Durham, 28th Sept 2018

Fall 2018 Symposium

EMERGING CONTAMINANT MONITORING IN SWISS SURFACE WATERS

Targeted and Non-targeted Strategies for Water Quality Assessment

Matthias Ruff

The 'Rhine story' – 4 different actors

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FOEN
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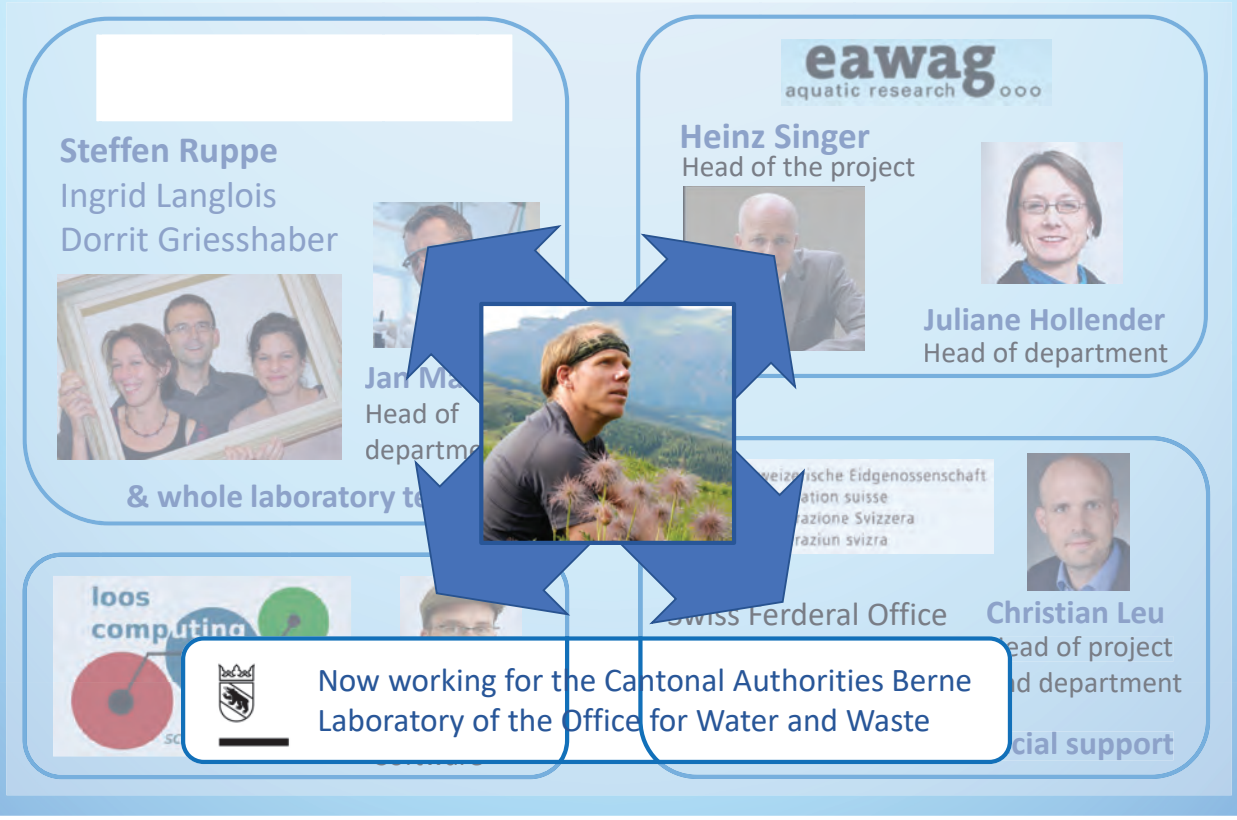
Christian Leu
Head of project and department

Project initiation & financial support

The Rhine story – 4 different acteurs



Europe…

The River Rhine

Length	1233 km
Catchment area	220,000 km^2
Total discharge	2,300 m^3/sec
Habitants living in the catchment	58 Mio
Habitants supplied with drinking water	20 Mio

But why monitoring?

The Accident September 1986

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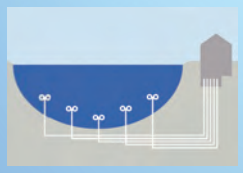


Monitoring Station

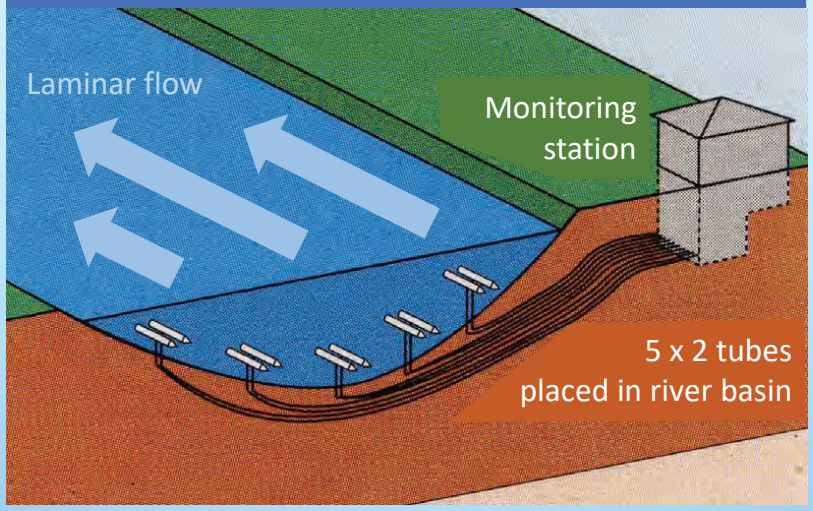
Eawag

The monitoring station

Goal and challenge

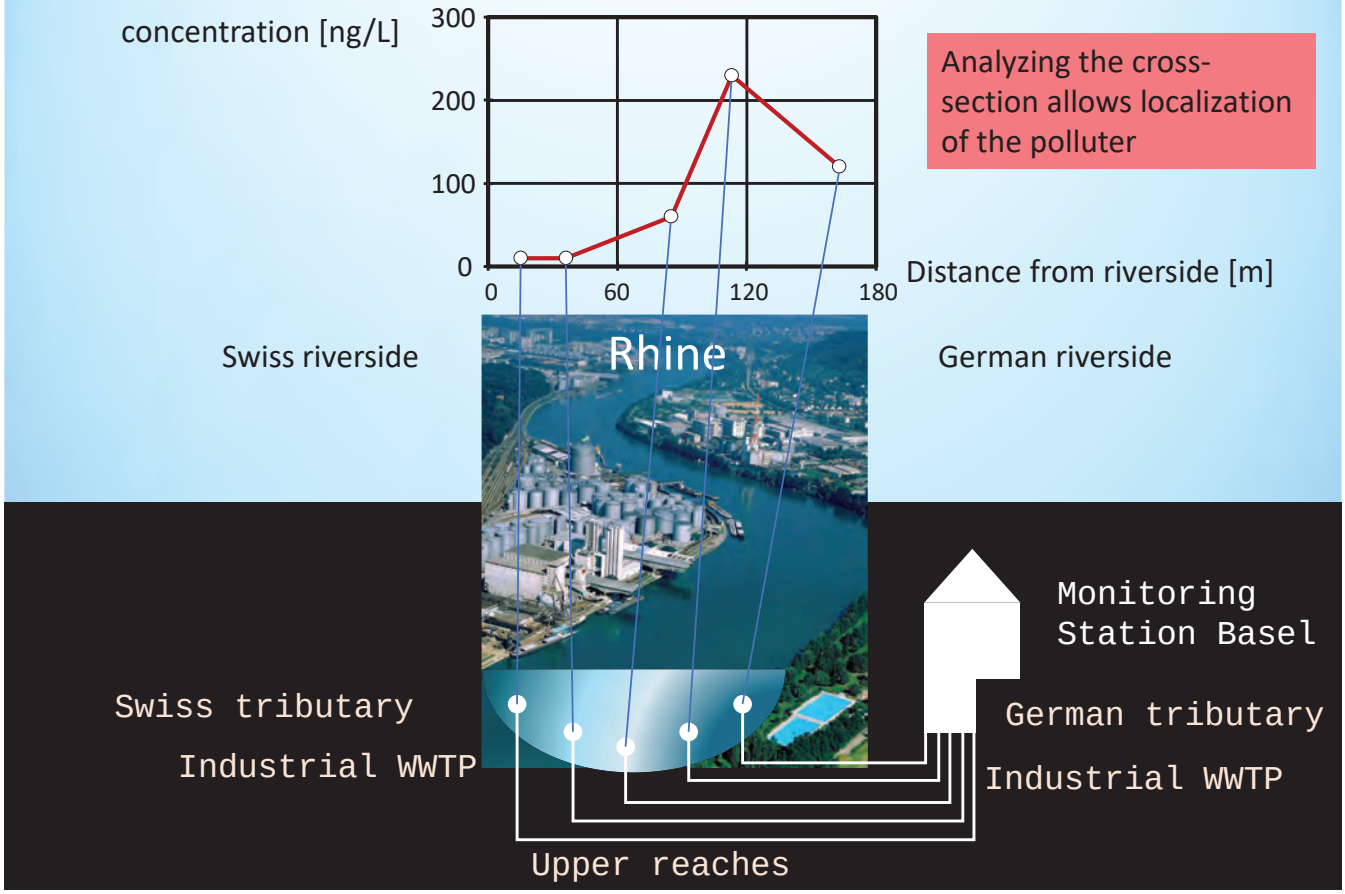
Goals

- Monitoring long term **trends**
- Detection of accidental **spills** and localization of the polluter



Scheme: AUE Basel

Event monitoring – Polluter localization



Rhine monitoring

Requirements and parameters

quantitative · universal · contemporary · actual · efficient

Rhine monitoring (until 2010)

Online-Parameters
Temp, pH, O_2, Leitfähigkeit

Sum parameters
DOC,TOC, N, P, GUS, °dH

Inorganic + Others
Heavy metals (10)
Anions + Cations (5+8)
Nutrients (N + P)
Chelating agents (3)
Others

Organic trace analysis

GC / GC-MS	HPLC-MS
Targets (42 + 56)	Targets (53)
Unknown Screening ∞)	

Water solubility
Volatility

Rhine monitoring

Requirements and parameters

quantitative | universal | contemporary

actual | efficient

Rhine monitoring (since 2012)

