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The potential of Non-Target Screening in environmental monitoring

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Non-target screening helps to explore the iceberg of chemicals

→ Confirmation with **reference standards**

→ Expected compounds whose **exact mass** can be screened

→ All remaining components with **no prior information**

Definitions from Schymanski et al., 2015, ABC

Content

General workflow

Three application examples

- Evaluation of wastewater treatment technologies
- Assessment of (political) mitigation measures using sediment archives
- Daily monitoring of river Rhine

NORMAN experiences

Conclusions

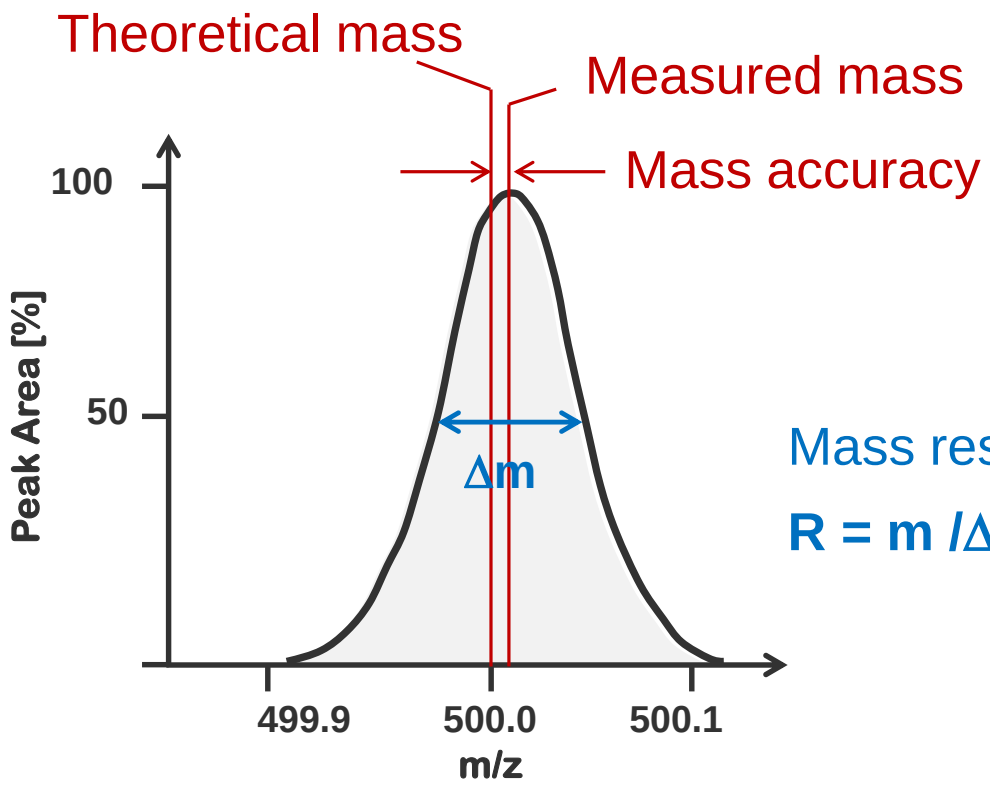
Target versus Non-target Screening

Target versus Non-target screening

Core needs – HRMS instruments & databases

- high mass accuracy (< 0.001 Da)
- high mass resolution (> 40’000)
- high sensitivity in fullscan mode
- high stability over time

- Compound databases
- Suspect lists
- Spectra libraries
- Computational tools



Mass resolution

R = m /Δm

NORMAN Suspect lists

http://normandata.eu/normansusdat/

Workflow for identification of contaminants using HRMS/MS

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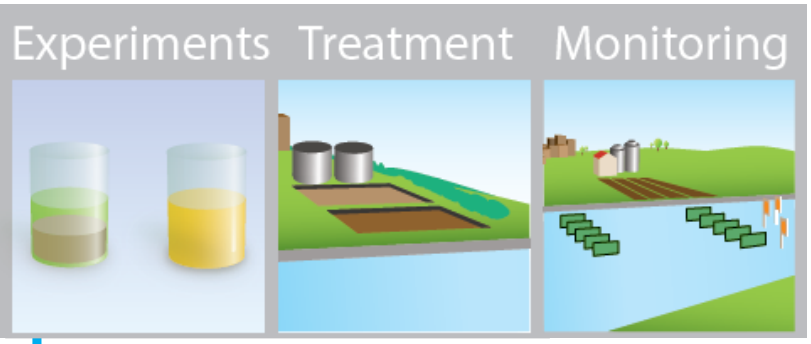
First, comprehensive target & suspect screening

Water



Sediment

Biota

Sampling
Space & Time
Before & After
Hot spots

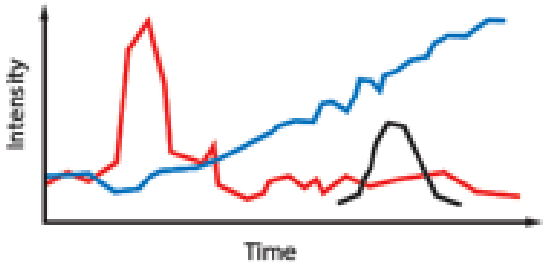
Sample Archive

Hollender et al, EST, 2017

Strategy to prioritize for identification

In Environmental Monitoring

- Frequency of occurrence
- High intensity
- Spatial trend along river
- Trend over time at monitoring site
- High toxicity (effect-directed analysis)



Pattern

For Chemicals Management

- Effectiveness of regulation: e.g. occurrence in water, sediment and biota (using suspect screening)
- Effectiveness of mitigation measure
  e.g. wastewater treatment:
  - persistence, elimination,
    formation of transformation products

