not enough to explain toxicity

target compounds contribution to algae toxicity in wastewater samples



Based on concentration and known literature about toxicity

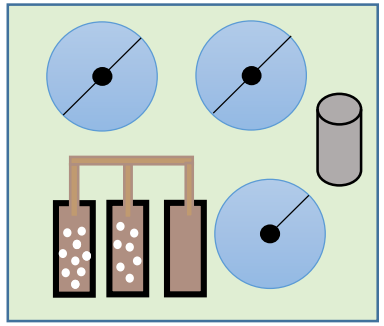
→ Toxic unit calculation



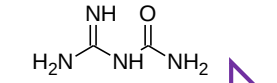
→ 74 % of the toxicity can not be explained by the 75 detected target compounds

Why are so many unknown compounds in the wastewater?

100 % Metformin

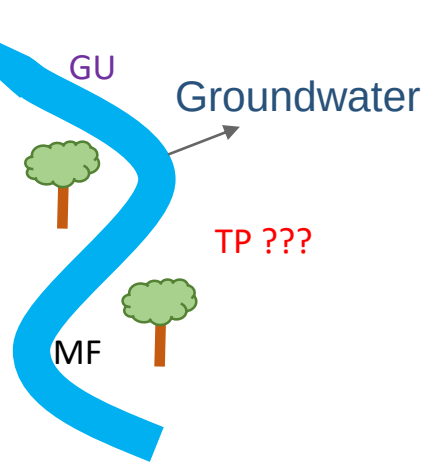


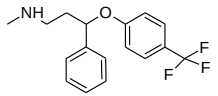
1 % MF



5-99 % Guanyl urea

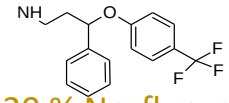
Transformation product???



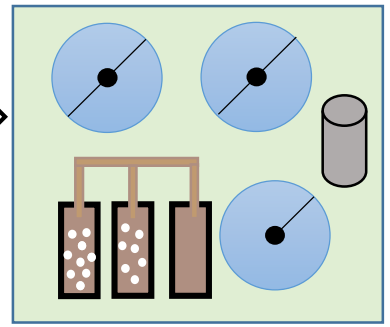


(+ GLUC)