Online-Parameters

Temp, pH, O_2, Leitfähigkeit

Sum parameters

DOC,TOC, N, P, GUS, °dH

Inorganic + Others

Heavy metals (10)
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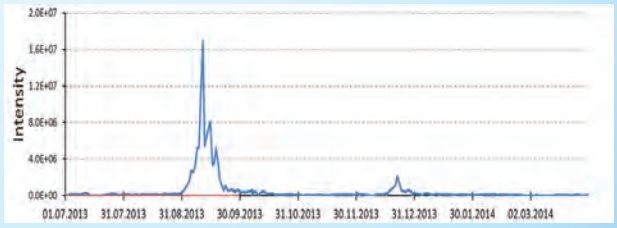
Organic trace analysis

Trend monitoring vs Spill detection

Trend monitoring

Spill detection



- x ***Known*** substances
- x Limited number
- x Exact quantification

- x ***Unknown*** substances
- x *Unlimited* number
- x Detection
  Identification
  Rough estimation

Analytical strategy

LC-HRMS (LTQ-Orbitrap)
High resolved full scan spectra pos/neg mode & MS2 fragmentation spectra
10 - 15'000 peaks per measurement

Target analysis

50

Priority substances

250

Site specific substances

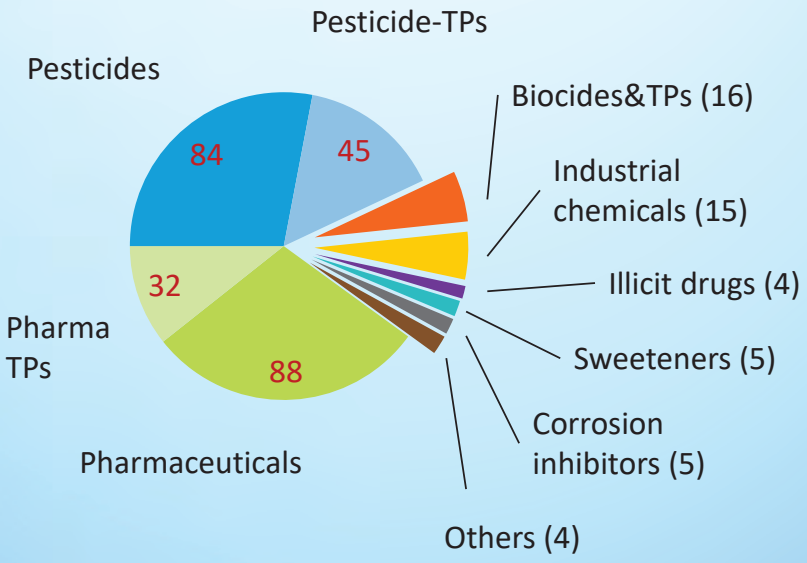
Non-target analysis

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

- x Std calibration
- x automated processing
- x 'semi'-quantification

Targeted Screening

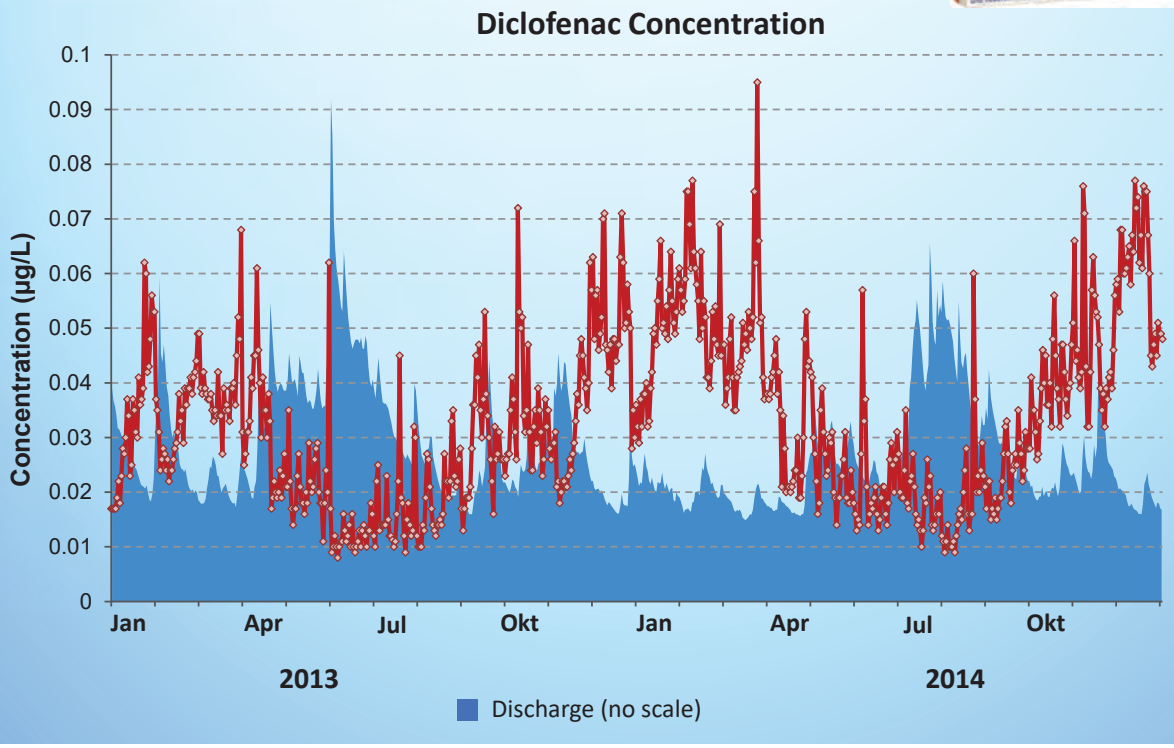
Substance diversity



Σ: 300

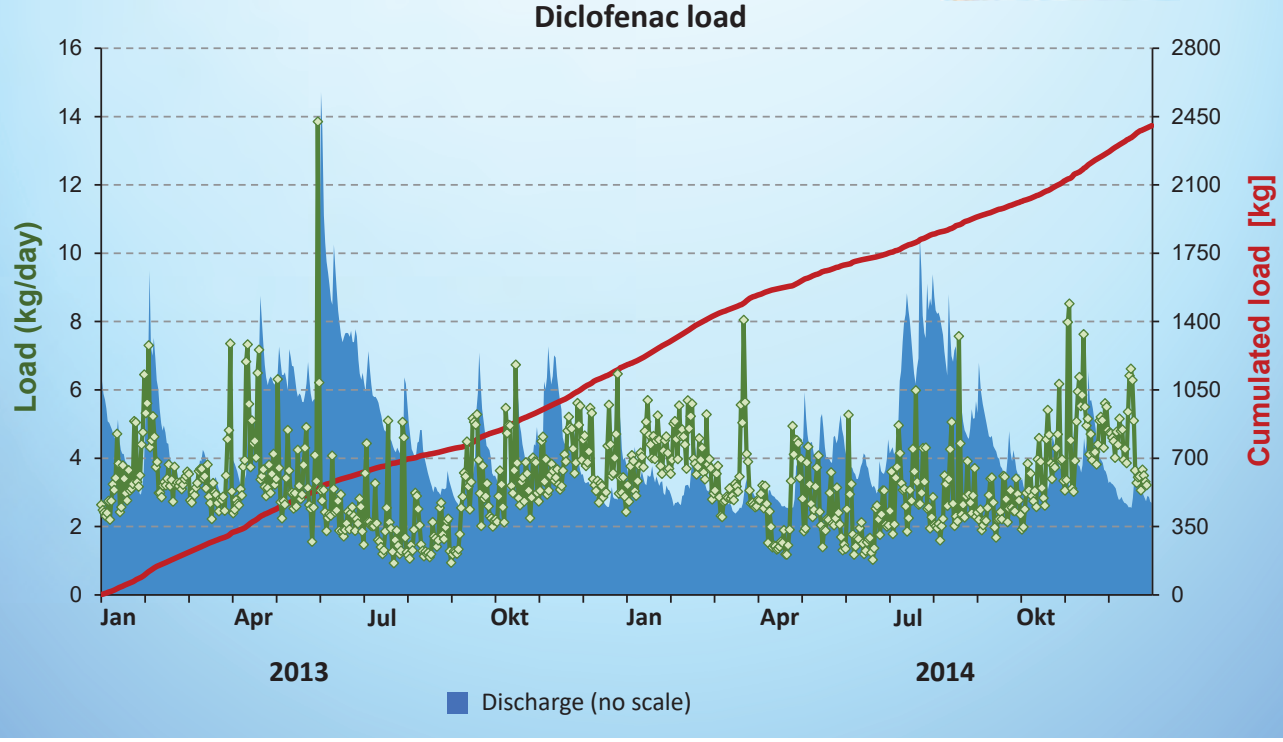
Diclofenac 2013 - 2014

Concentrations of 24 h composite samples



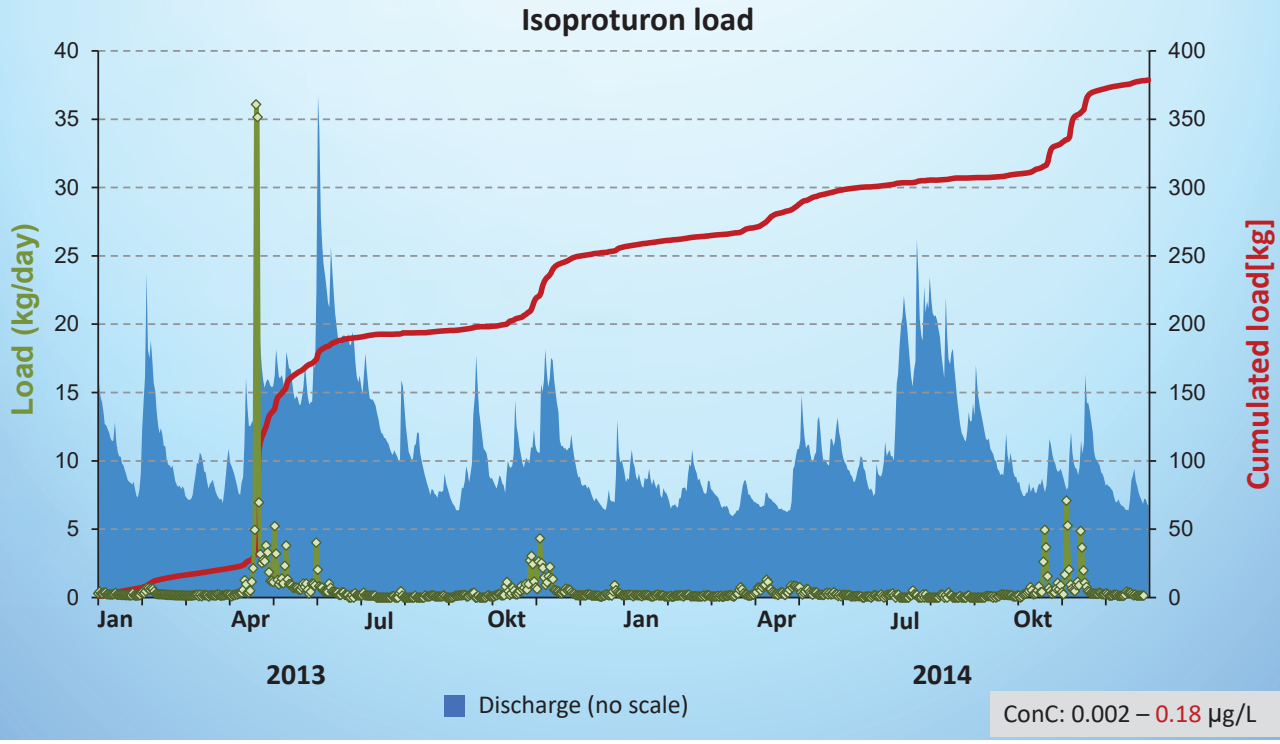
Diclofenac 2013 - 2014

Loads of 24 h composite samples



Isoproturon 2013 - 2014

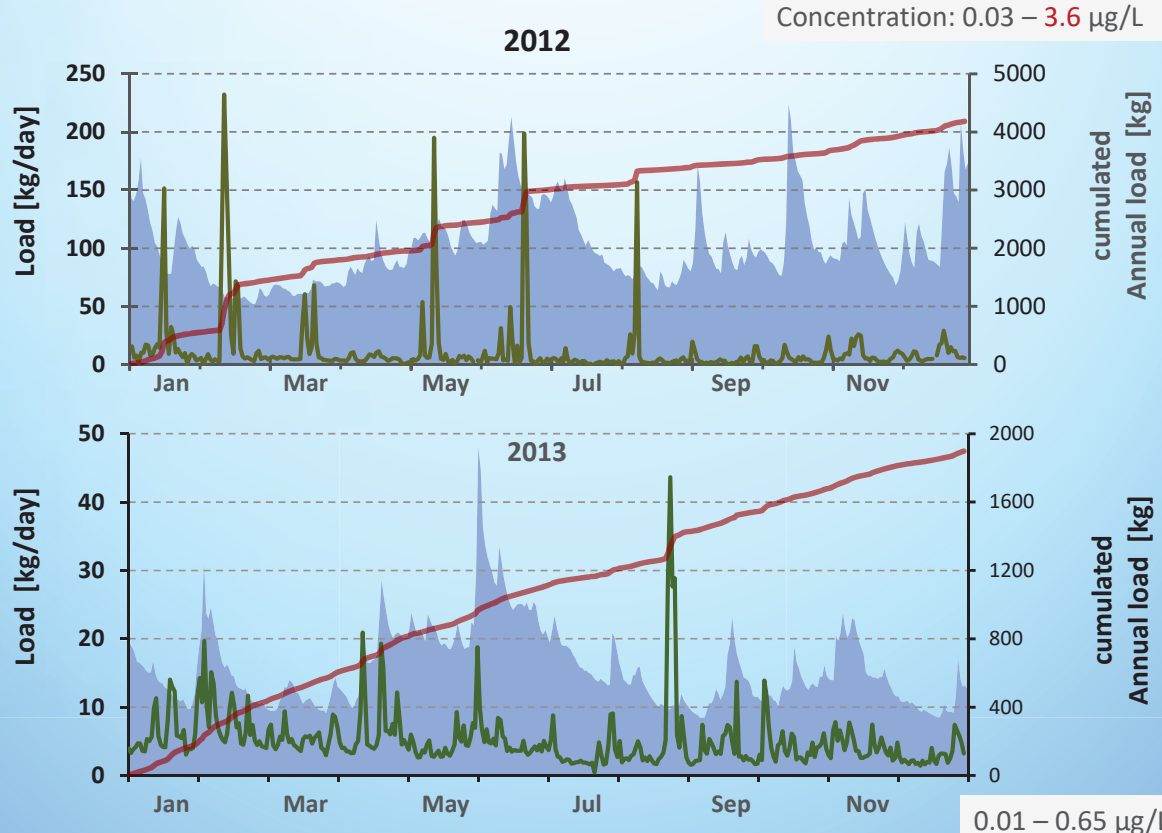
Loads of 24 h composite samples



ConC: 0.002 – 0.18 µg/L