Evaluation of wastewater treatment technologies

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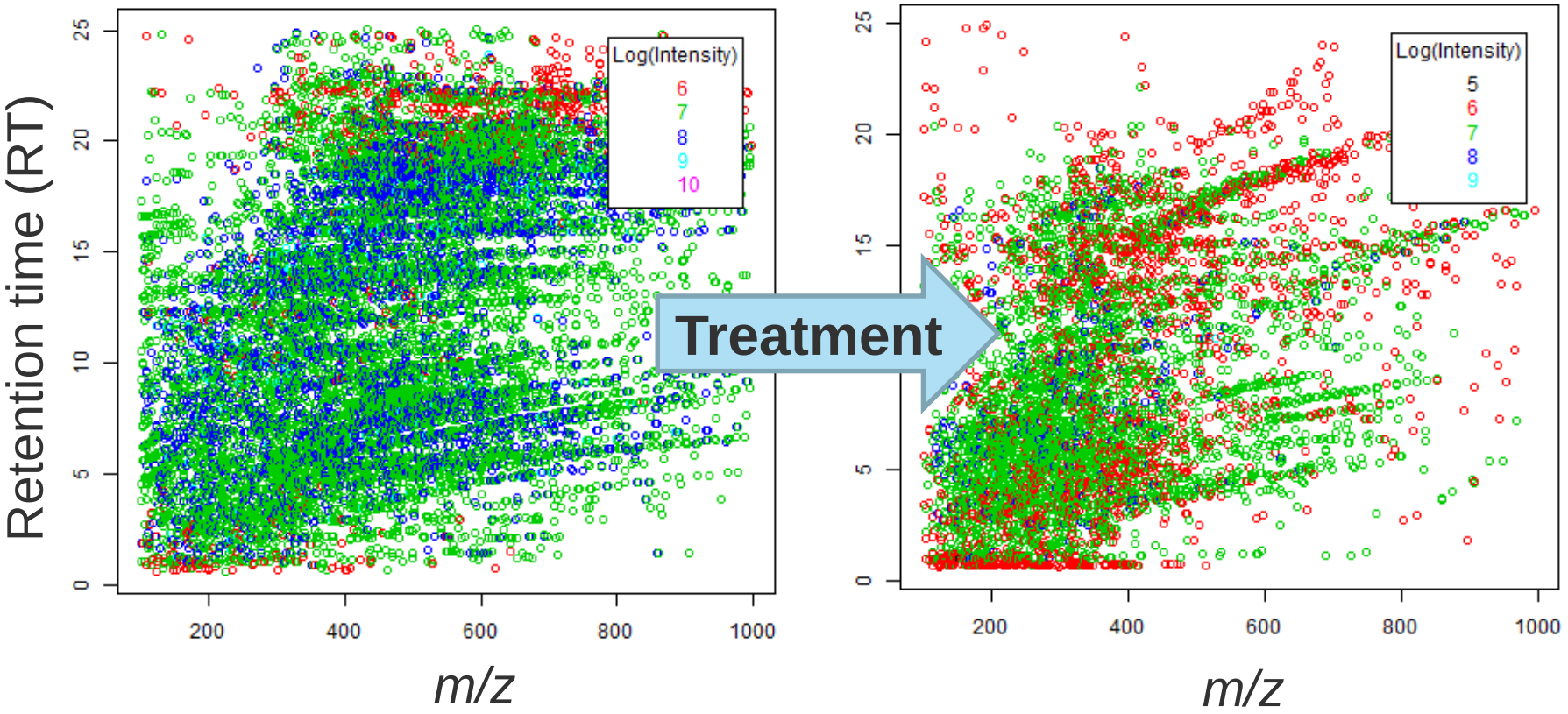
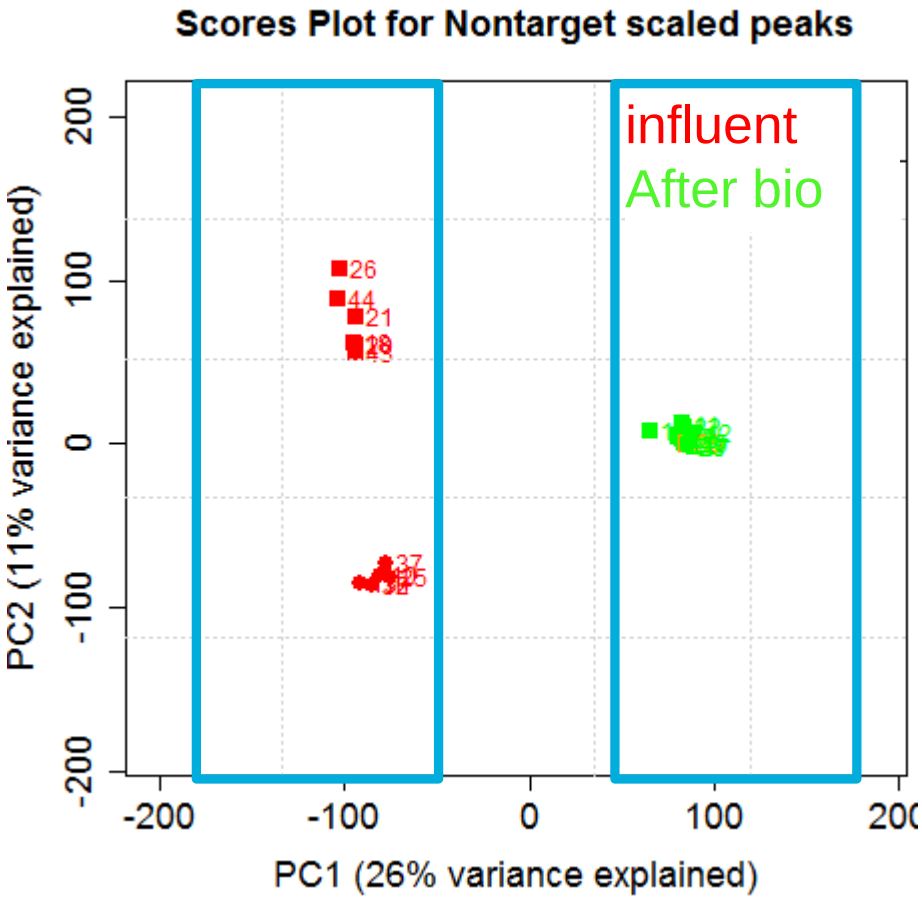
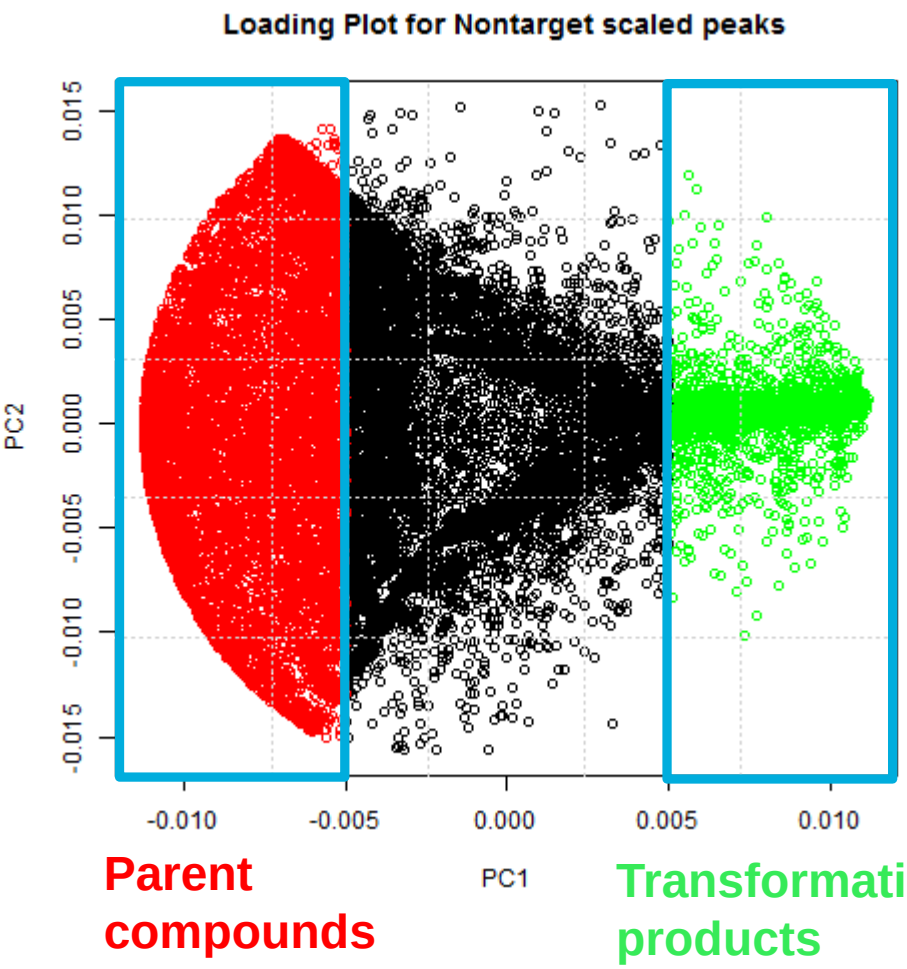
- **Compare before and after treatment**