80 % Fluoxetine



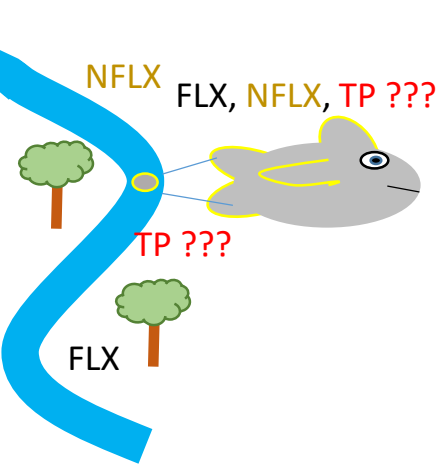
20 % Norfluoxetine



10-60 % FLX

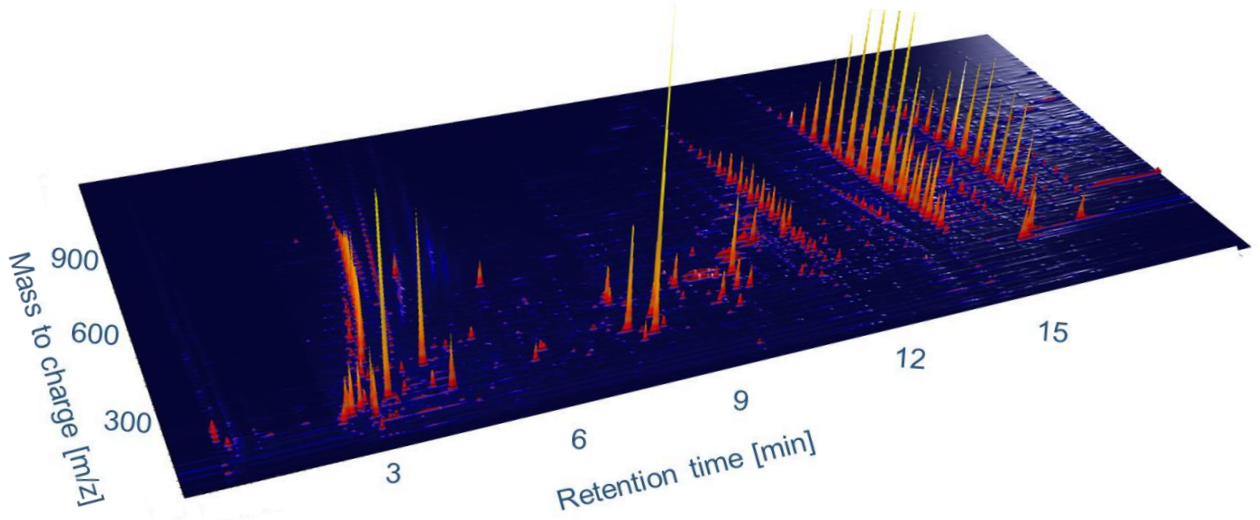
2-10 % NFLX

TP ??? e.g. TFA

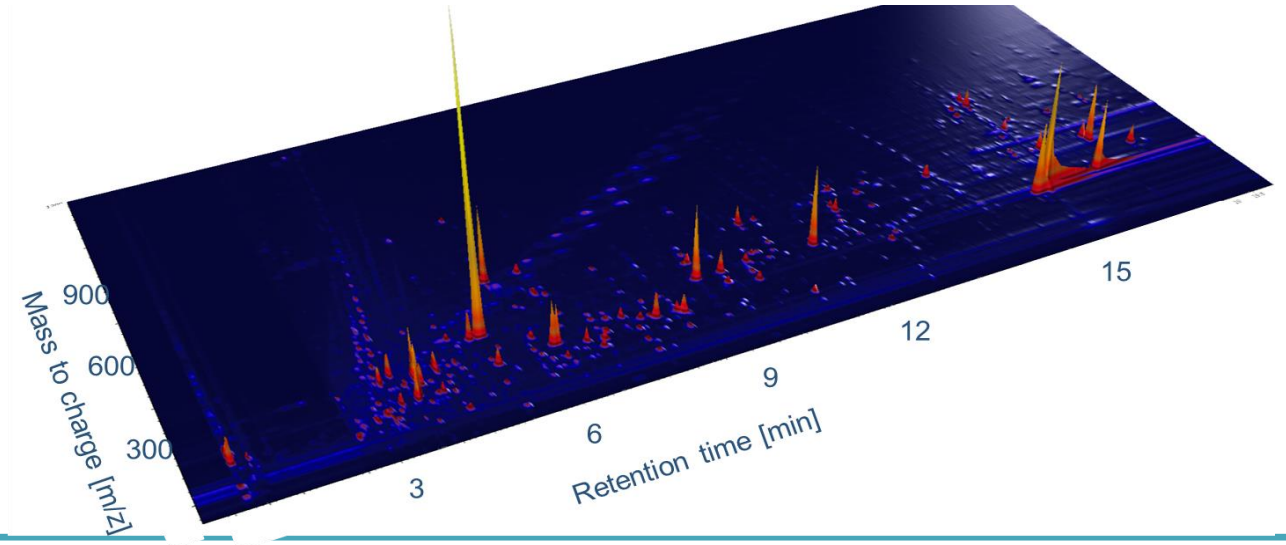


Influent vs. Effluent

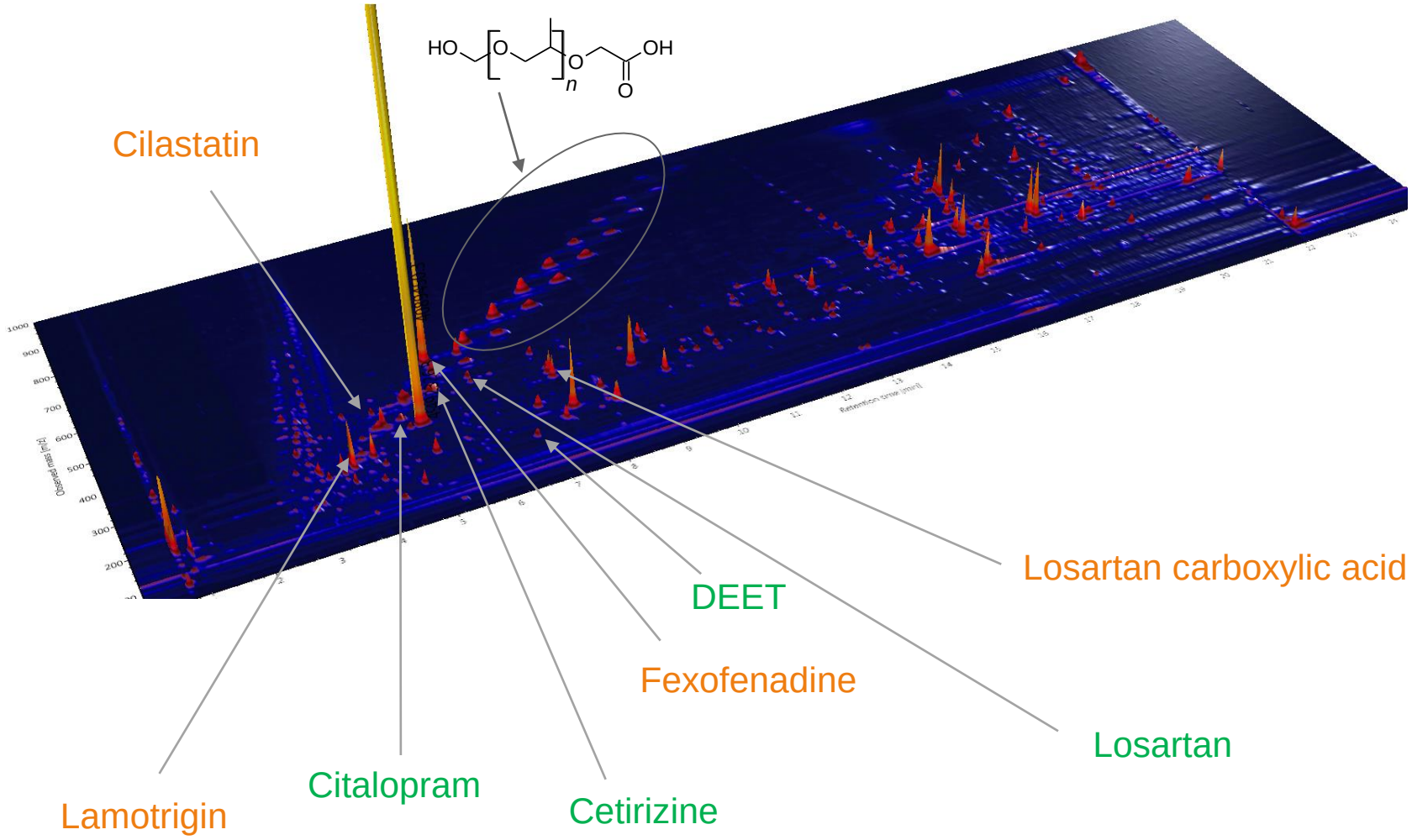
Influent