Saccharine

Concentration: 0.03 – 3.6 µg/L



0.01 – 0.65 µg/L

Analytical strategy

LC-HRMS (LTQ-Orbitrap)
High resolved full scan spectra pos/neg mode & MS2 fragmentation spectra
10 - 15'000 peaks per measurement

Target analysis

50

Priority substances

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

250

Site specific substances

- x Std calibration
- x automated processing
- x semi-quantification

Non-target analysis

remaining masses

Unknown substances

- x no calibration
- x concentration estimated
- x automated processing

Analytical strategy

LC-HRMS (LTQ-Orbitrap)
High resolved full scan spectra pos/neg mode & MS2 fragmentation spectra
10 - 15'000 peaks per measurement

Target analysis

50

Priority substances

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

250

Site specific substances

- x Std calibration
- x automated processing
- x semi-quantification

Non-target analysis

remaining masses

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

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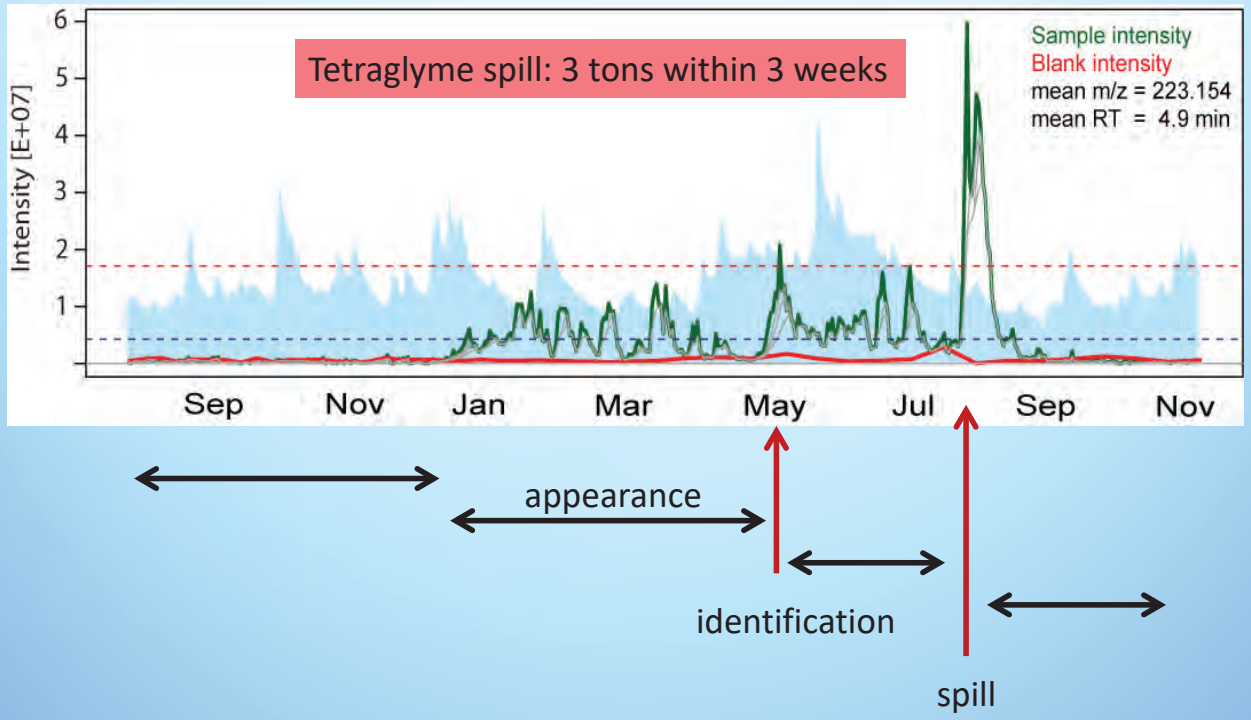
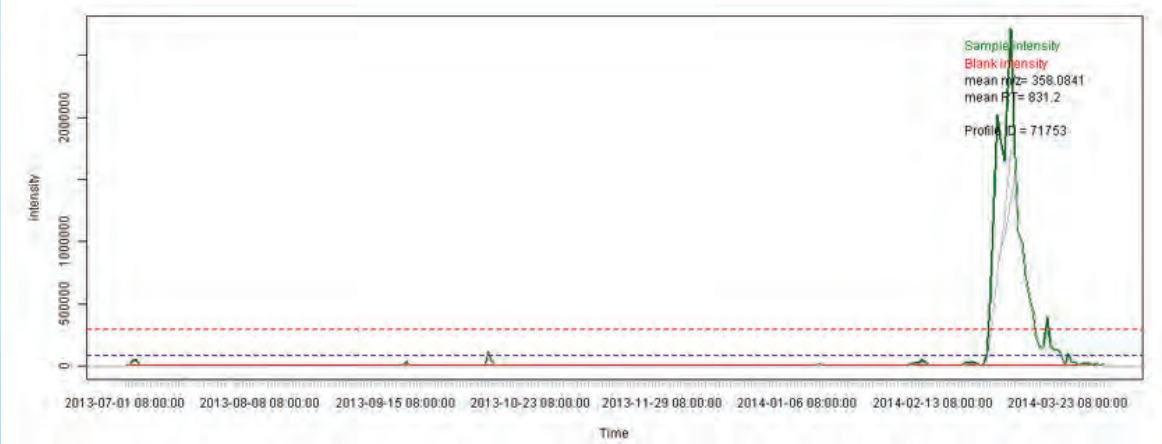
Prioritization using time profiles



March 2014: Indomethacin

March 2014	1	2	3	4	5	6	7	8

Indomethacin spill: single event



Concentration (max):	> 0.4 µg/L
Load (over 14 days):	170 kg

Source was located!

