

Immediate detection of accidental spills into the River Rhine using automated time series

Matthias Ruff, Martin Loos, Heinz Singer, Juliane Hollender

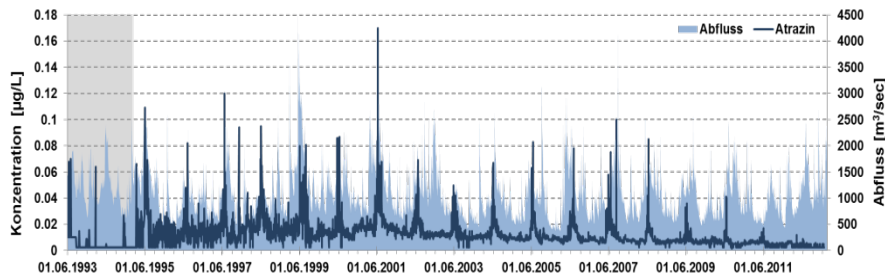
In cooperation with AUE Basel-City

Steffen Ruppe, Dorrit Griesshaber, Ingrid Langlois, Jan Mazacek



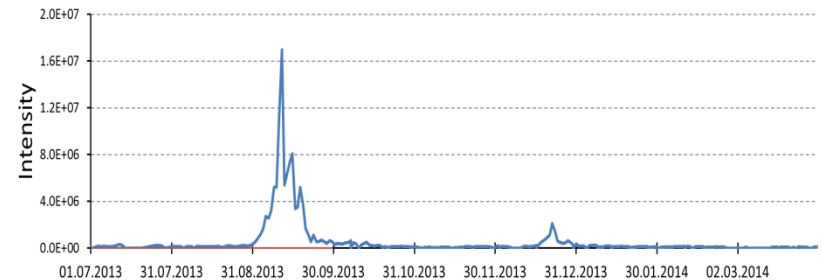
Goal of the Rhine monitoring

Trend monitoring



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

Spill detection



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

Analytical strategy

LC-HRMS (LTQ-Orbitrap)