Effluent

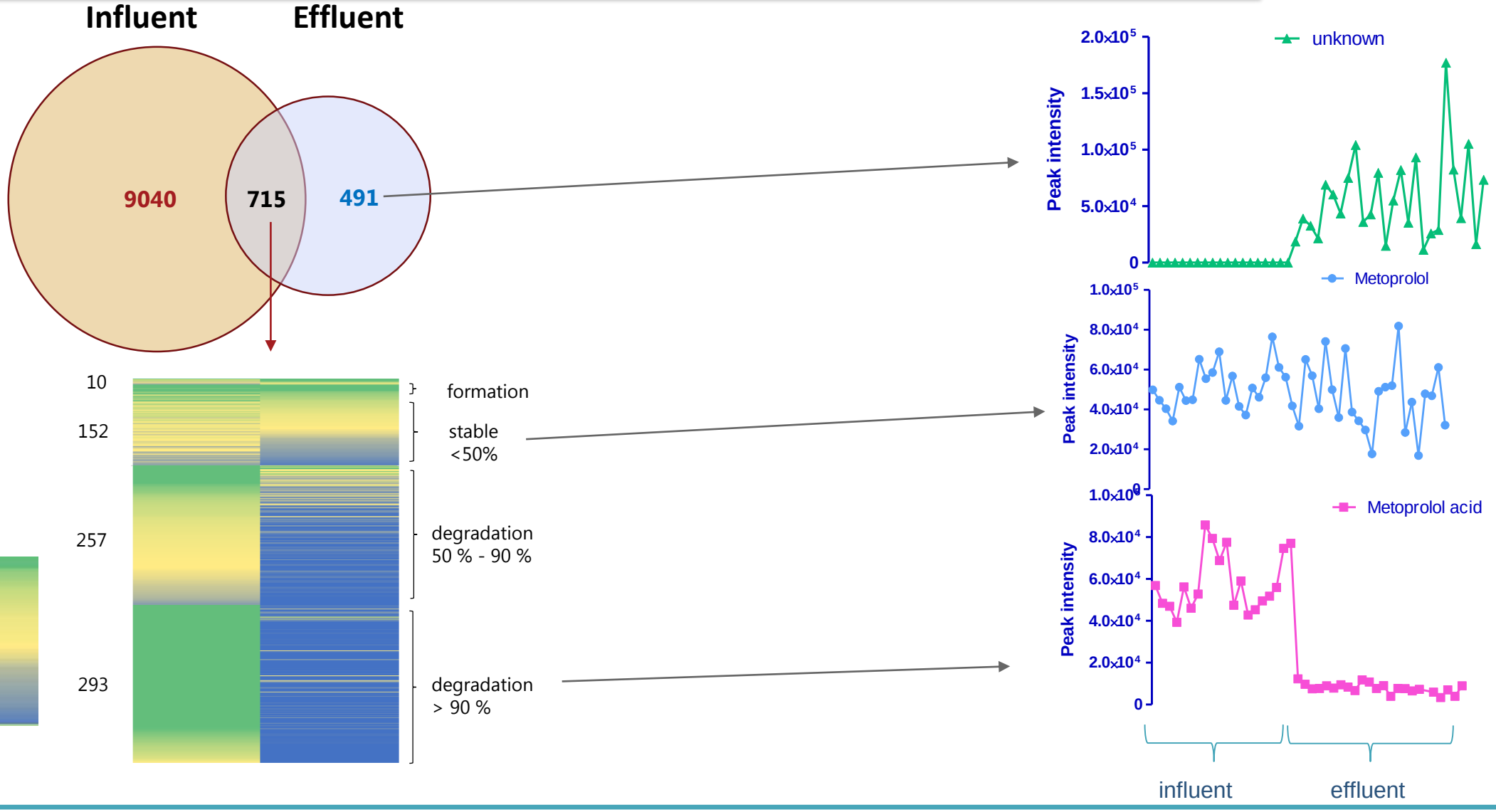


Target and suspect screening (wastewater effluent)

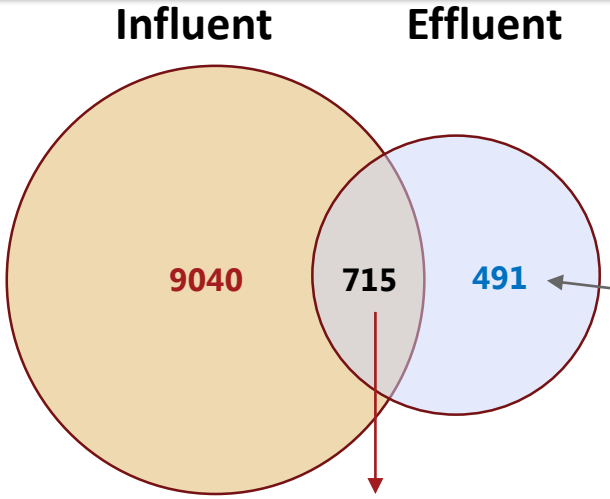


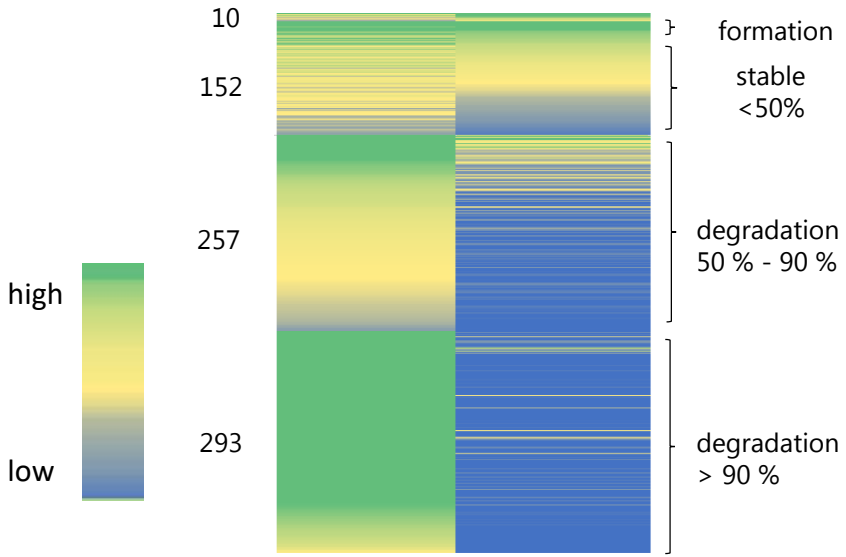
→ Thousands of compounds- other approaches are needed for compound prioritization:

Prioritization of compounds by Non-target screening

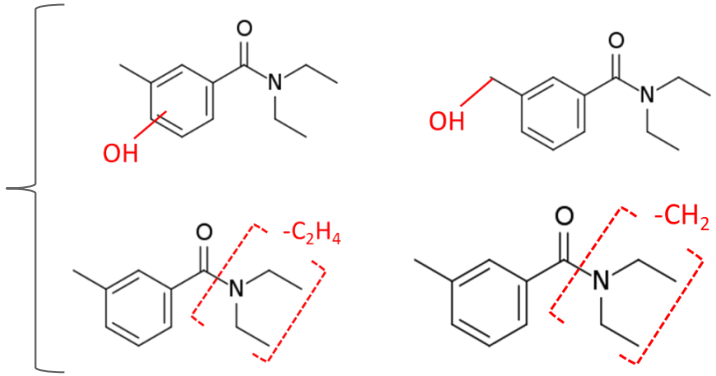


Identification of transformation products; example DEET

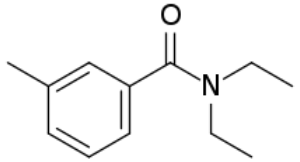




Detected only in effluent samples (=formed in WWTP)



Which compounds are degraded?