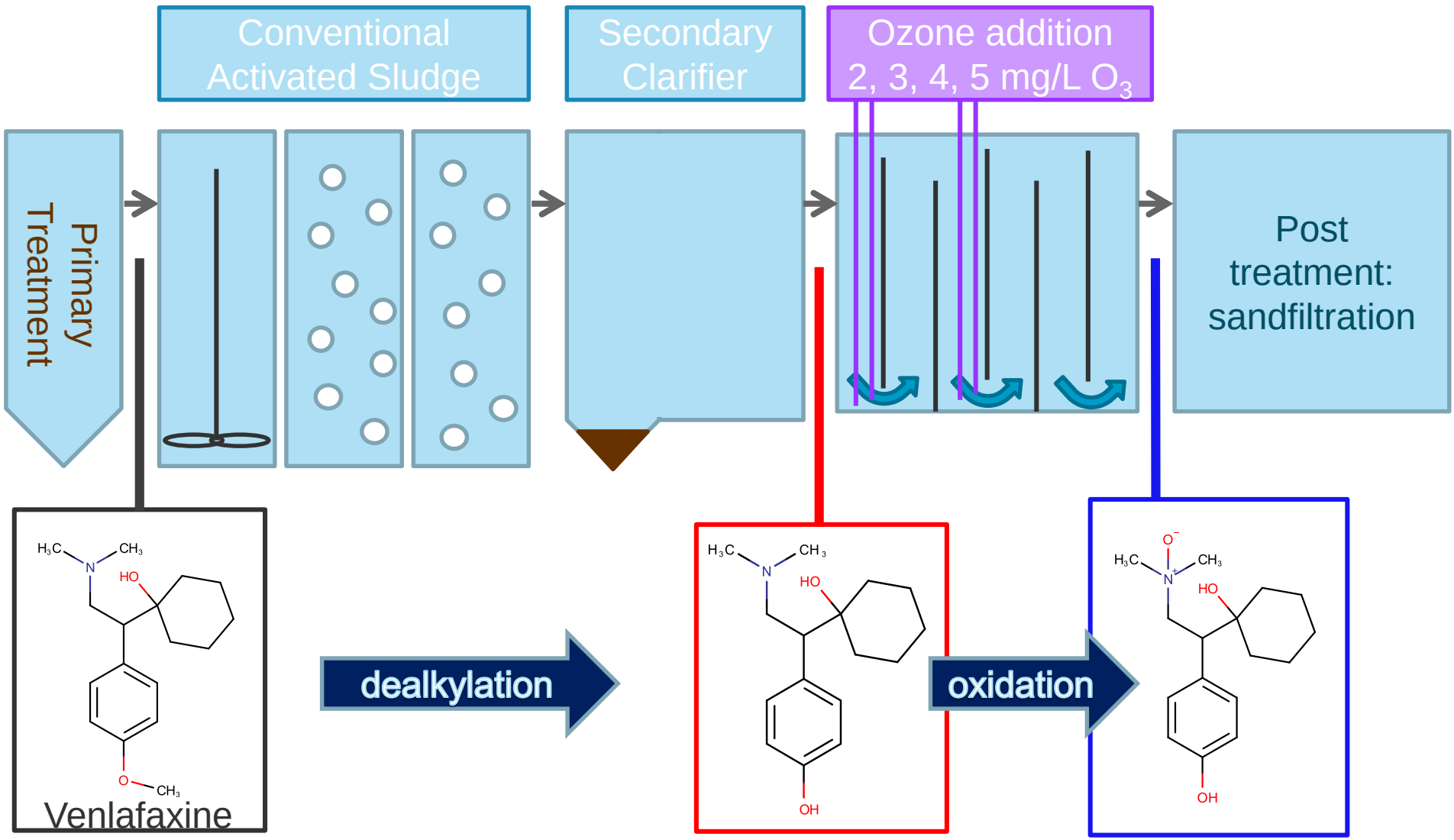
Statistical tools: Principal component analysis of Non-target Peaks





Schollée et al., 2015, Anal. Chem.

Identification of transformation products along the wastewater treatment chain including ozonation

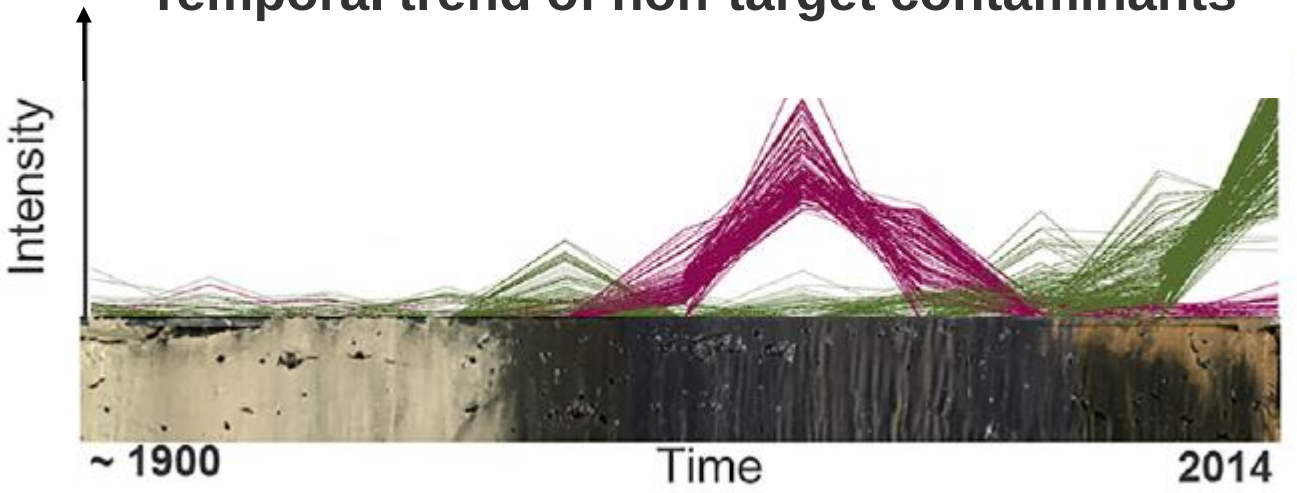


Schollée et al., Wat. Res. 142 (2018) 267-278; Venlafaxine TPs in: Rúa-Gómez et al. 2012; Gulde et al. 2016