High resolved full scan spectra & MSMS fragmentation spectra

Target analysis

50

250

Priority substances

Site specific substances



Non-target analysis

x Std calibration

x manual data processing

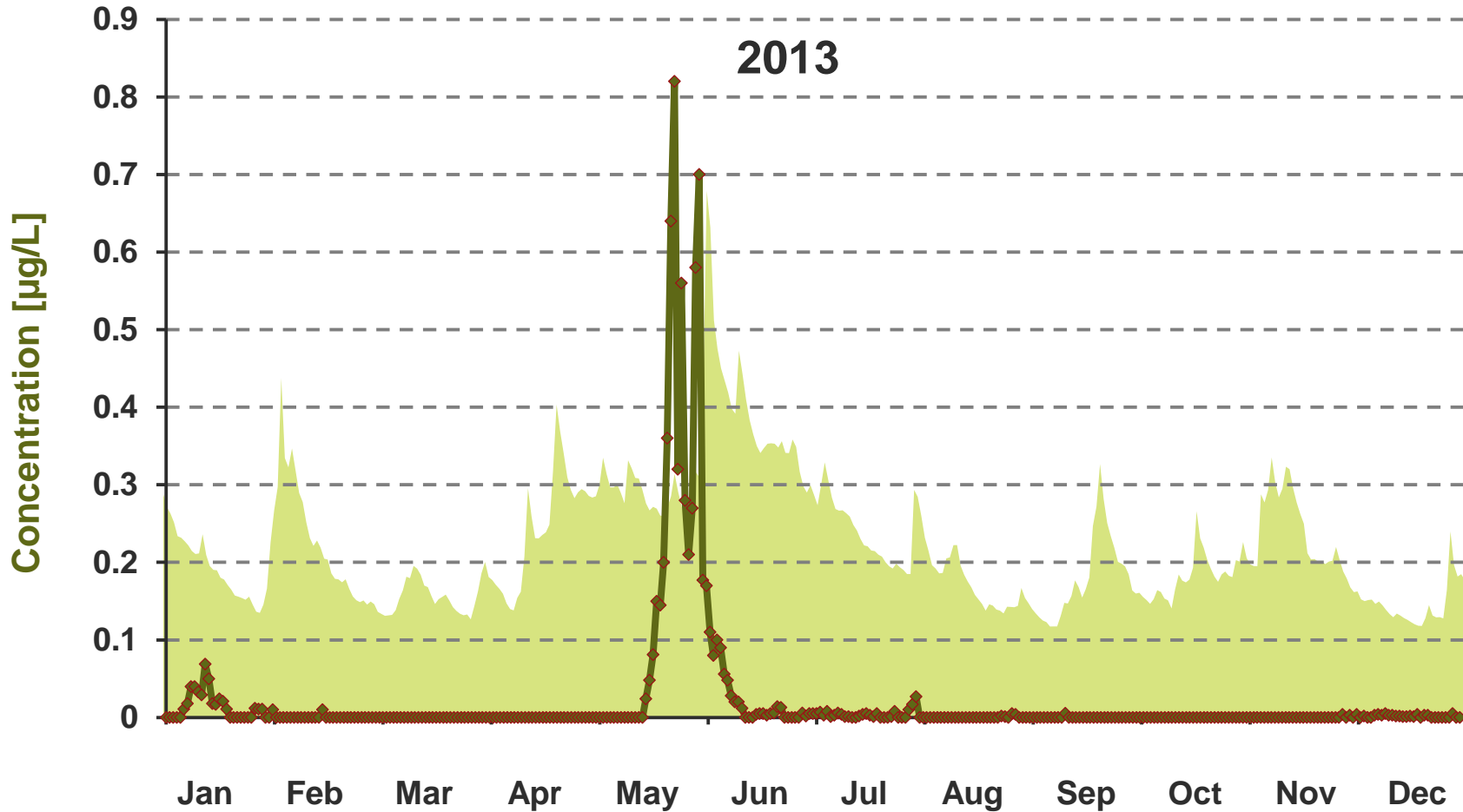
x exact quantification

x Std calibration

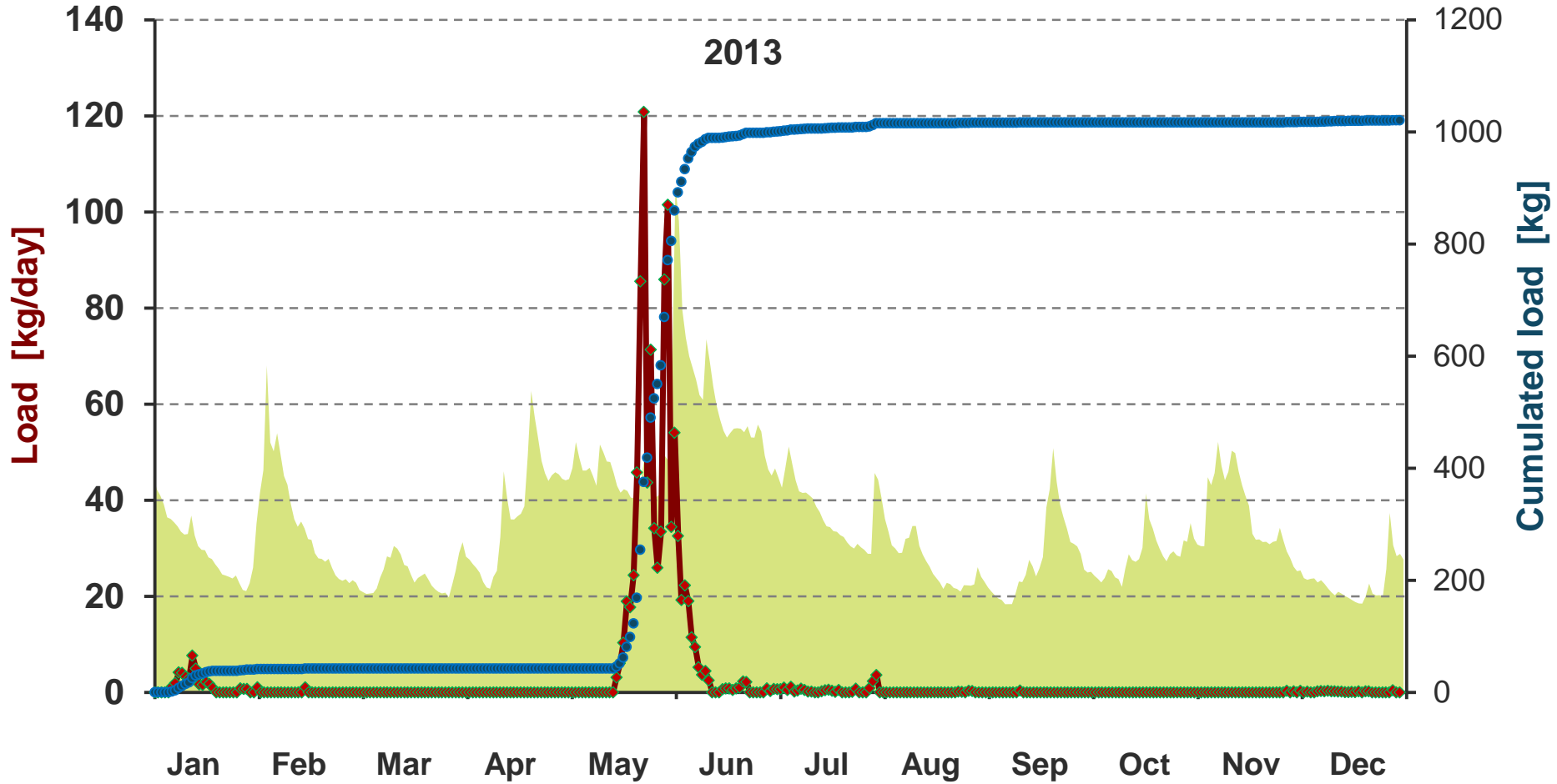
x automated processing

x semi-quantification

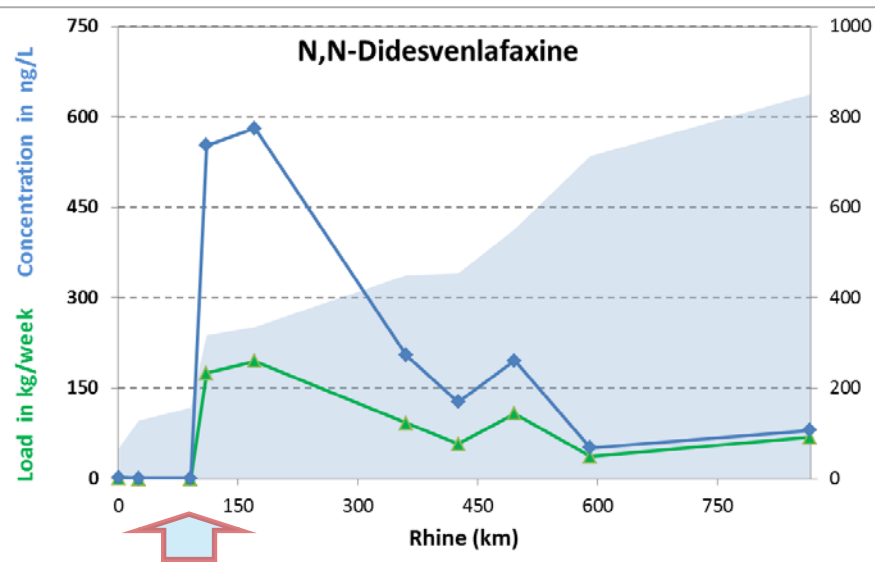
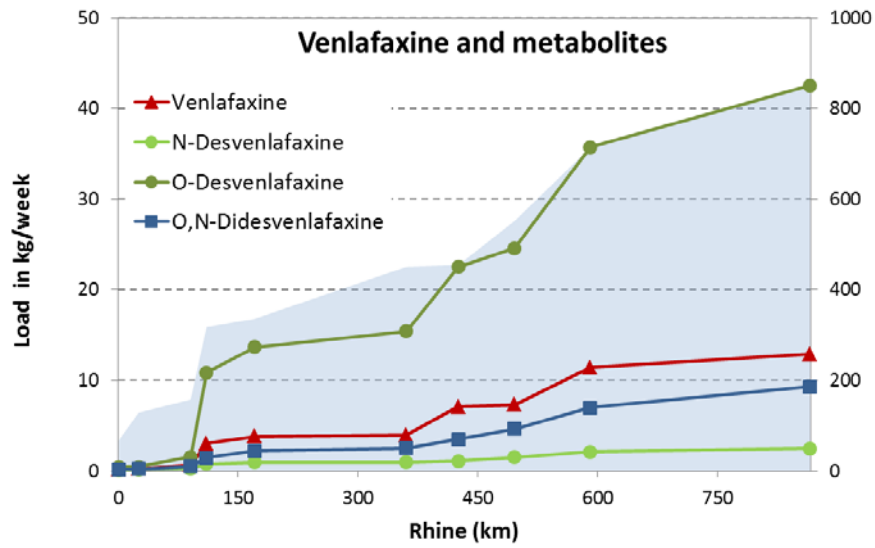
Target analysis: N,N-Didesmethylvenlafaxin



Target analysis: N,N-Didesmethylvenlafaxin



Venlafaxine in the river



Analytical strategy

HRMS (LTQ-Orbitrap)

High resolved full scan spectra & MSMS fragmentation spectra

Target analysis

50

250



Non-target analysis

remaining masses

∞

Priority substances

Site specific substances

Unknown substances

x calibration

x exact quantification

x manual data processing

x calibration

x semi-quant. quantification

x automated processing

x no calibration

x concentration estimated

x automated processing

Analytical strategy

HRMS (LTQ-Orbitrap)

High resolved full scan spectra & MSMS fragmentation spectra

Target analysis

50

250

Priority substances

Site specific substances



Non-target analysis

remaining masses
 ∞

peak picking

recalibration/alignment

componentization

prioritization

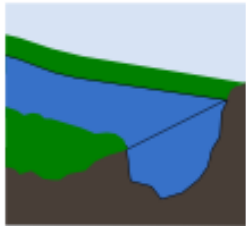
- x calibration
- x exact quantification
- x manual data processing