Non-target screening: m/z 141.0207 $[M-H]^-$

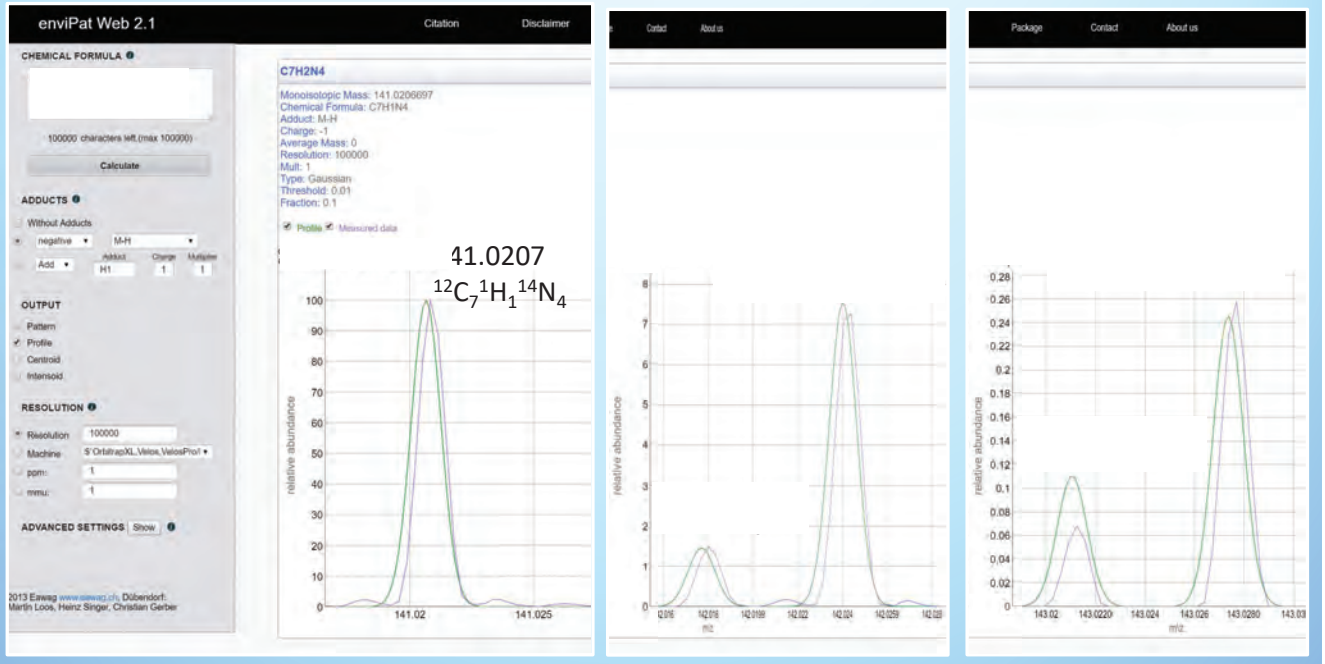
Unknown compound 141

- Almost continuous emission throughout the year
- Zero emission during long vacation in Germany

Determination of molecular formula

Isotope pattern and molecular formula fit

at a mass resolution of 100’000 (@ m/z 400) and mass accuracy < 2ppm



http://www.envipat.eawag.ch/

Database search: just 6 entries for $C_7H_2N_4$

- ChemSpider Database:

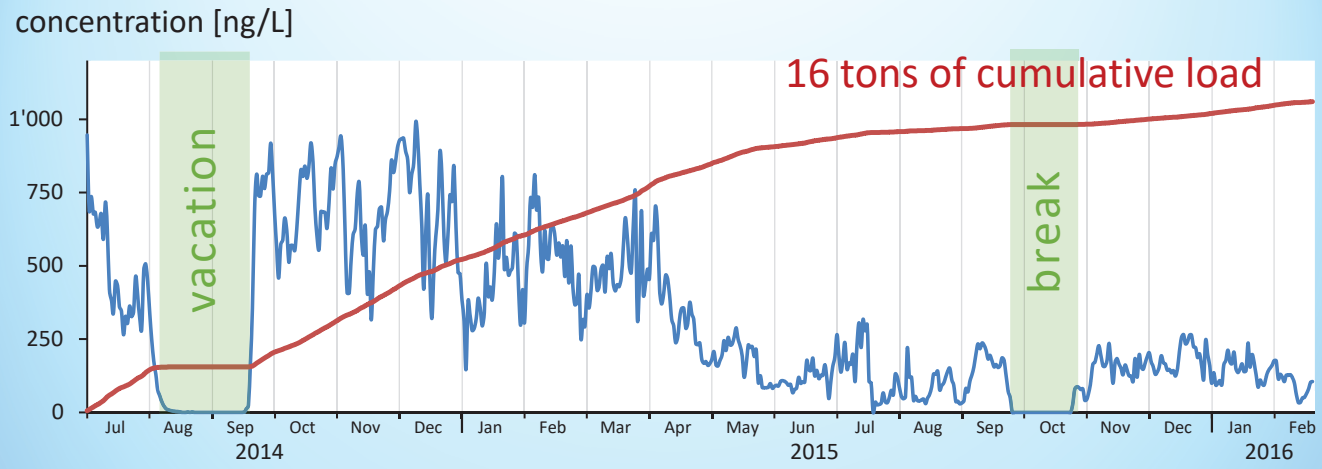
- In-Silico fragmentation: 3 structures likely
- Spectral databases: no entries
- No vendors for chemical reference substance

Usually, the story would end here…

BUT

Due to cooperation with the local chemical industries, the polluter reacted on our request and provided a reference substance.

Identified as Tetracarbonitrile-1-propene



- Unwanted by-product of an chemical synthesis
- Average load of 0.8 tons per month into the river
- Company reacted, emission about 80 % reduced

International monitoring network

- 7 Headquaters
- 7 Monitoring stations

Threshold concentration levels for alarm activation [µg/	regional	internati
Pesticides, Biocides, Pharmaceuticals	0.1	0.3
other Substances	1	3

Alarms for the river Rhine at Basel

Compound	Use	Type	Load	Source	Dynamics
Acetaminophen	Drug	target	**0.3 t**	WWTP	Peak
Mecoprop	Pesticide	target	**0.3 t**	Agriculture	Peak
Aliskiren		uspect	**1.4 t**	Industry / WWTP	Peak / continuous
Tizanid		uspect	**0.2 t**	Industry	Peak
Indon		spect	**0.2**		Peak
p-Tol		spect	**1.5**		Peak
2-Phe acetal		n-target	**0.6**		Peak
Unknow		non-target	**1.3 t**	Industry	Peak
Unknow		non-target	**0.1 t**	Industry	Peak
Unknown_325		non-target	**5 t**	Industry	Continuous
Tetracarbonitrilpropen	Industry	non-target	**14 t**	Industry	Continuous

Summarized detected load from municipal **WWTPs** and **agriculture**

100 tons/a

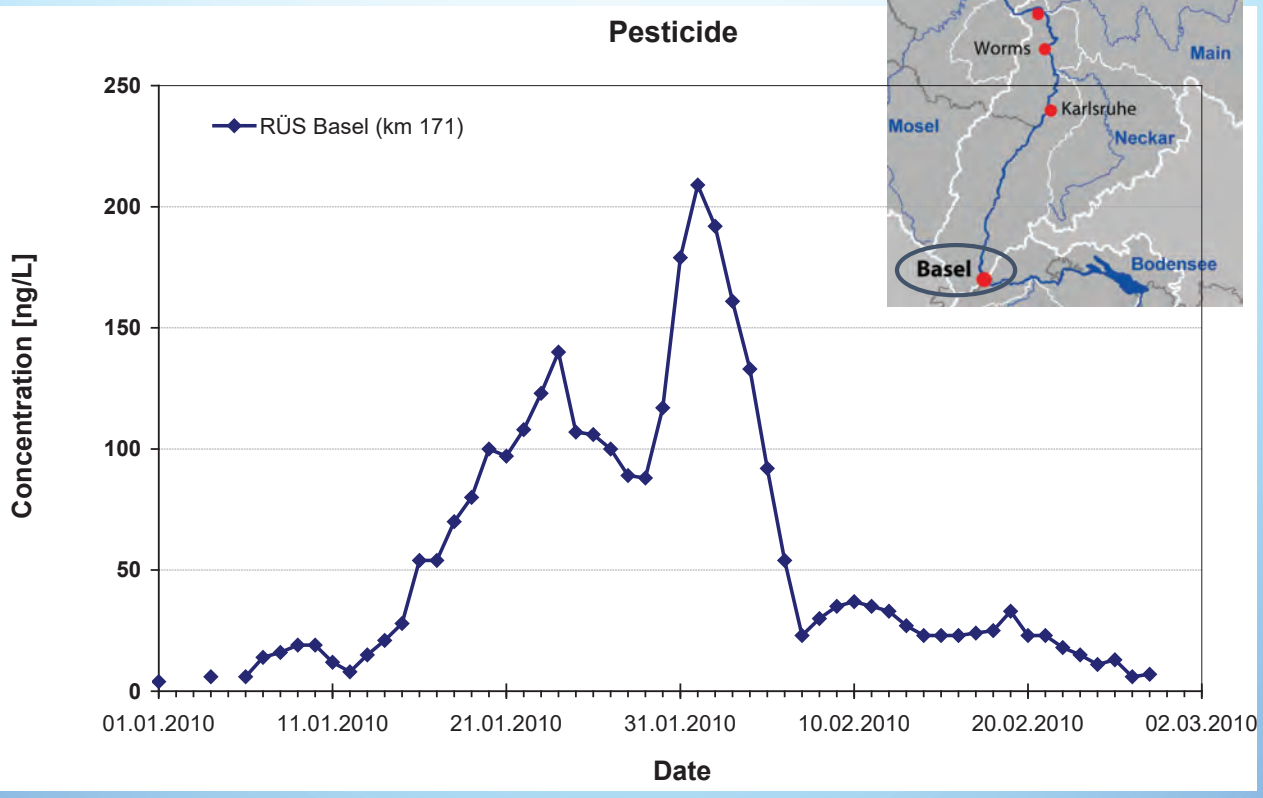
Load industry

24 t/a

Does the monitoring concept work?