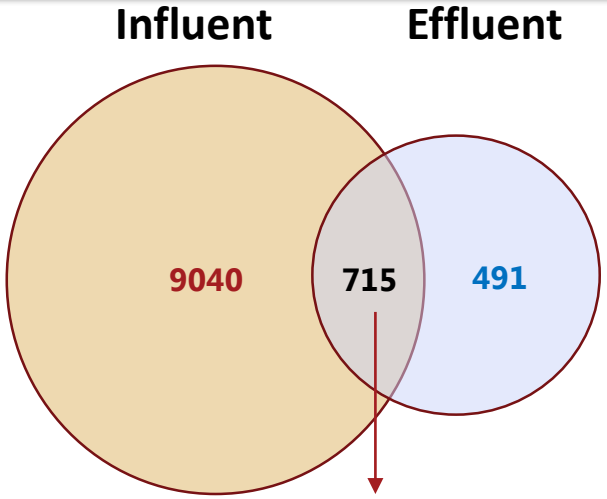


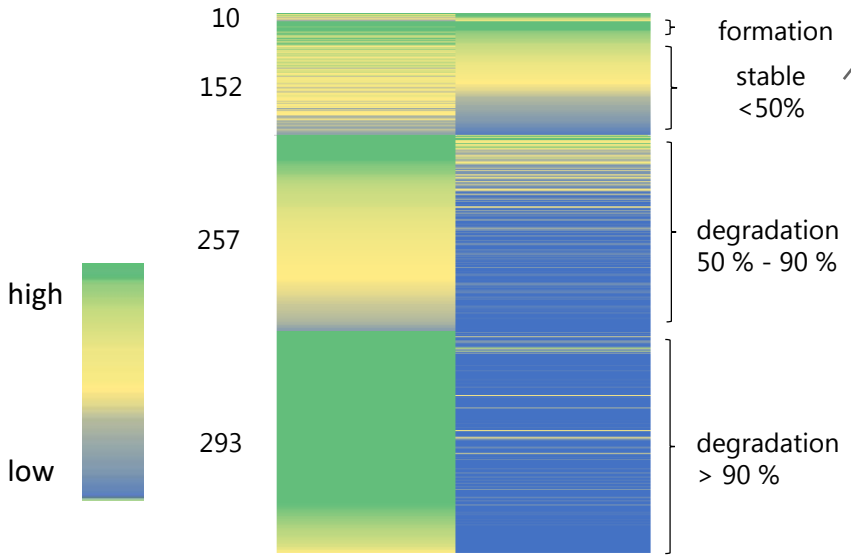
Example: DEET

No! Transformation

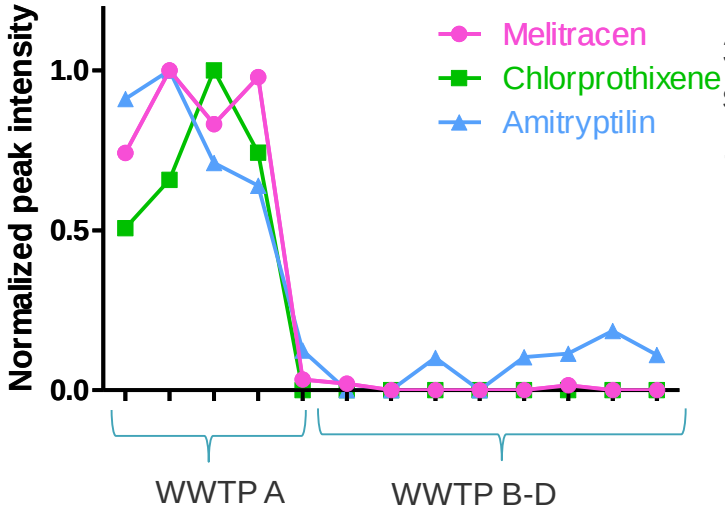
Degradation
= mineralization?

Stable compounds- identify specific sources





Wastewater effluent samples



3 antidepressants, all produced by the same company- coincident?