Assessment of mitigation measures using sediment archives

Lake sediment cores

Temporal trend of non-target contaminants

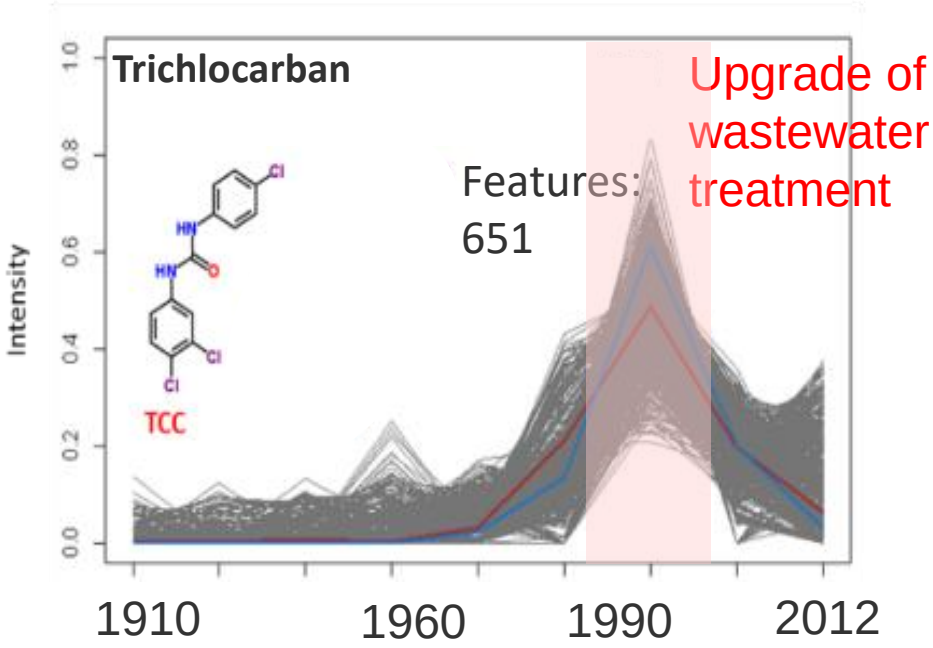


Analytical method

- Freeze-drying & homogenization
- Extraction & purification
- Chromatographic separation
- Orbitrap-ESI-HRMS/MS

Chiaia-Hernandez et al. *ES&T* 2013, 47(2) pp. 976-986

Time trends of non-target contaminants in Lake Lugano sediment using clustering



Characterize time trends in Lake Lugano sediment using non-target screening & clustering

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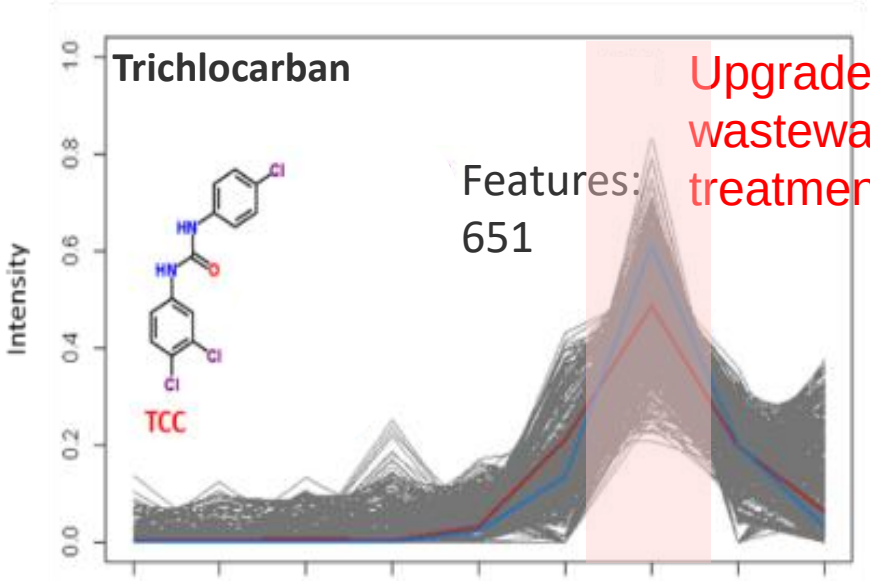
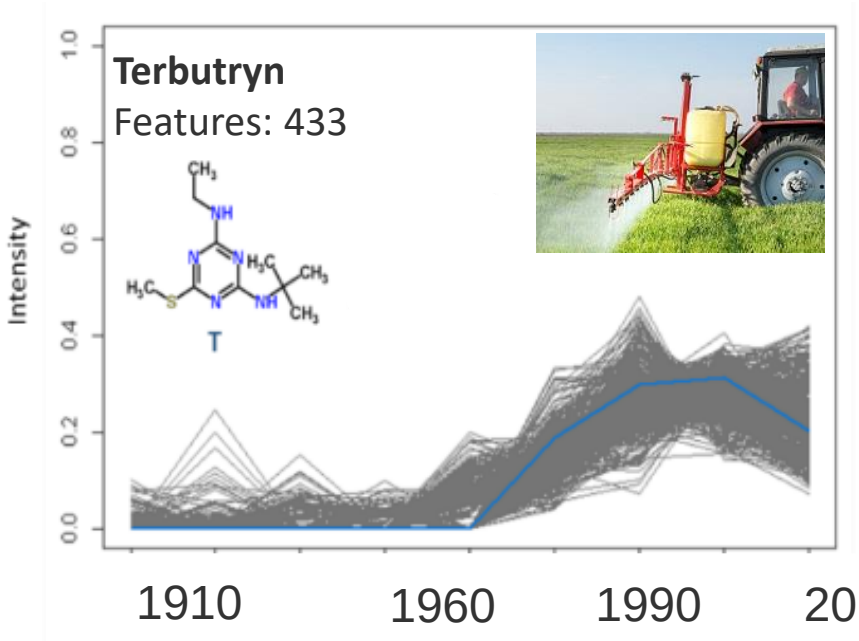
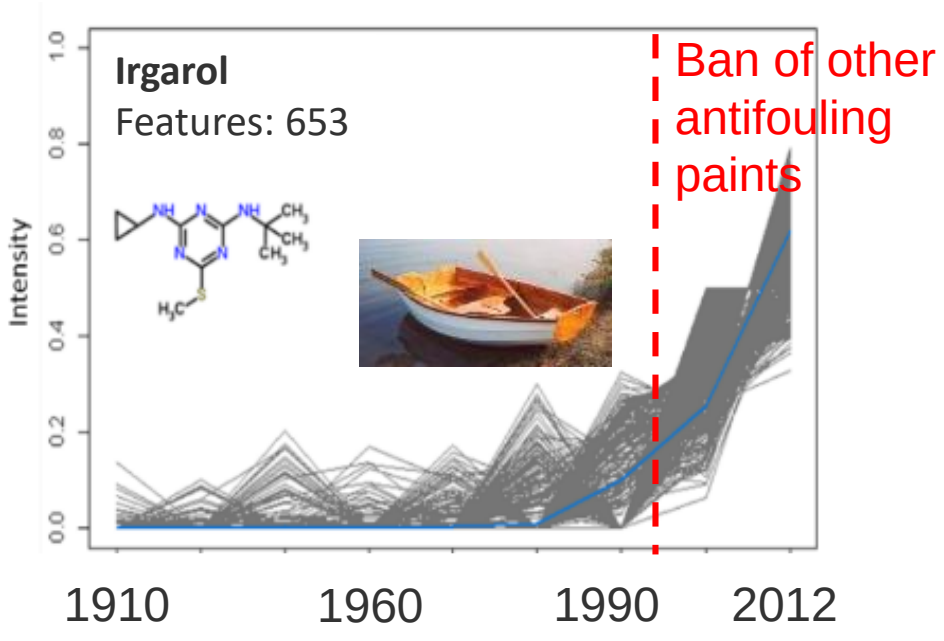
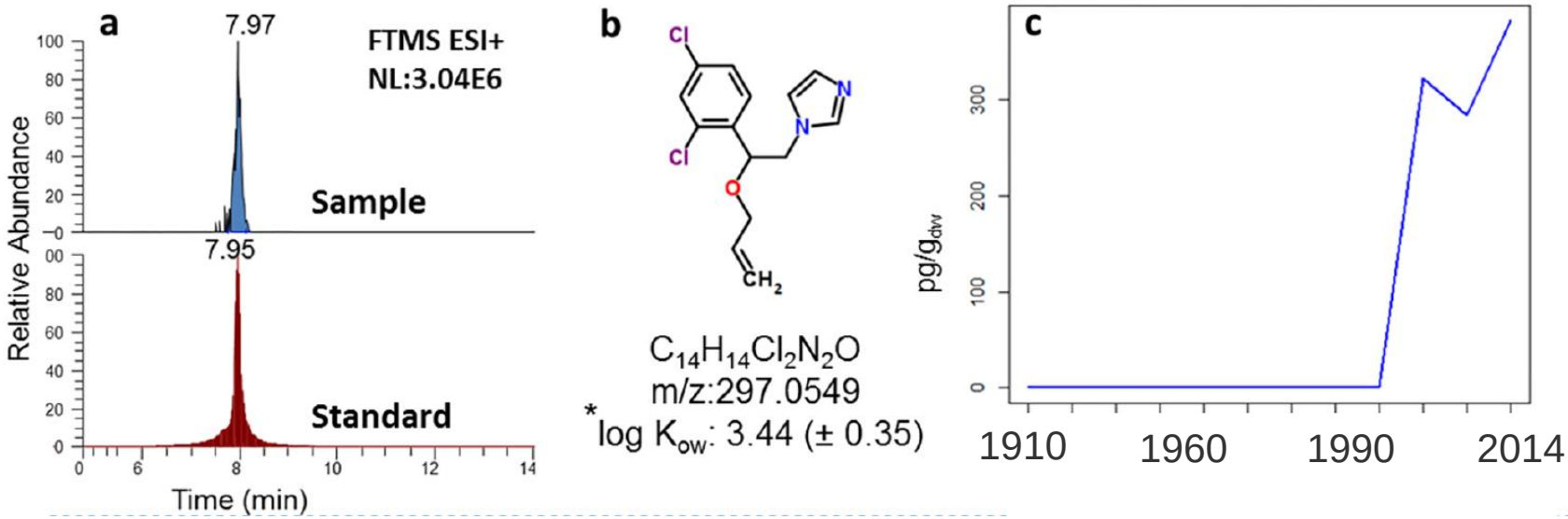