3 convincing examples

1 Spill with origin Basel



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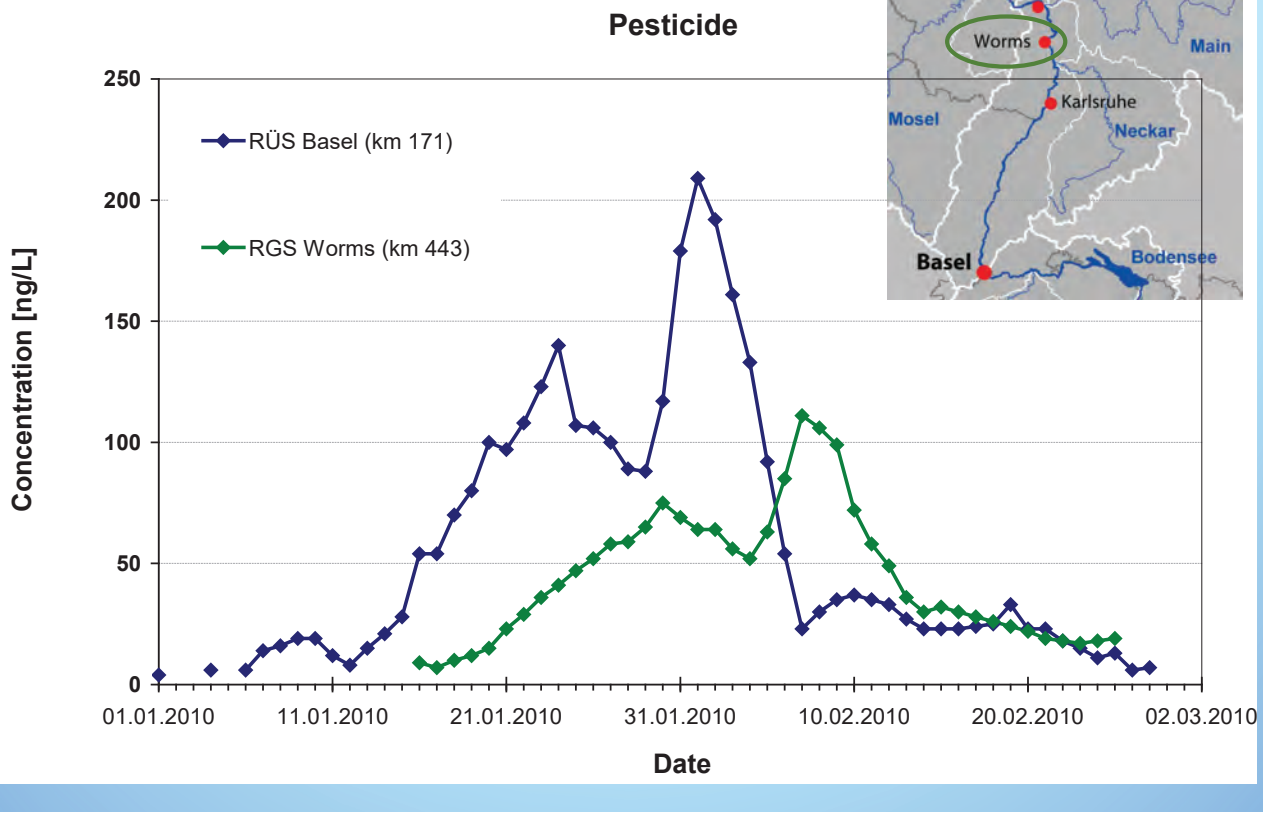

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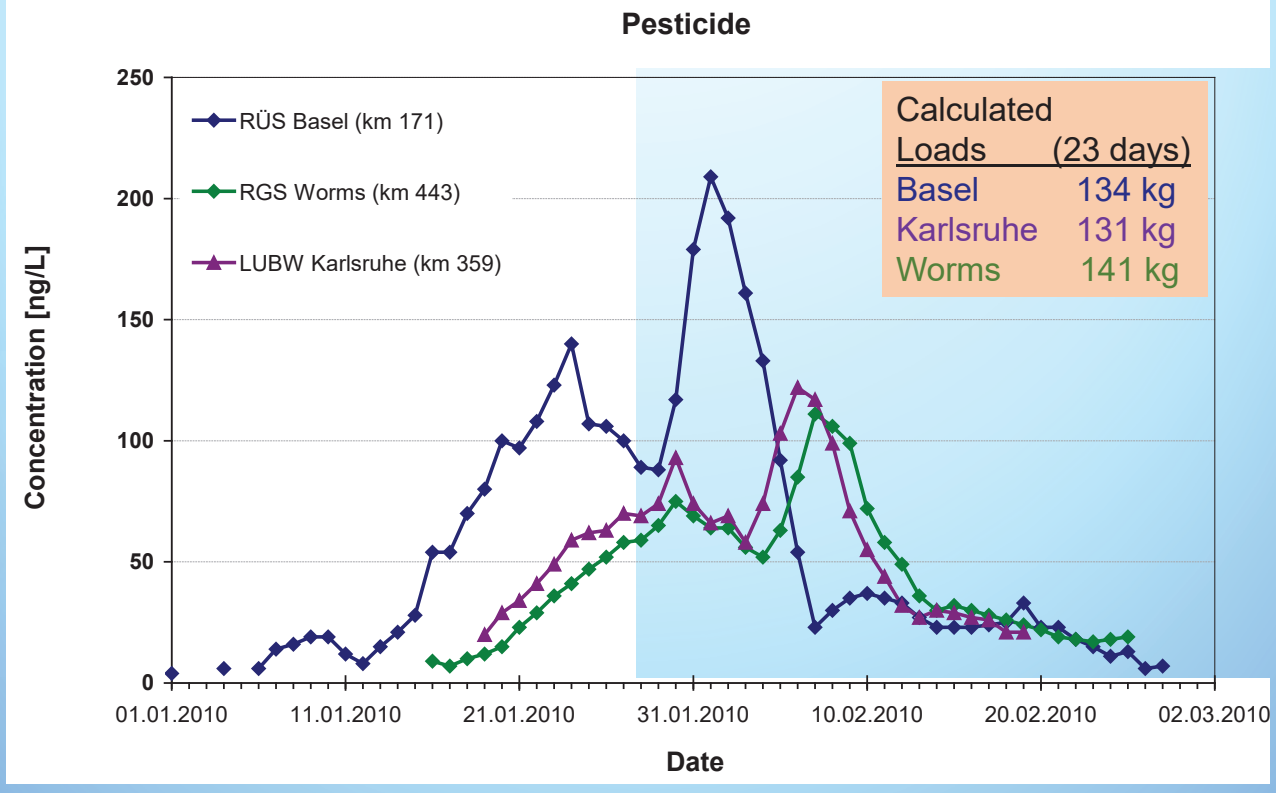
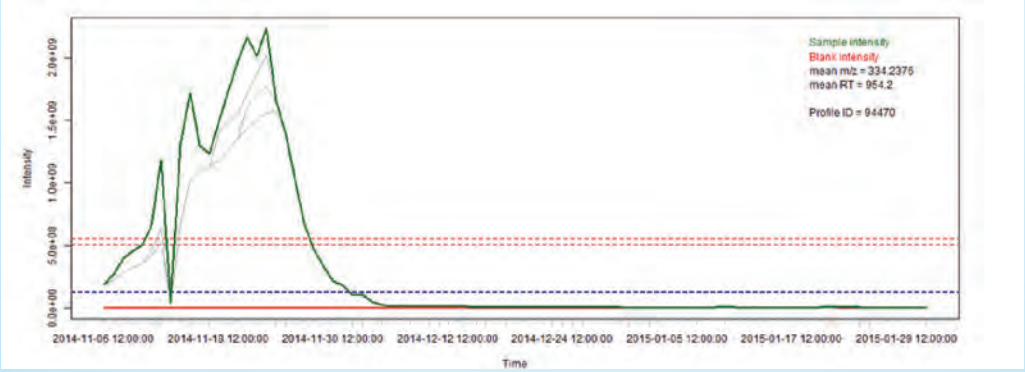