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

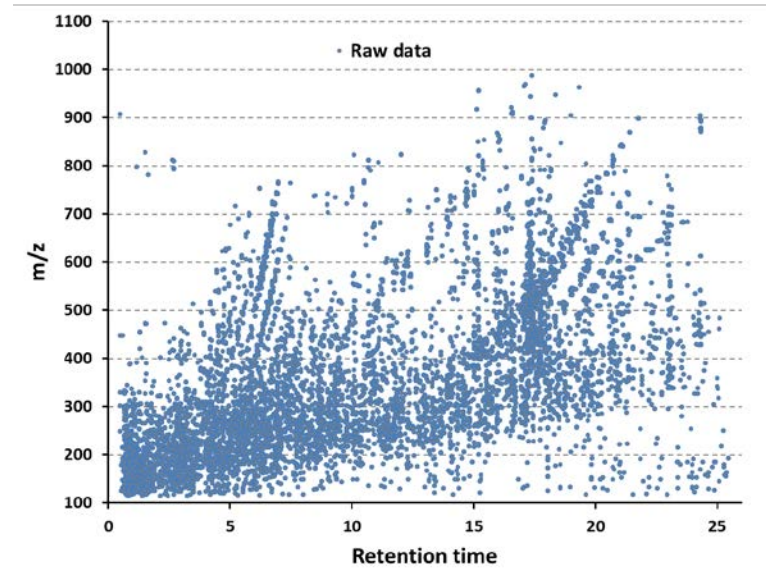
enviMass2

Principle of using time series

Sampling

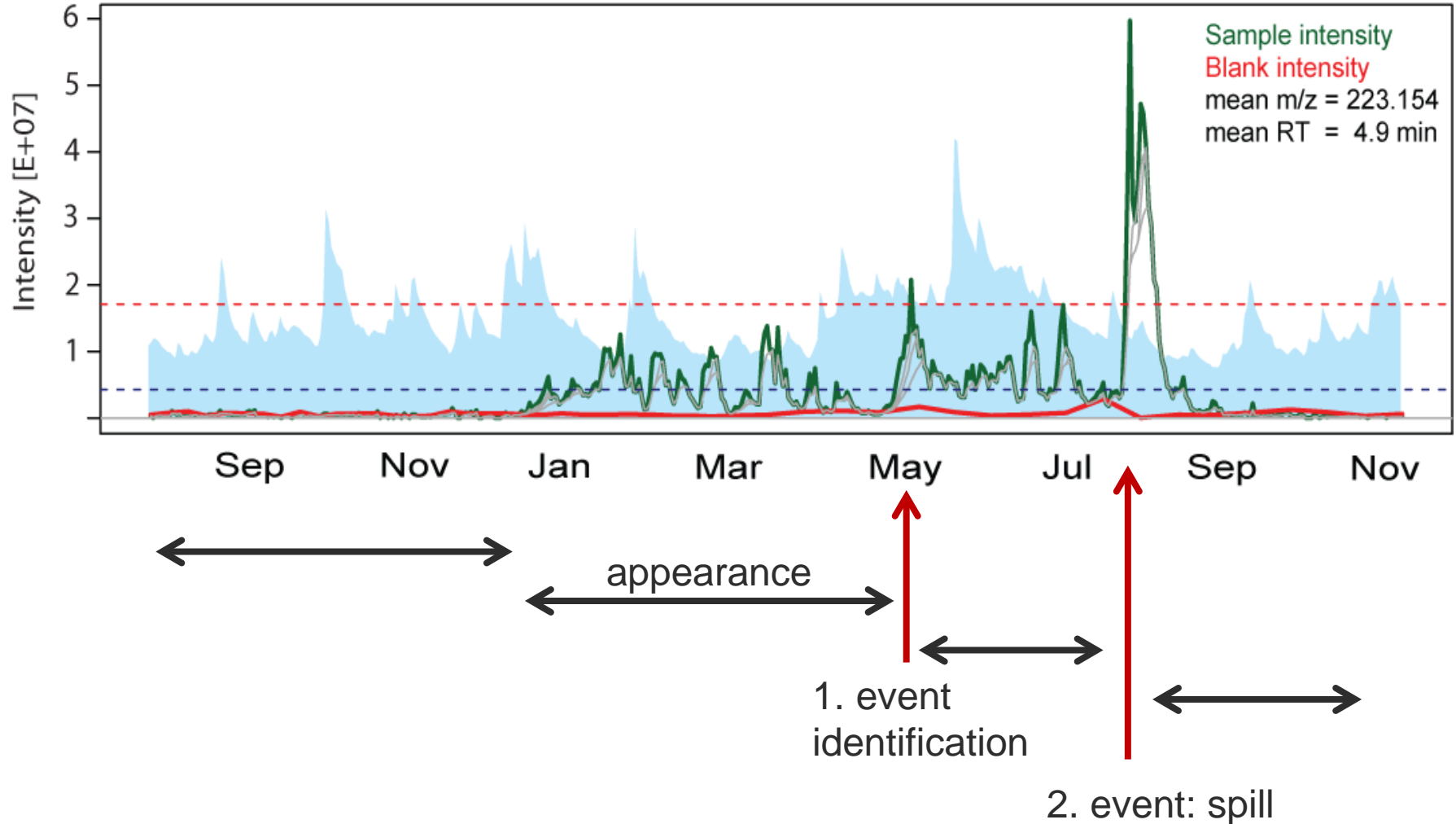


LC-HRMS

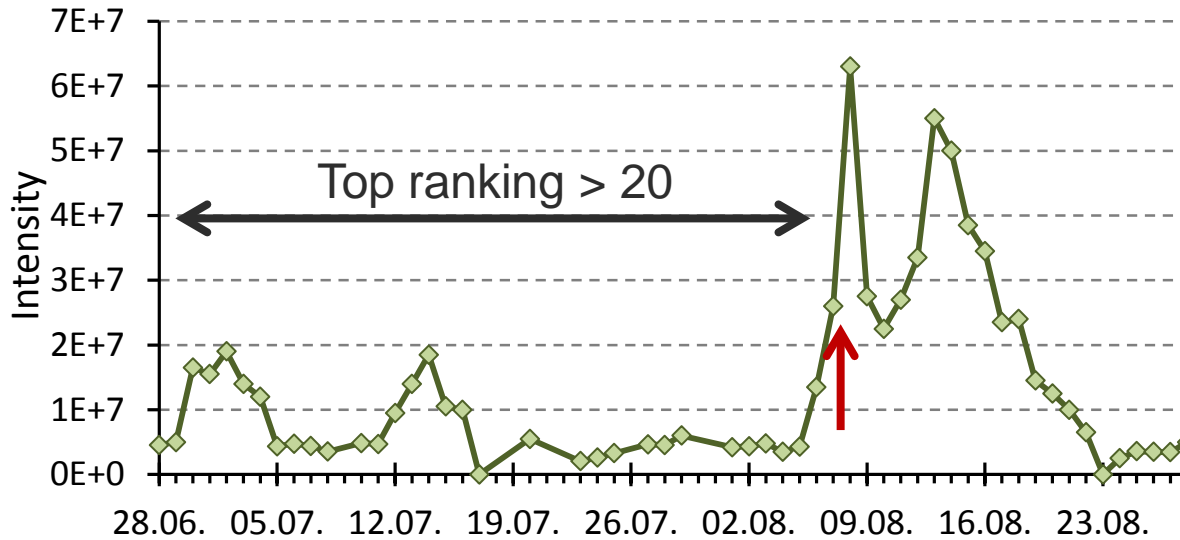
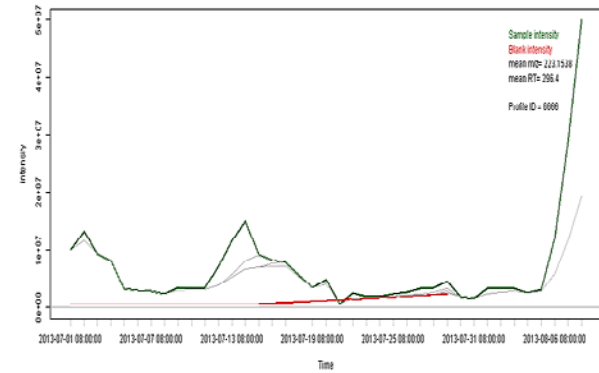
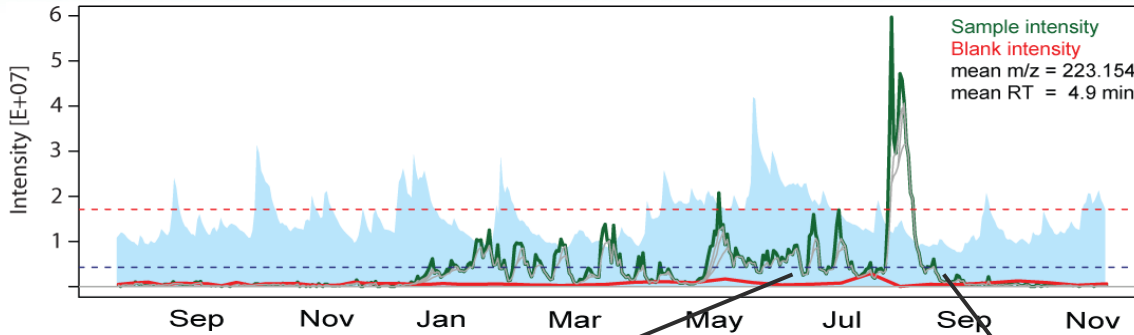