Identification of compounds with increasing concentrations

Imazalil



- Postharvest fungicide for citrus fruits
- Almost no application in Switzerland
- Entering Switzerland with imported fruits?

Chiaia-Hernandez et al. *ES&T* 2017, 51, 12547−12556

Daily screening at the International Rhine monitoring station

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Departement für Wirtschaft, Soziales und Umwelt des Kantons Basel-Stadt

Amt für Umwelt und Energie

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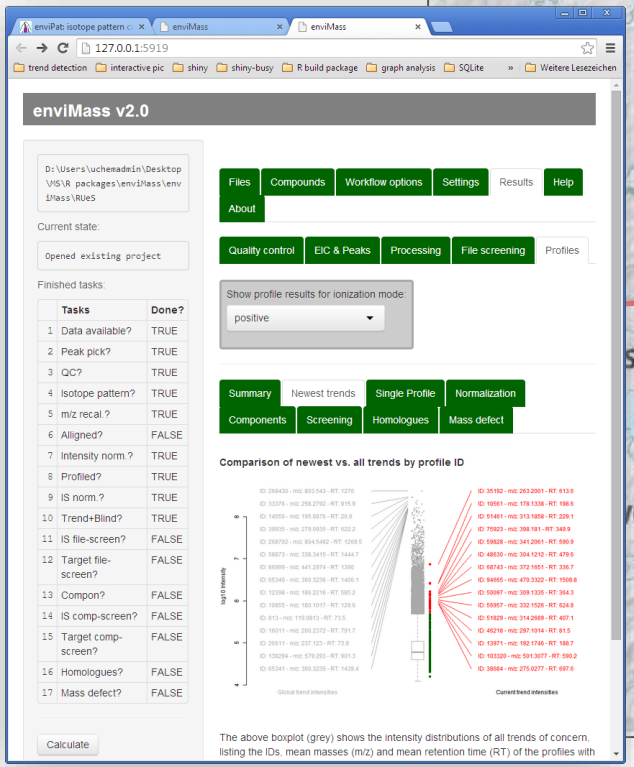
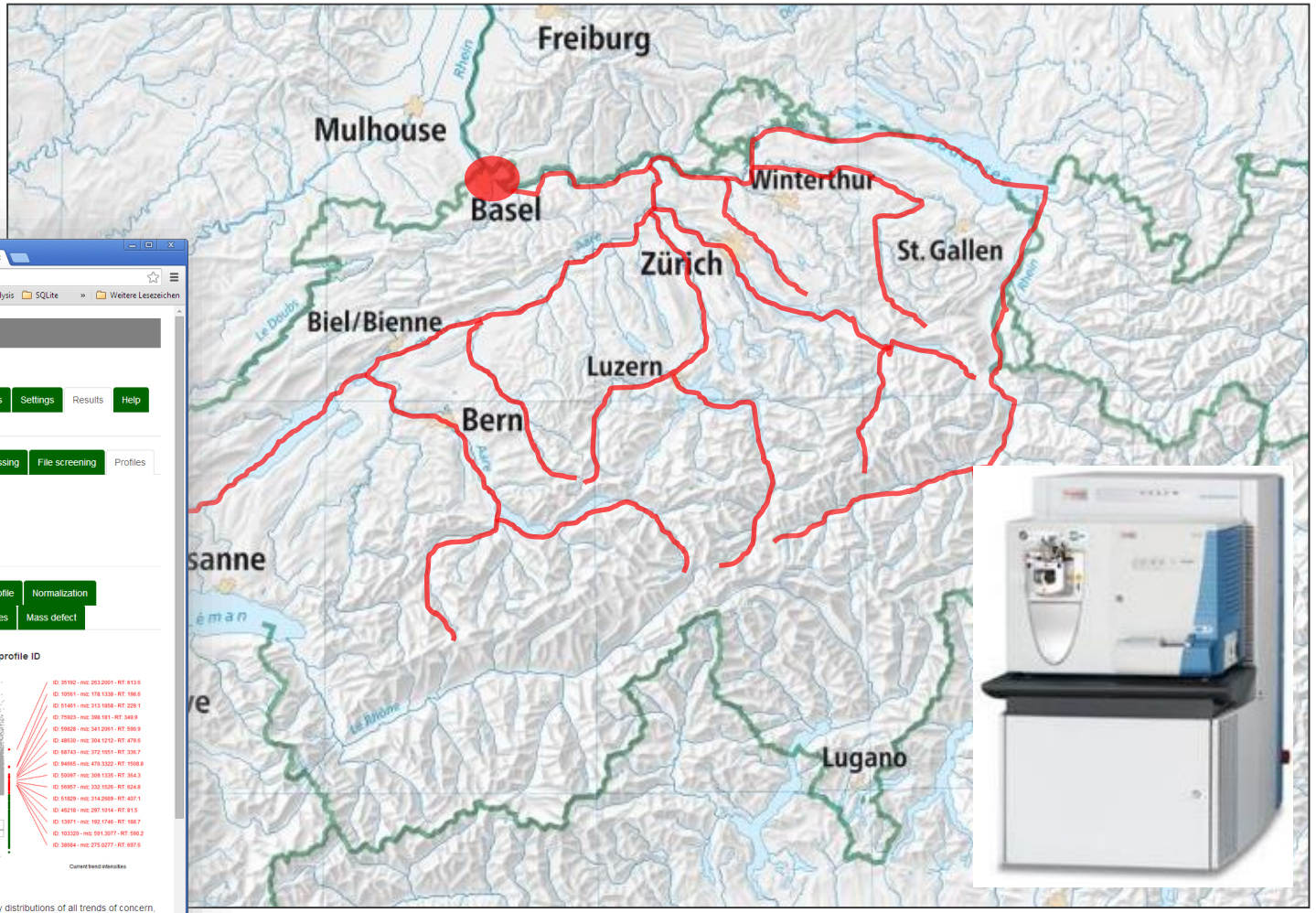