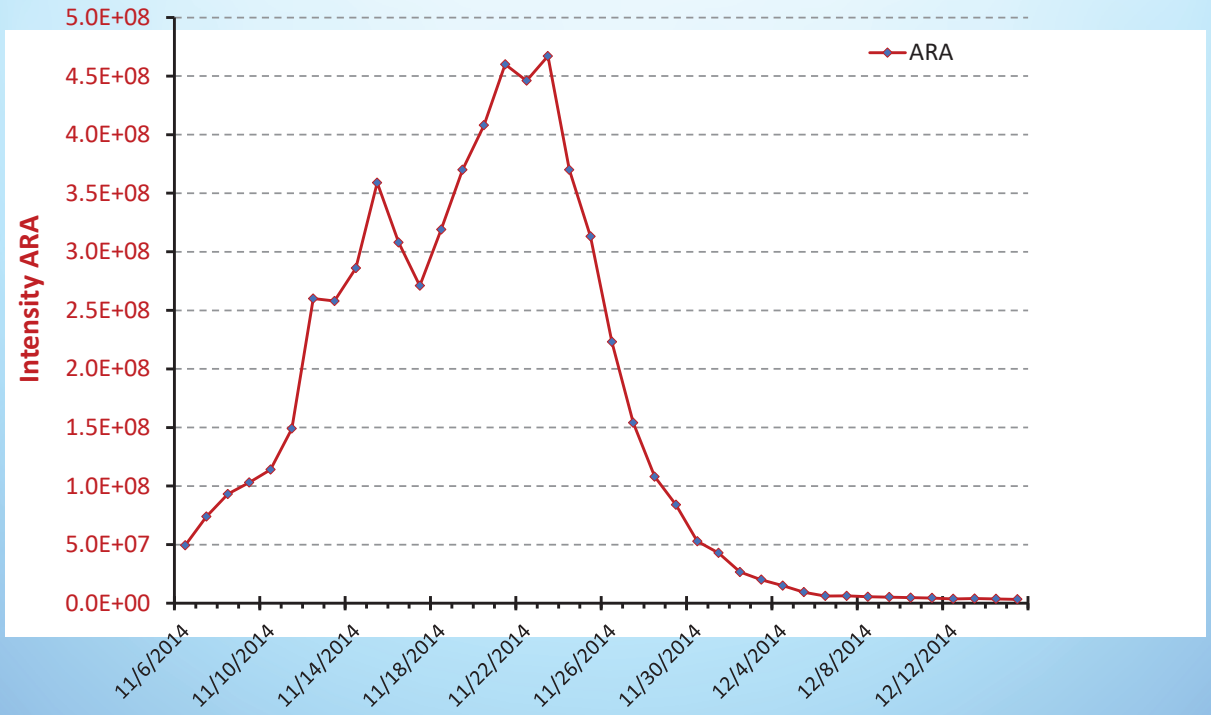
2 Point-Source at WWTP: NT 334.2376



WWTP effluent

Rhine Monitoring Station

2 Overlay WWTP and monitoring peak



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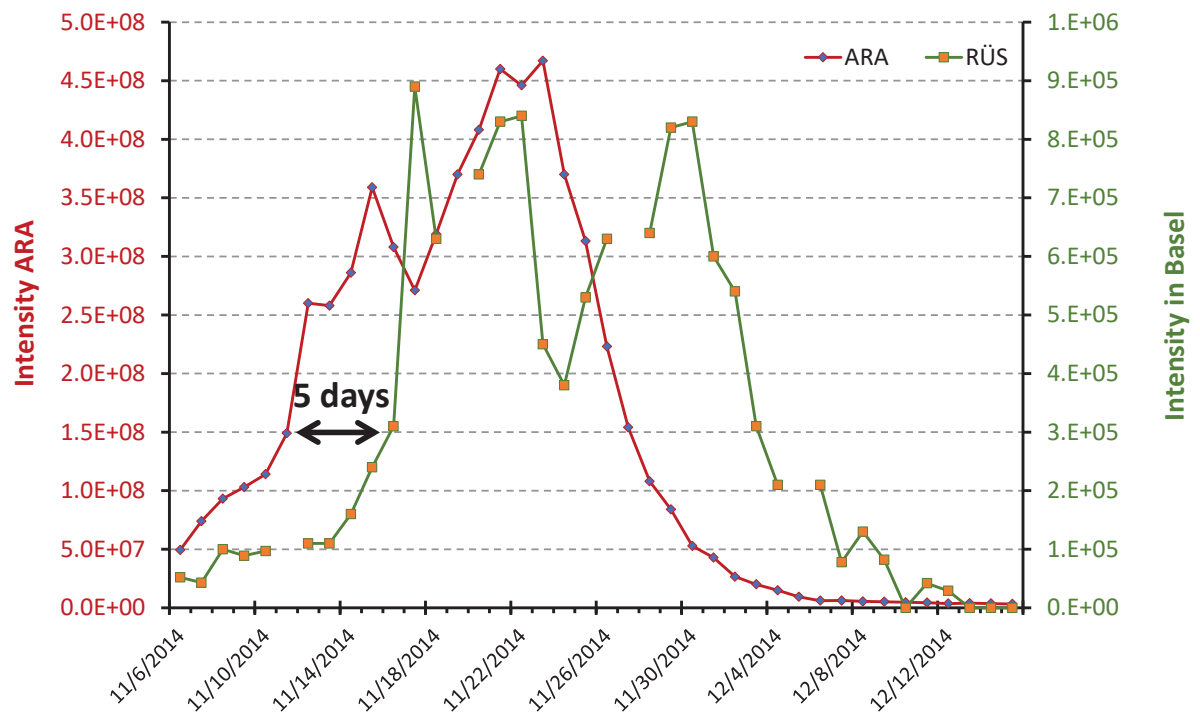
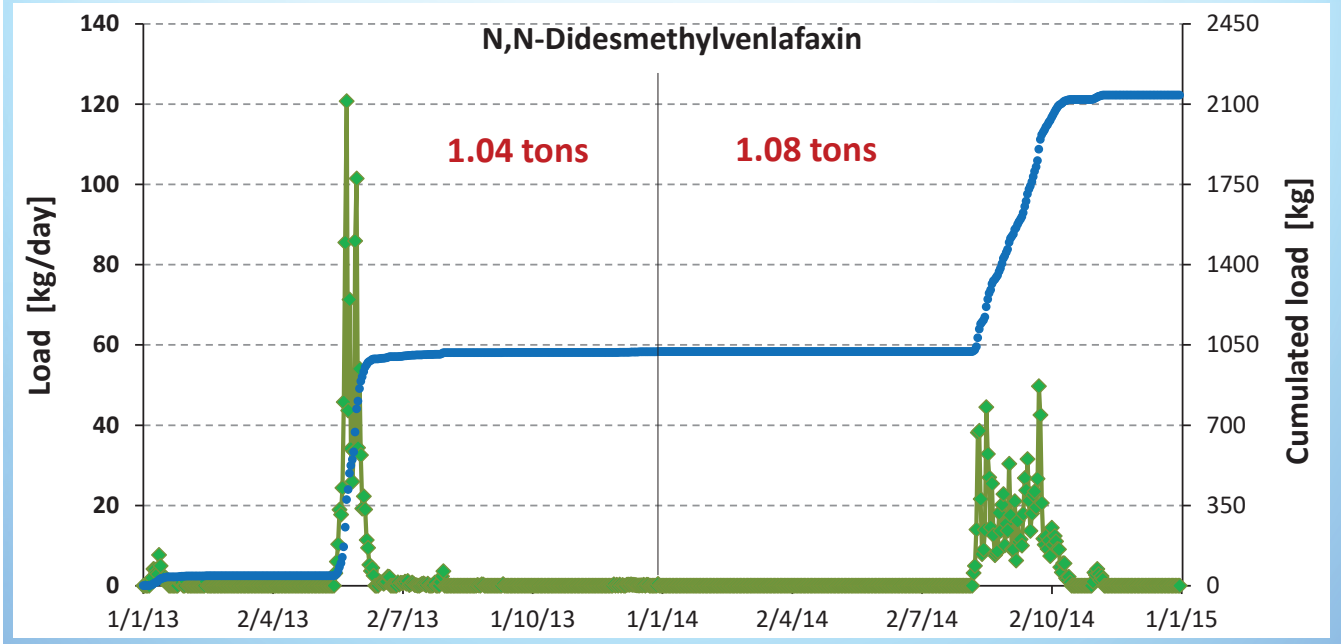


3 Recurring production patterns

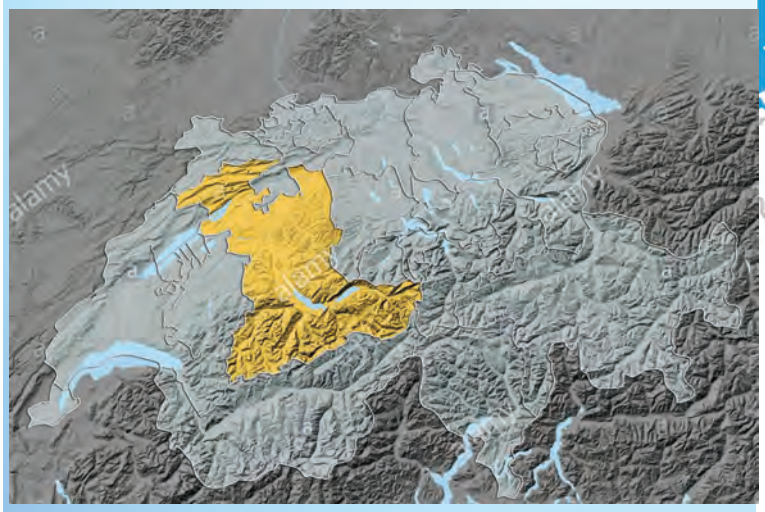
Loads of 24 h composite samples



No reduction, just a dilution!

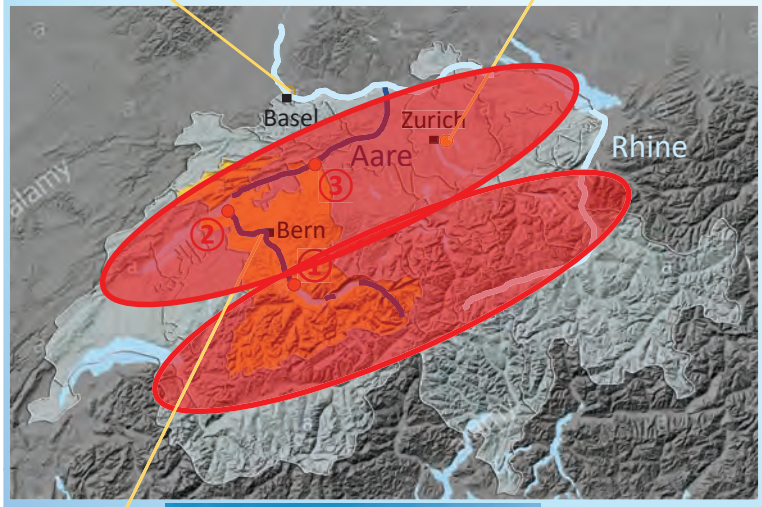
Swiss Rhine Monitoring extended?

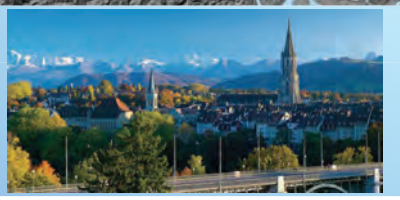
River Aare in Cantone Berne



Swiss Rhine Monitoring extended?

Planned next year: Screening of River Aare by Cantone Berne





① Alpine river Aare and lake monitoring

② Monitoring the midland plateau with most population and agriculture

③ Monitoring the midland plateau and the water leaving the cantonal border

Conclusion

- The monitoring station provides a deep insight into the river
- Trend monitoring by using a targeted approach
  Spill detection by using a non-targeted approach
- Data processing just possible using adapted, intelligent algorithms
- The monitoring works over hundreds of km and within a complex catchment area
- Best is a communicating network of stations
- Loads can be reduced by identifying the polluter

The 'Rhine story' – 4 different actors

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Steffen Ruppe
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eawag aquatic research

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Thanks for listening!