Statistical
analysis

Prioritization using time series

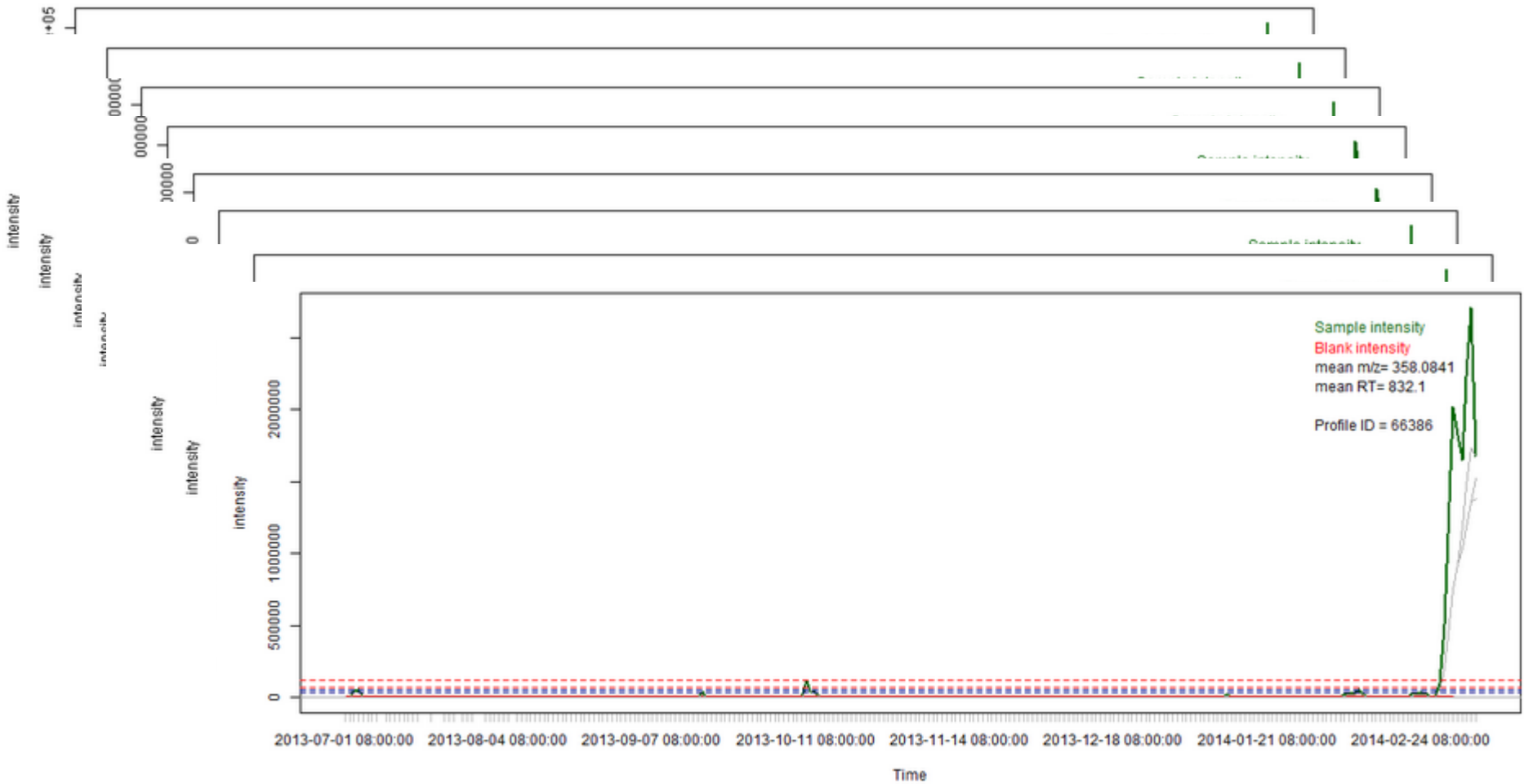


Tetraglyme spill



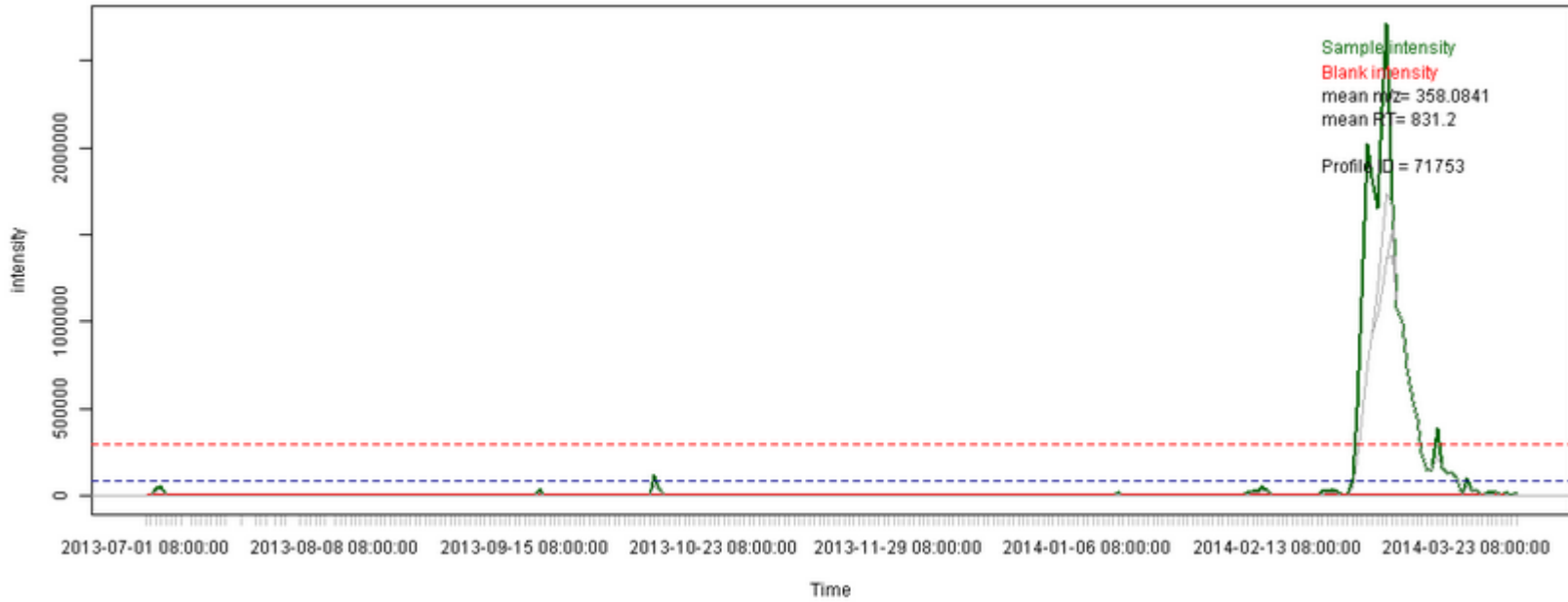
Load (2 weeks): > 2 tons