	Tasks	Done?
1	Data available?	TRUE
2	Peak pick?	TRUE
3	QC?	TRUE
4	Isotope pattern?	TRUE
5	m/z recal.?	TRUE
6	Aligned?	FALSE
7	Intensity norm.?	TRUE
8	Profiled?	TRUE
9	IS norm.?	TRUE
10	Trend+Blind?	TRUE
11	IS file-screen?	FALSE
12	Target file-screen?	FALSE
13	Compon?	FALSE
14	IS comp-screen?	FALSE
15	Target comp-screen?	FALSE
16	Homologues?	FALSE
17	Mass defect?	FALSE



http://www.eawag.ch/en/department/uchem/software/

Analytical strategy

Solid phase extraction followed by LC-HRMS/MS (Orbitrap)
High resolved full scan spectra & MSMS fragmentation spectra

Target analysis

50 → Priority substances

- x calibration
- x exact quantification
- x manual data processing

250 → Site specific substances

- x calibration
- x semi-quant. quantification
- x automated processing

Non-target analysis

remaining masses ∞

- Time profiles
- Statistical analysis
- Changes / trends
- Prioritization

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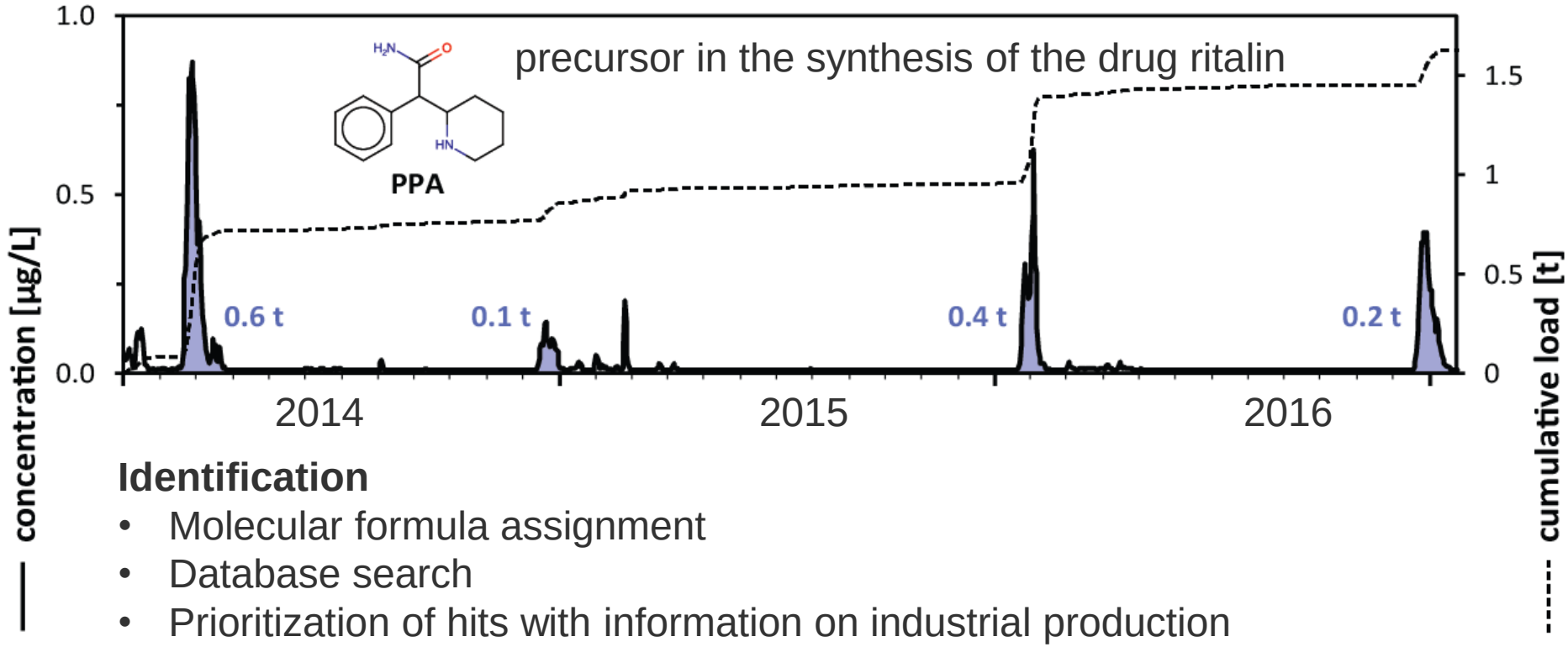
Ruff et al., Aqua & Gas 2013, 5: 16-25

Daily non-target screening of the Rhine River

Prioritization using time profiles

Previously unknown chemicals detected due to “stand-out” patterns



Identification

- Molecular formula assignment
- Database search
- Prioritization of hits with information on industrial production
- Confirmation with reference standard