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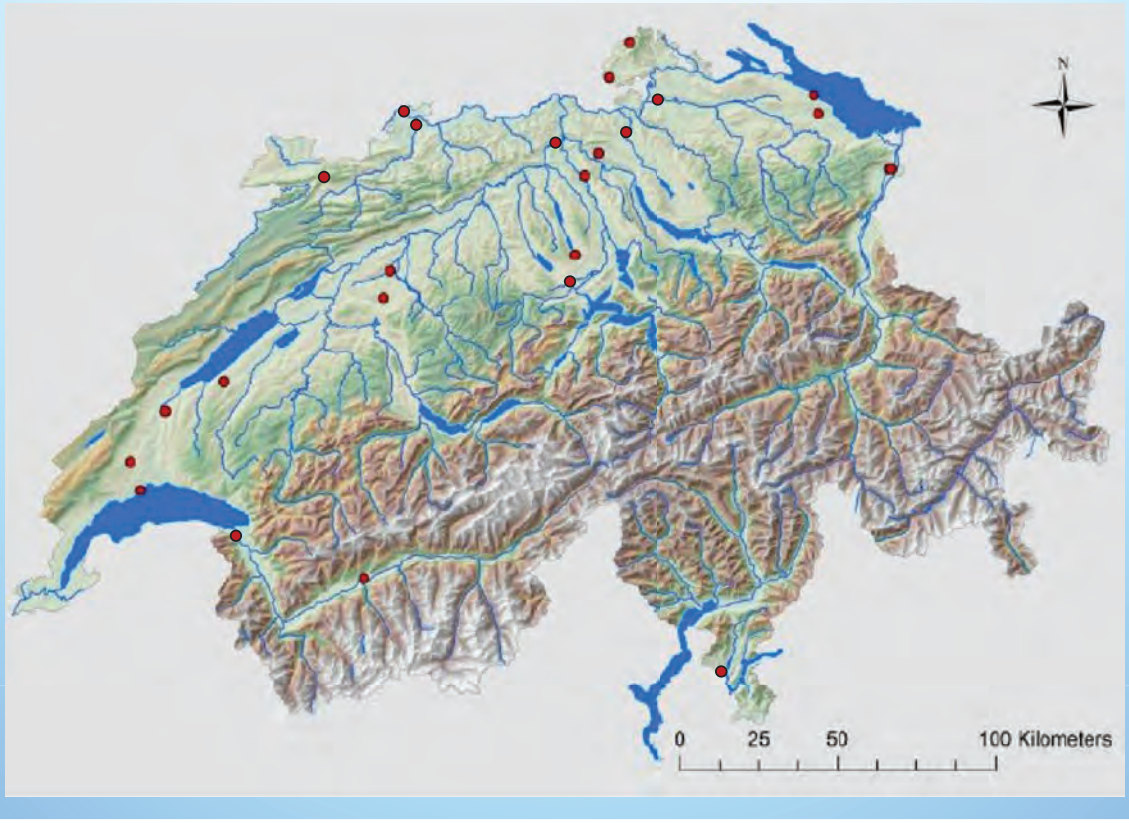
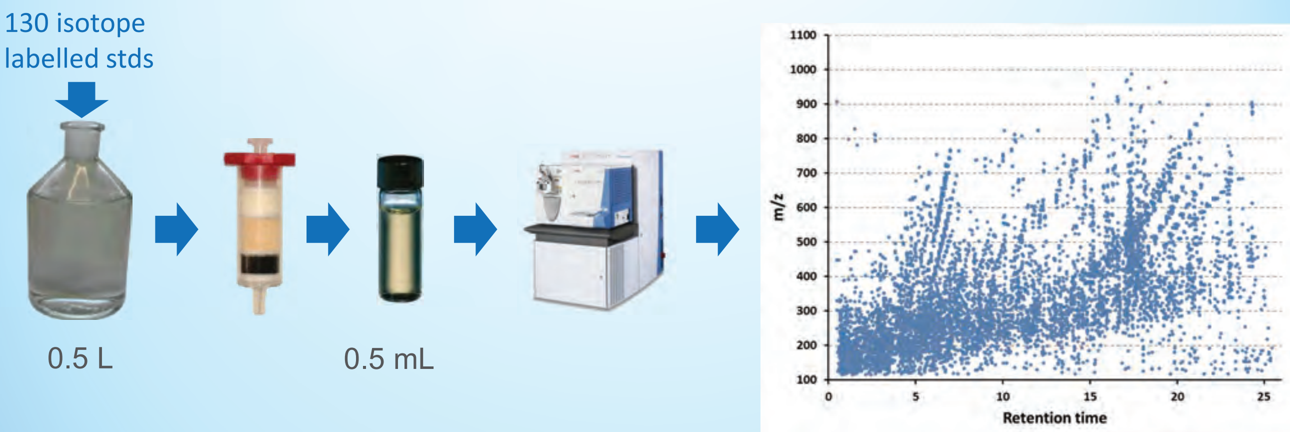
Project initiation & financial support

National network of monitoring stations



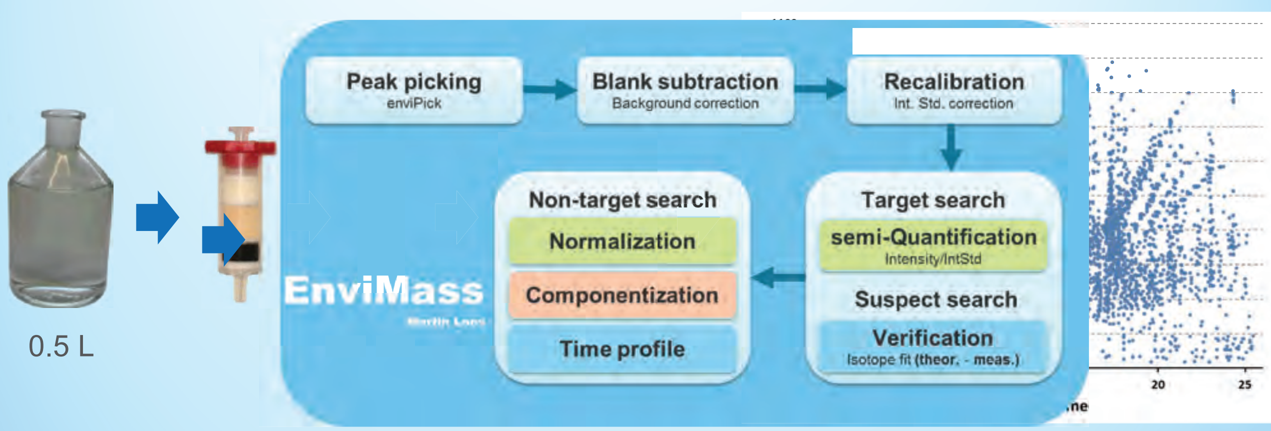
Challenge - Time restriction for alarm



- 24 hours composite sample over the river cross section
- RP LC-ESI-Orbitrap measurement in positive and negative mode
- Sample enrichment by factor of 1000 using a Multi-layer SPE
- MS Scan (R=100'000) with data-dependent MSMS (R=17'500)

15'000 peaks per file

Challenge - Time restriction for alarm



enviMass

target, suspect, and non-target workflow

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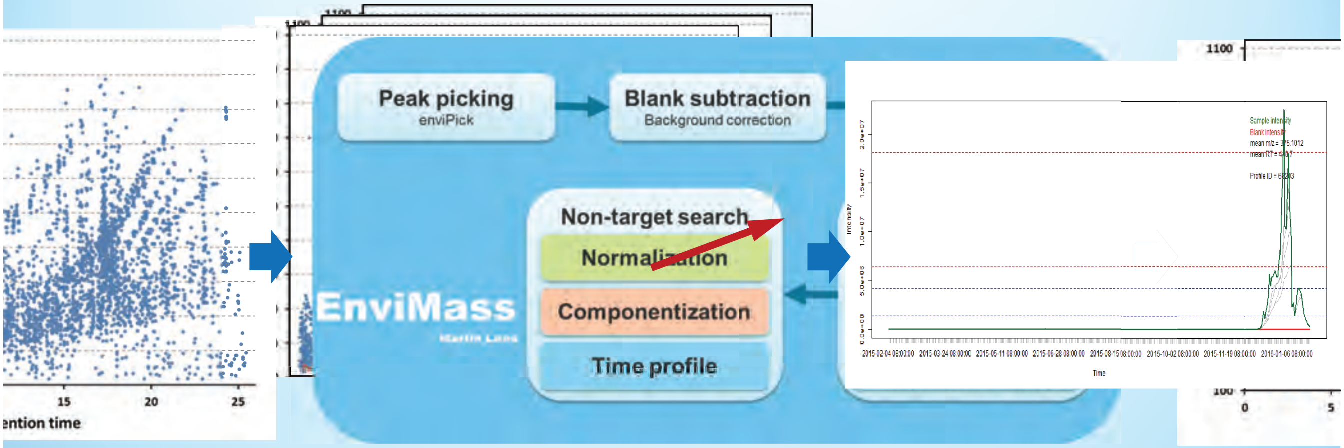