Concentrations: > 3 µg/L

Indomethacin spill



March 2014	1	2	3	4	5	6	7	8
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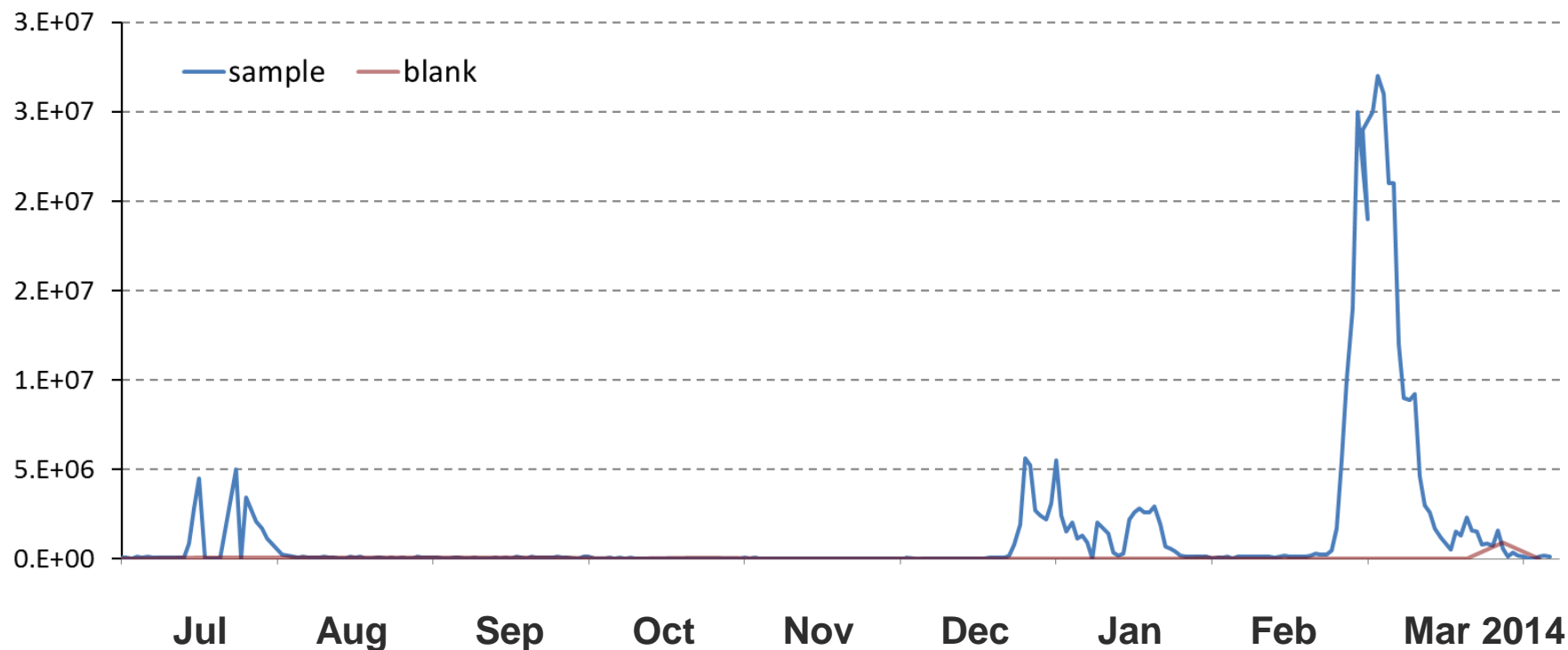
Indomethacin spill