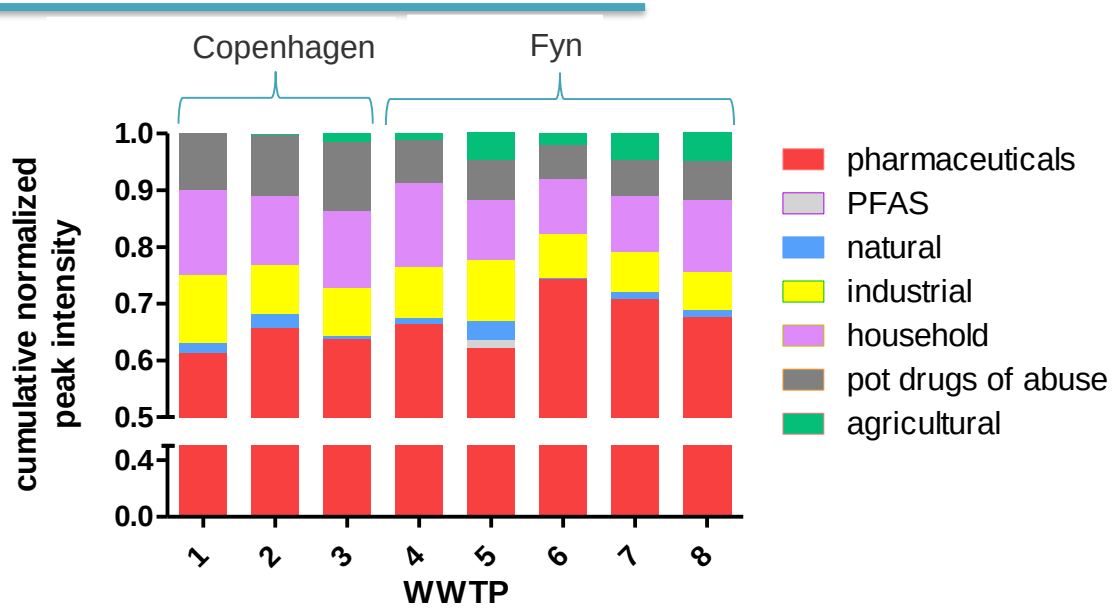
→ concentration?? Risk??

NTS list

Melitracen- antidepressant (not usual described)

- Why detected only in WWTP A? Psychiatric hospital?
- R&D department of producer in catchment area
- Going back into the data (retrospective) to search for more of the chemicals this company is producing

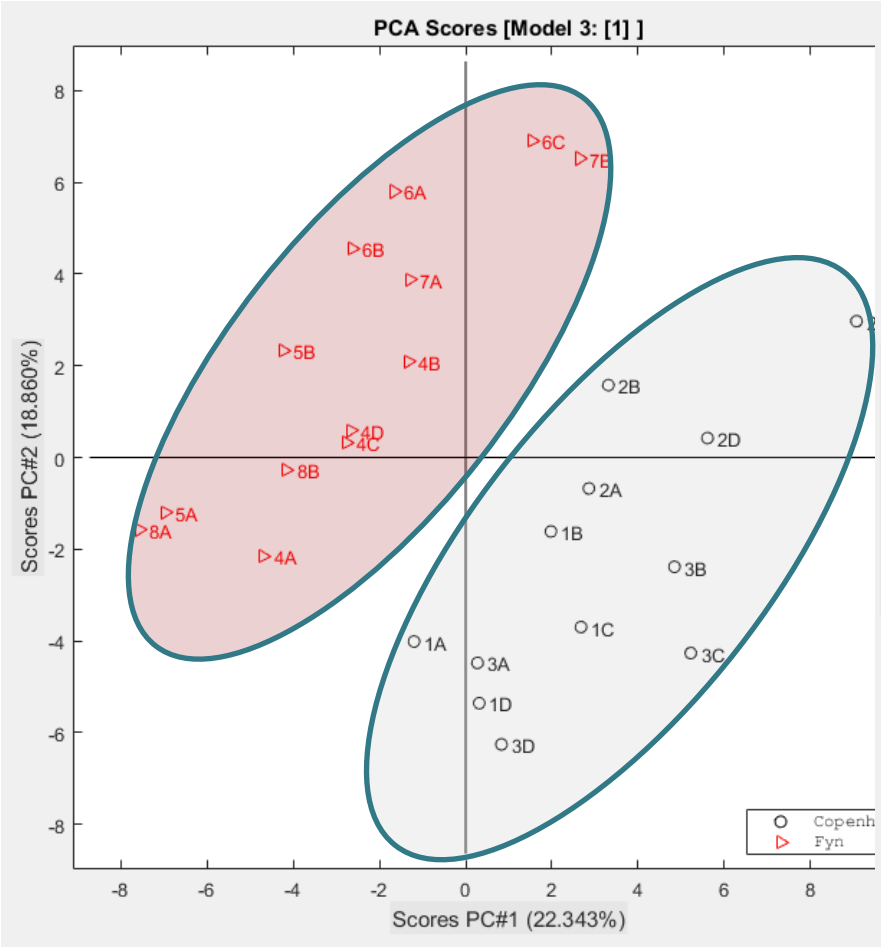
Overview about the current status of identified compounds