- Trend detection for targets, suspects, and non-target peaks

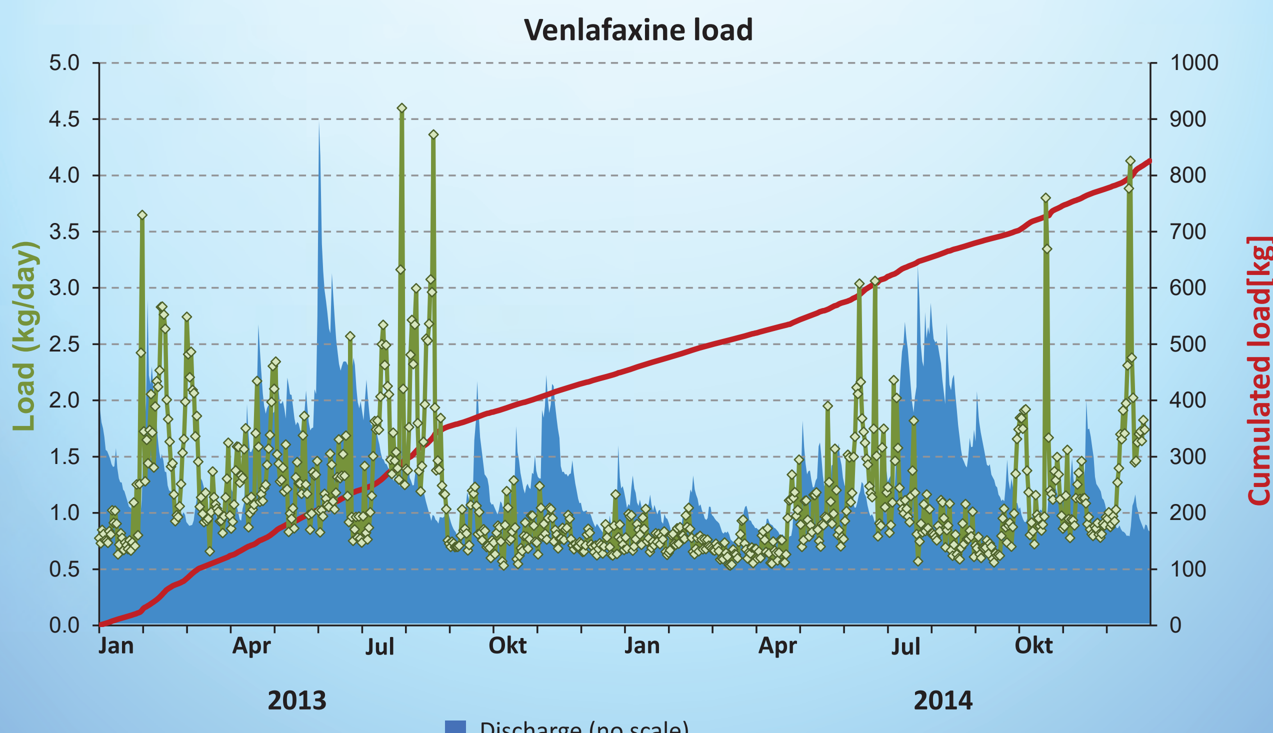
enviMass

target, suspect, and non-target workflow

- 8500 peaks/sample, 1800 files/year (1500 sample files + 300 blank files):
  15.5 Million peaks per year

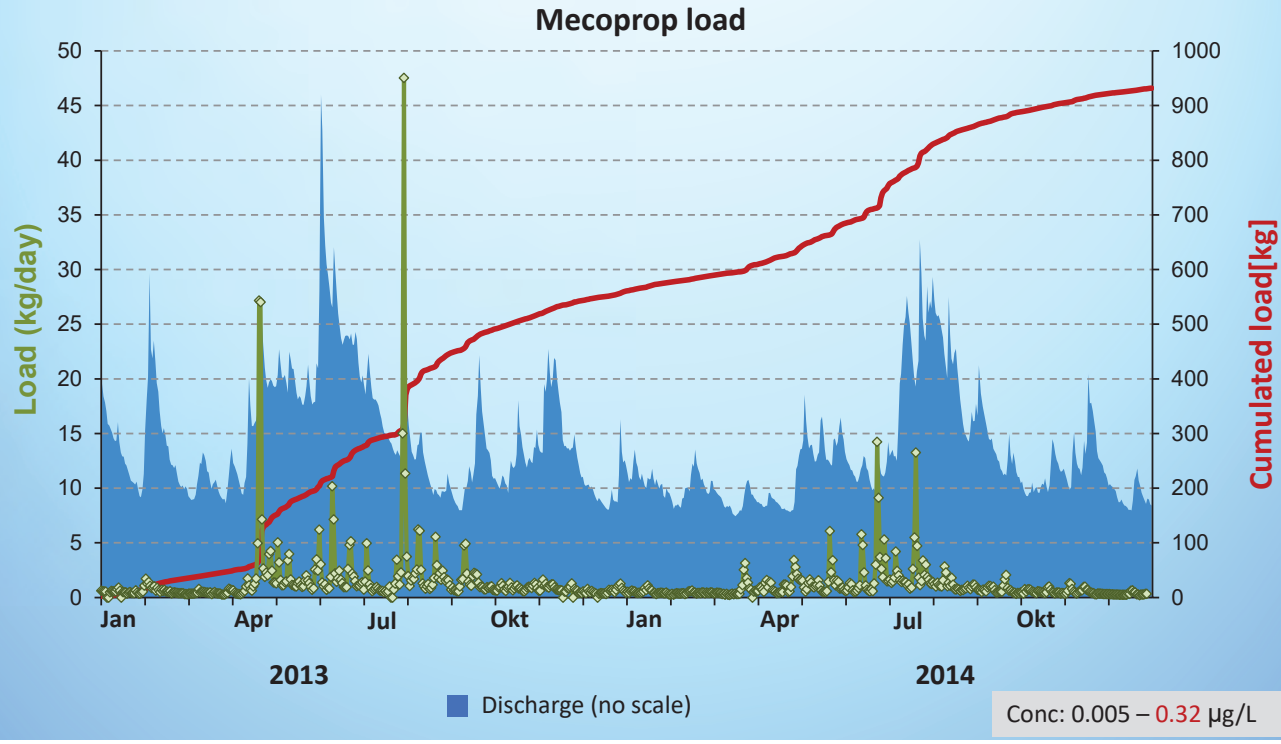
Venlafaxine 2013 - 2014

Loads of 24 h composite samples



Mecoprop 2013 - 2014

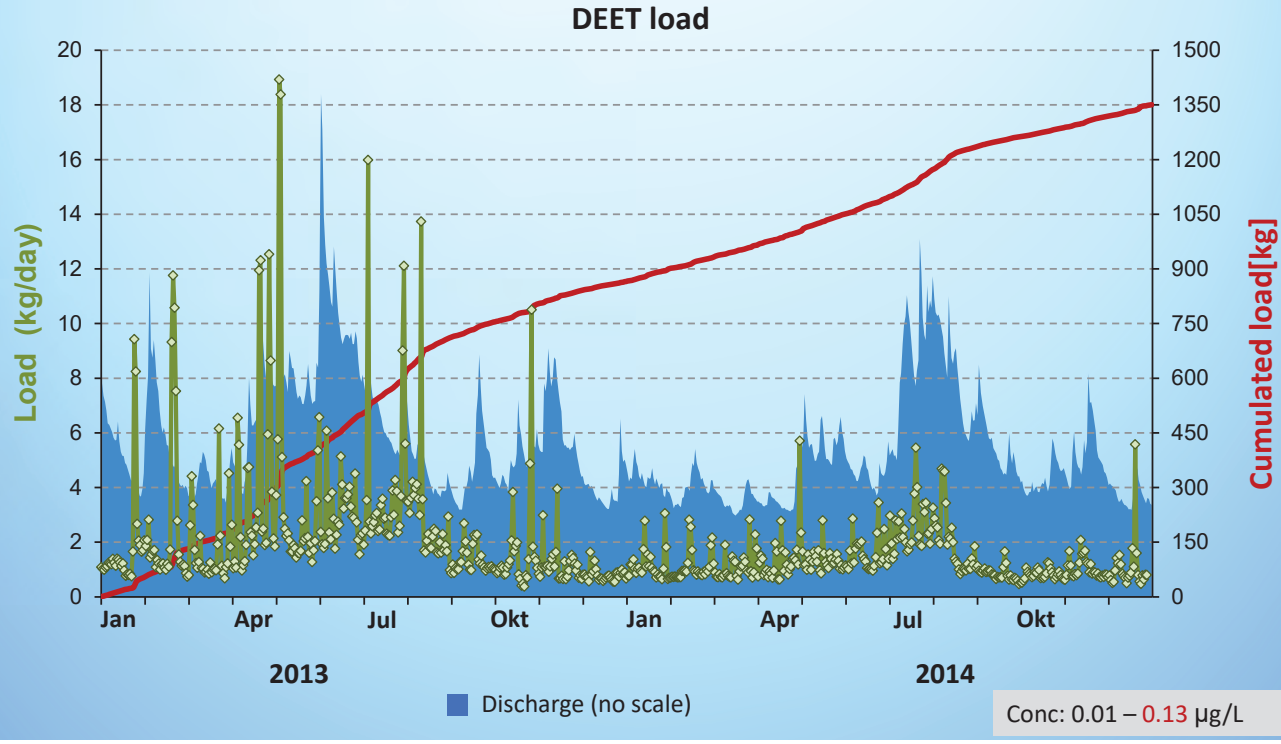
Loads of 24 h composite samples



Conc: 0.005 – 0.32 µg/L

DEET 2013 - 2014

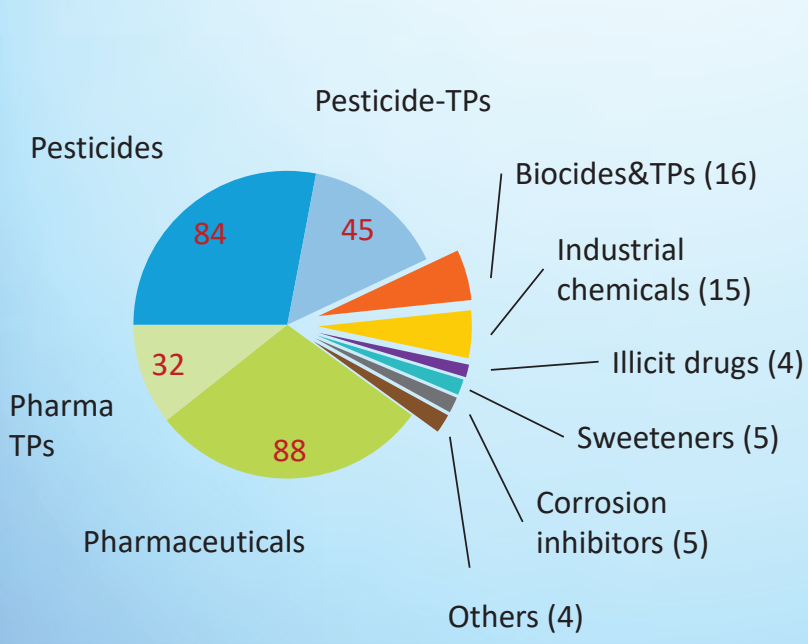
Loads of 24 h composite samples



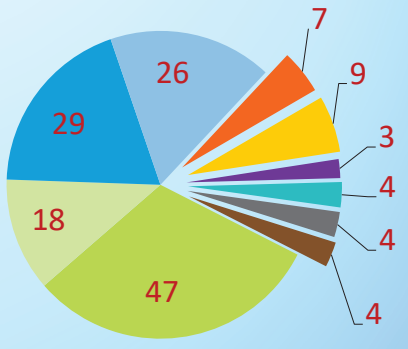
Conc: 0.01 – 0.13 µg/L

Modern Rhine monitoring

Substance diversity and results



results



Σ: 300 151