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

Polluter could be located!

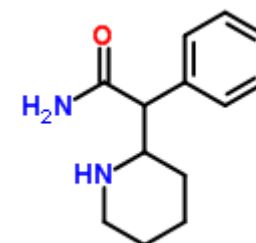
Unknown spill 1



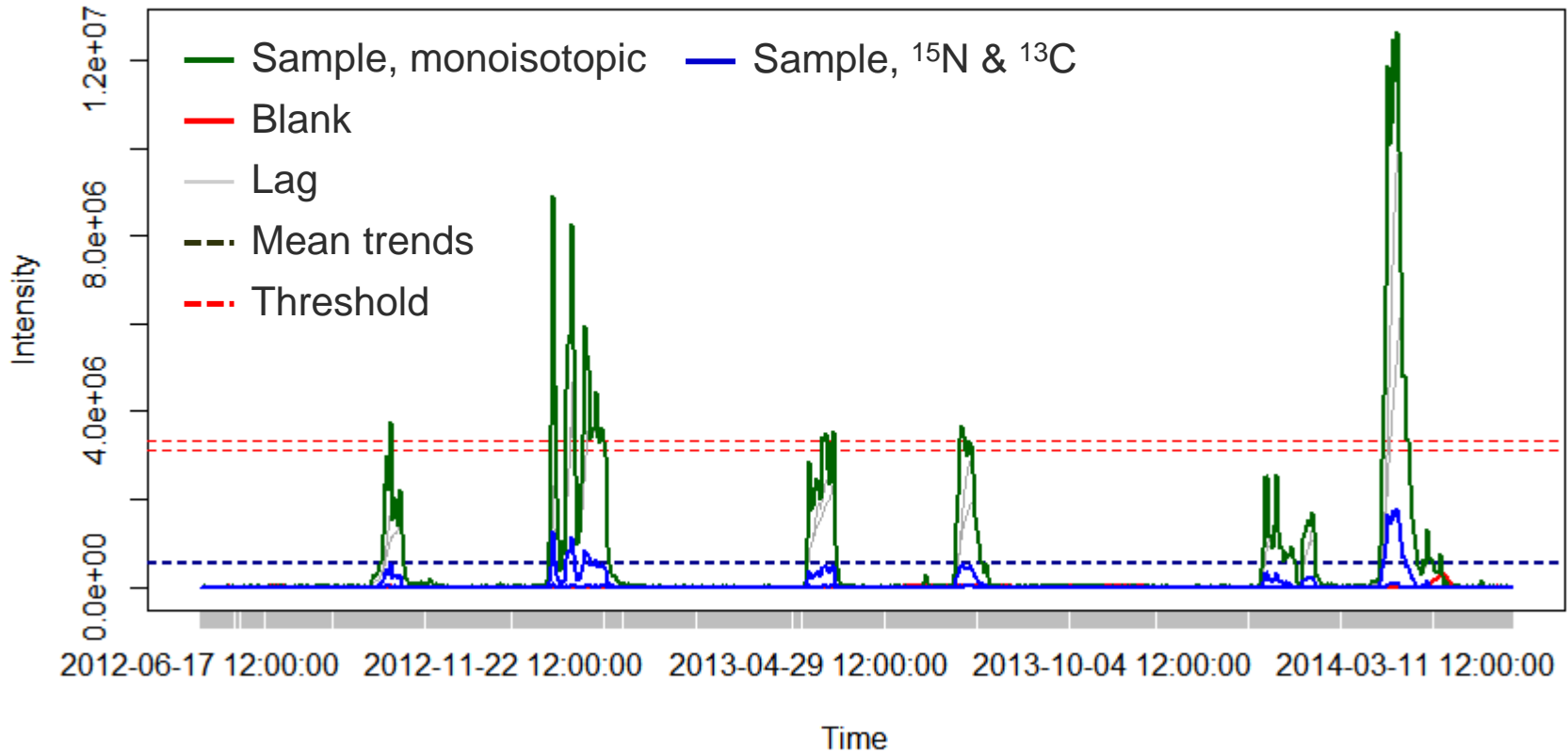
Elemental composition: $C_{13}H_{18}N_2O$