► **10 major spills of non-target compounds in 2014 with > 25 tons of load**

Hollender et al, Env. Sci. Technol. 2017, 51: 11505-11512

Data of the Rhine monitoring station

NORMAN experiences since 2012

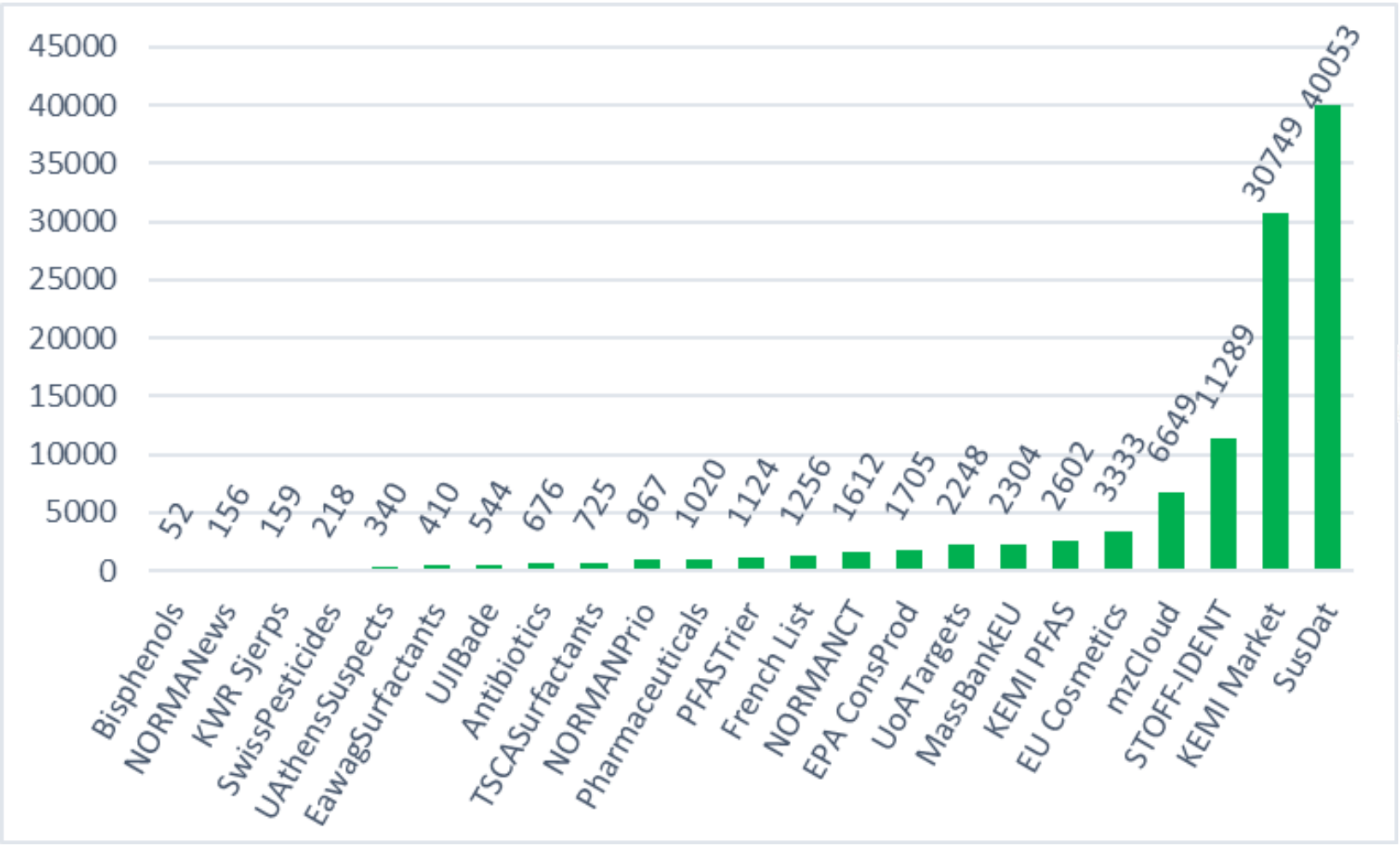
Goal: Comparison & harmonization of NTS methods in Europe

Collaborative trials on water (Schymanski *et al*. ABC (2015) 407: 6237-6255) and dust (Rostkowski et al, in prep.)

- ► Liquid & gas chromatography are complementary
- ► Need for exchange of suspect lists & mass spectra

NORMAN Suspect List Exchange

- http://www.norman-network.com/?q=node/236
- 28 lists available … specialist collections to market lists
  - Integrated in NORMAN Databases & CompTox Chemistry Dashboard



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Schymanski, Aalizadeh *et al*. in prep; https://www.researchgate.net/project/Supporting-Mass-Spectrometry-Through-Cheminformatics

Open access mass spectra library

- currently 51’000 spectra of 15’622 compounds from 15 main instrument types and 32 institutions

MassBank norman

High Resolution Mass Spectral Database

Home | Quick Search | Peak Search | Record Index | Statistics | Imprint/Data privacy MassBank ID: Go

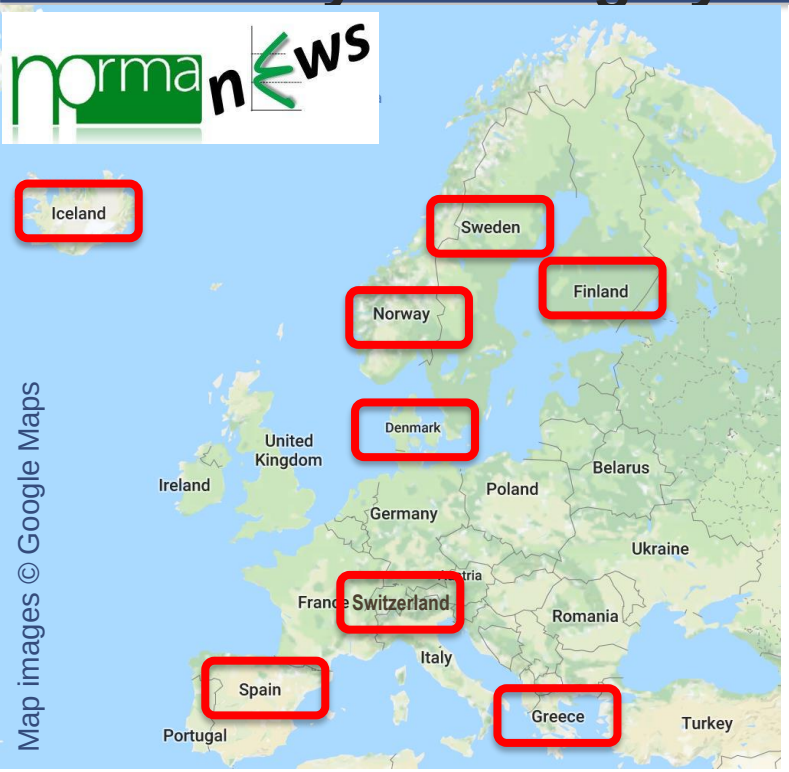
European MassBank (NORMAN MassBank)