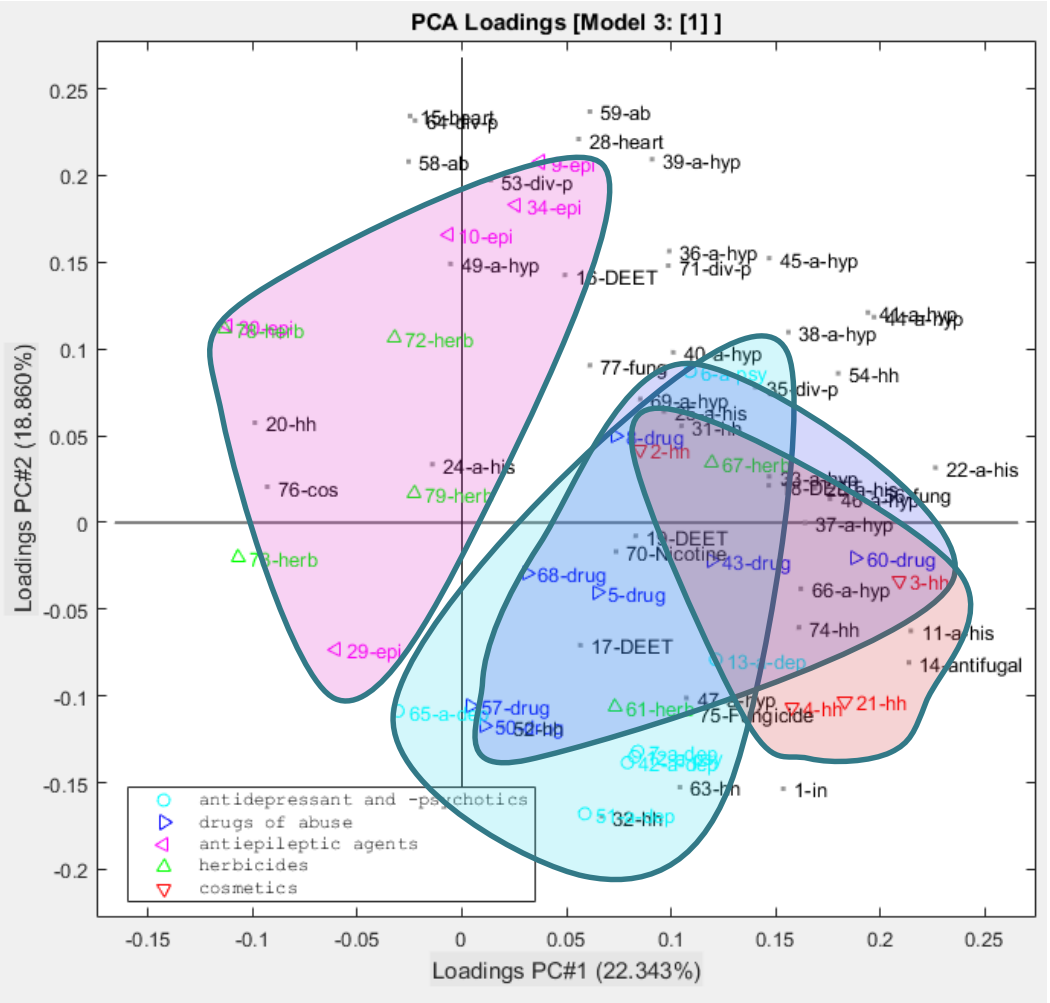


Around 250 compounds identified

- Most of them are pharmaceuticals
- Copenhagen area more drugs of abuse detected
- Fyn more pesticides detected
- PFAS only in one WWTP detected
- Identification ongoing…

Differences between Fyn and Copenhagen





Are the identified chemicals a risk?

→ Data about toxicity available?

Gap in toxicity data for uncommon reported compounds-

VEDA approach in VANDALF chance to increase toxicity knowledge

→ Known concentration?

Not for suspect and non-target compounds. Can be determined in a subsequent step, if analytical standards are available. If not: semi-quantification is needed

→ Even without known concentration and toxicity- NTS can provide a fundament for decision making

European legislation defines the goal of achieving good ecological and chemical status of water bodies (Water Framework Directive)

Conclusion

- The number of chemicals in the environment is too high to capture them by target screening

→ Different sources and transformation leads to high variety of compounds

- Suspect screening helps, but still constraint by specific compound classes you are looking for – TPs are often not included
- Non-target screening: prioritization strategy needed
- Overall picture (e.g. how many compounds degraded and formed), or identification of specific compounds possible
- Retrospective analysis possible

Acknowledgment

Thanks to

- Innovation fund Denmark for funding the VANDALF project
- Mathias Blichert from Biofos
- Kristoffer Kilpinen from Eurofins
- The analytical chemistry group from University of Copenhagen