Several fragments, BUT:

>1800 structural hits using ChemSpider database



Unknown spill 1

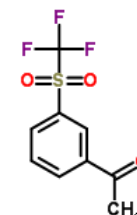
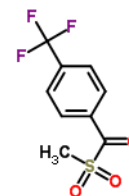
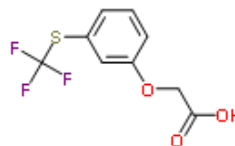
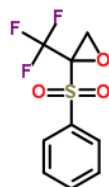
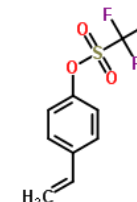
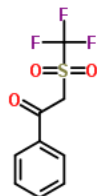
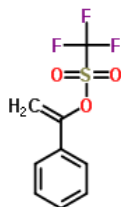
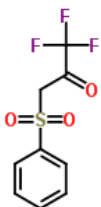
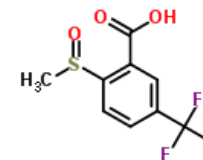
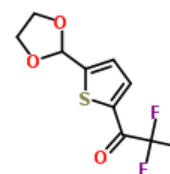
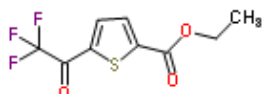
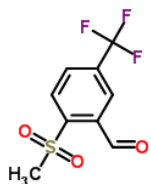


Unknown spill 2

Elemental composition: $C_9H_7F_3O_3S$

Several fragments, AND:

just 15 structural hits using ChemSpider database

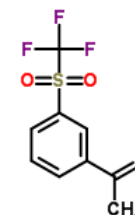
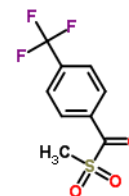
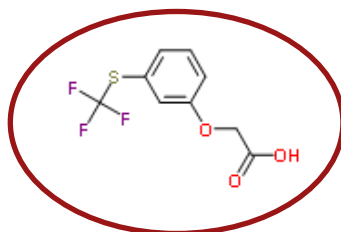
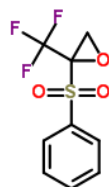
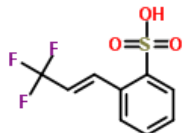
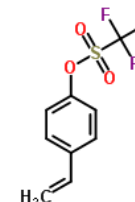
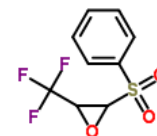
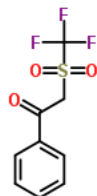
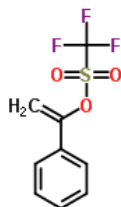
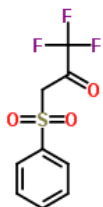
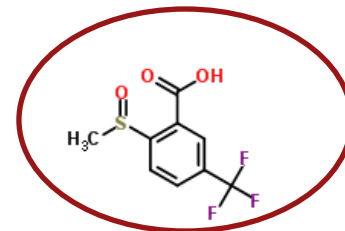
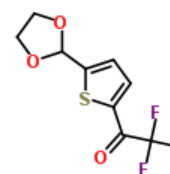
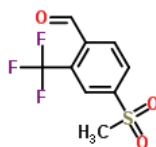
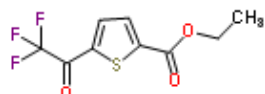
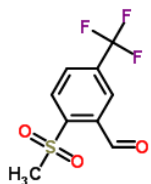


Unknown spill 2

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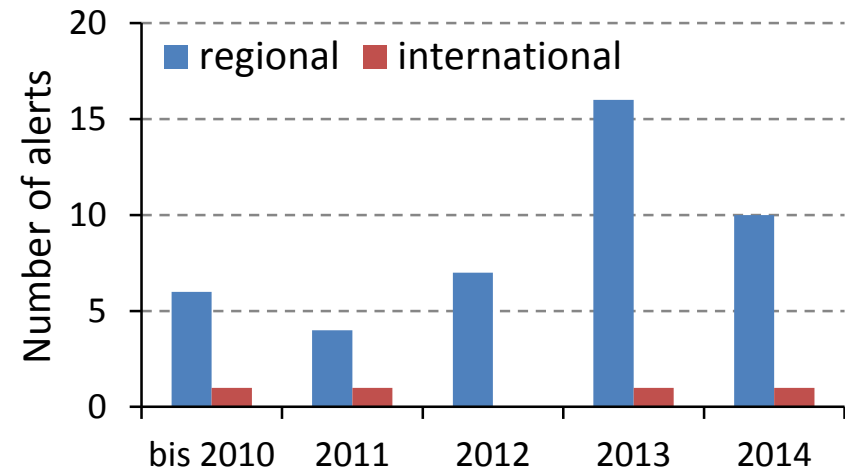
Several fragments, AND:

just 15 structural hits using ChemSpider database



Summary

- Comprehensive daily monitoring:
Broad target screening of relevant substances
and
daily non-targeted data-analysis
- Dataset prioritization using the enviMass time-series-analysis allows an
automated, time narrow detection of accidental spills
- Localization of polluter is laborious,
but often successful
- Significant increase of alerts with
high loads at the monitoring station



THANK YOU

for your attention!

Thanks also to

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