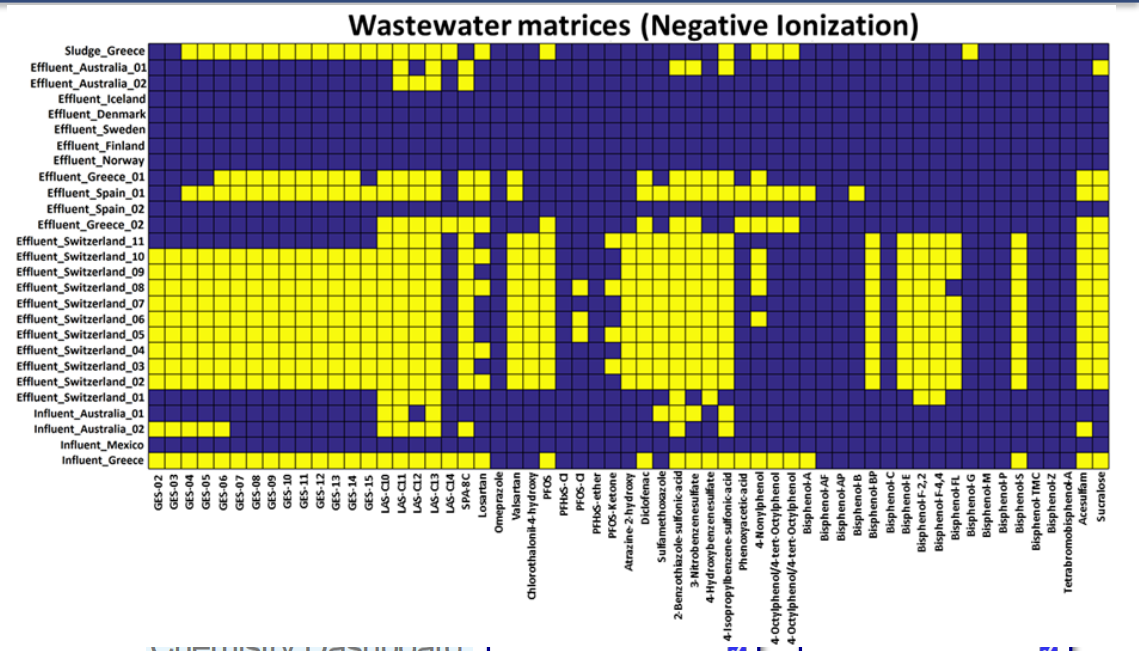
Quick Search

Peak Search

Record Index

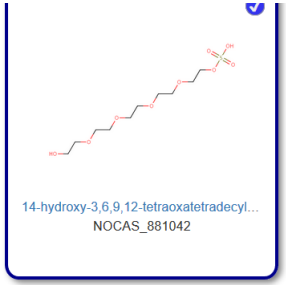
Retrospective screening of emerging suspects - an early warning system

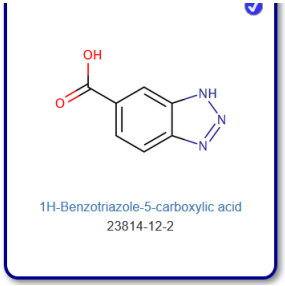


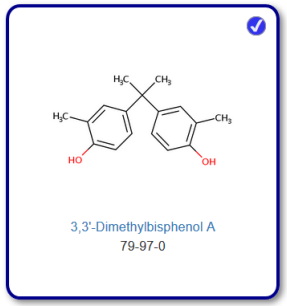


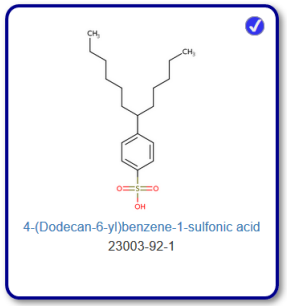
Chemistry Dashboard

NORMANEWS





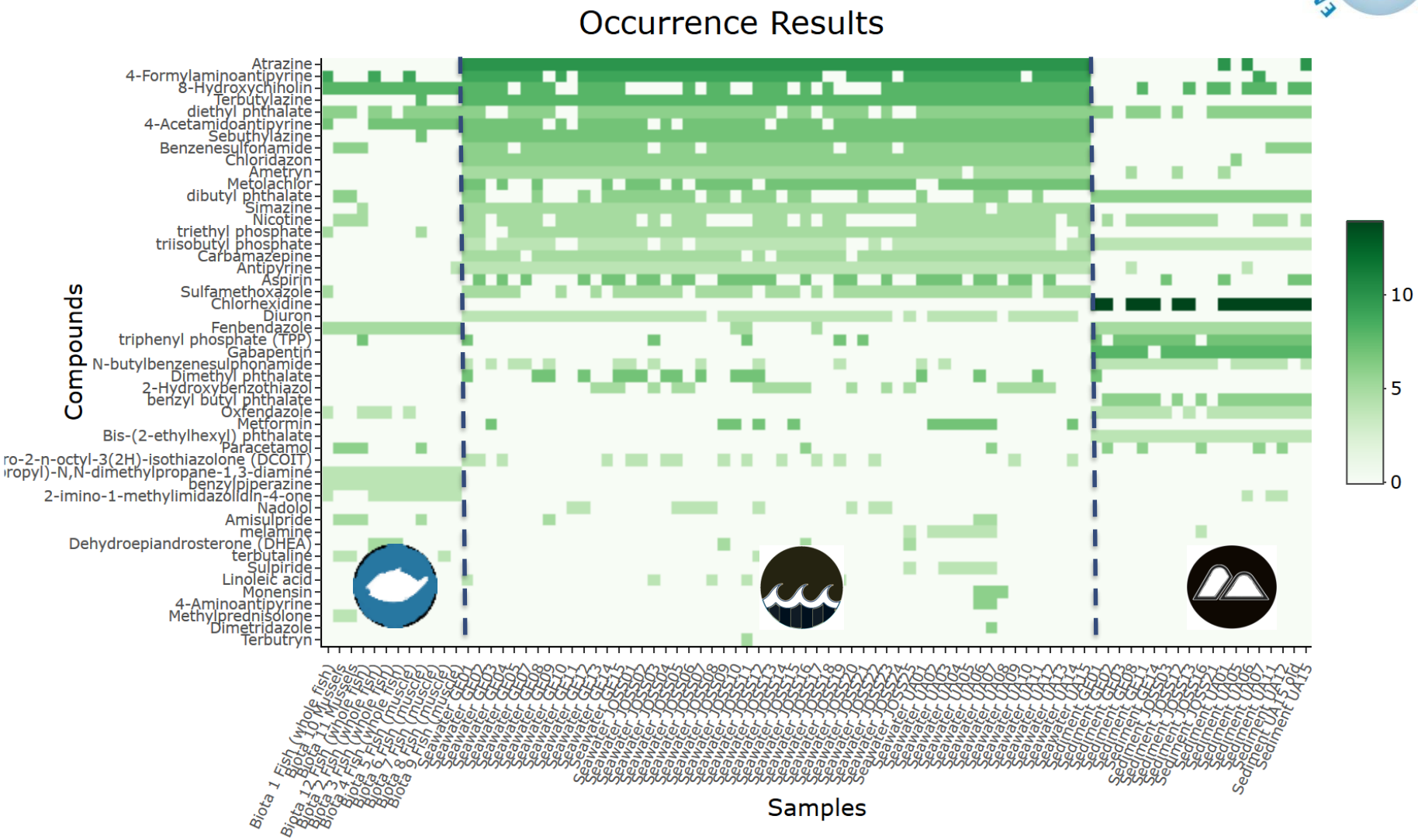




Alygizakis et al. 2018 ES&T & https://comptox.epa.gov/dashboard/chemical_lists/normanews

NORMAN Digital Sample Freezing Platform

Retrospective screening of REACH chemicals in Black Sea samples (various matrices)



Interactive heatmap available at http://norman-data.eu/NORMAN-REACH

Non-target screening ready to be used in regulation?

Yes!

- Successful examples like the Rhine monitoring stations exist
- Excellent instrumentation, databases and data analysis tools are available
- Digitalization & data sharing opens interesting opportunities for chemicals management in river basins and all over Europe

Next steps

- Further implementation in practice labs
- Improved management of the amount of data
- Linking of non-target data with chemical registration & management

Acknowledgements – Group effort

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http://norman-data.eu/