Additional slides

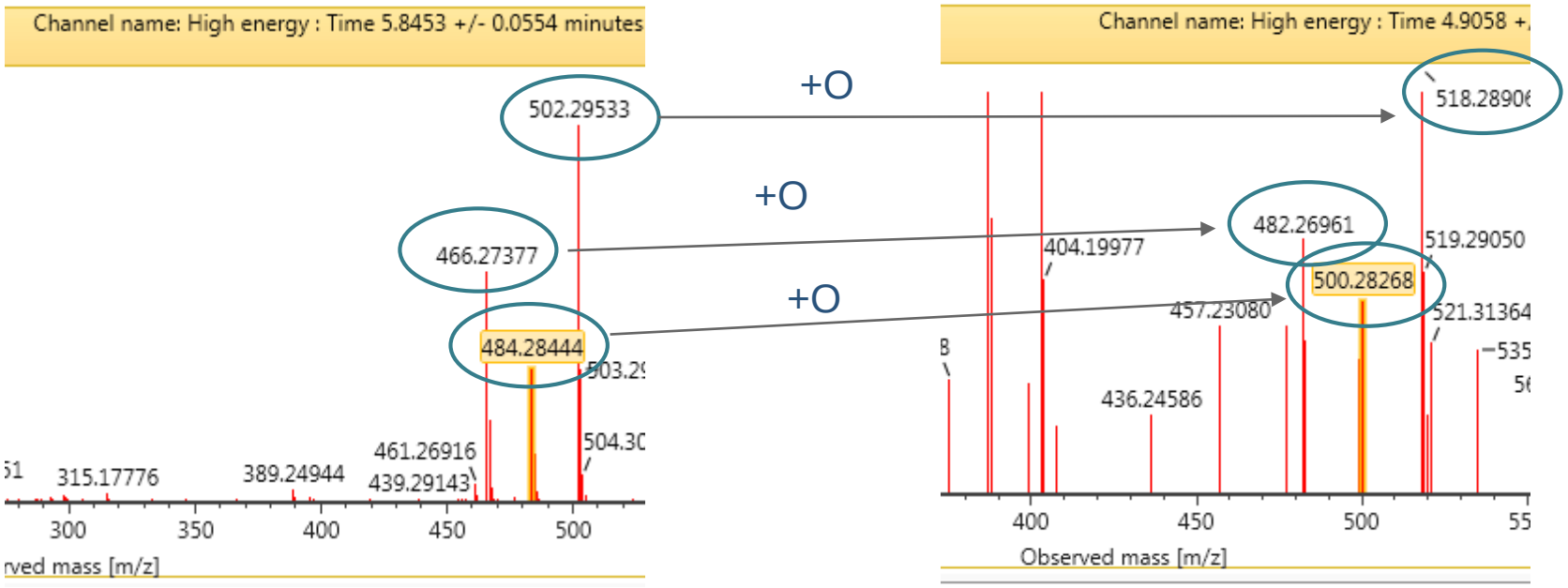
Example transformation product (TP) detection

Influent

Fexofenadine

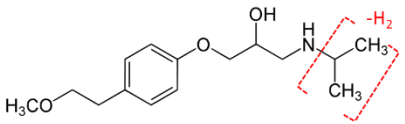
Effluent

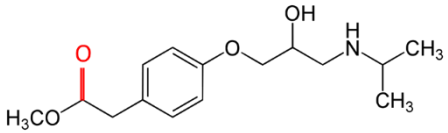
Fexofenadine+Oxygen



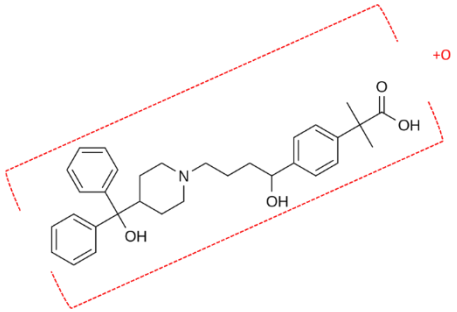
Example of identified TPs

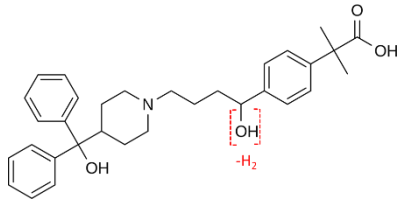
Metoprolol

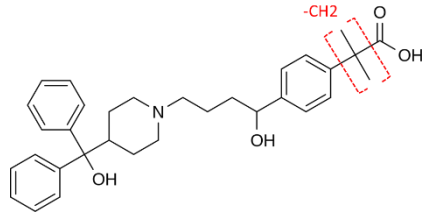


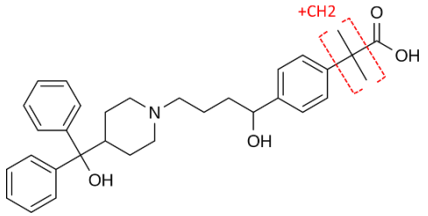


Fexofenadine









Losartan