MS²field: High-frequency in situ environmental sampling and HRMS in a transportable container

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OVERVIEW

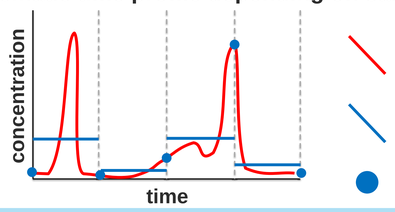
- Automated micropollutant measurement with filtration – online SPE – LC – HRMS from raw wastewater
- 1 week continuous uptime, 20 min measurement frequency
- Target quantification to ng/L and non-target feature extraction using spectral analysis

INTRODUCTION

Motivation

- **Traditional sampling methods** (grab samples, time-proportional samples) require enormous efforts to **capture real-life concentration dynamics** occurring in the environment, e.g.
  - daily/weekly dynamics of pharmaceuticals/PCPs in wastewater influent
  - micropollutant spills in rivers
  - herbicide runoff during rain events
- Manual **sampling and sample preparation** is labor-intensive and error-prone
- Sample **transport and storage** presents major logistical issues

Schematic time profile depending on sampling method



Objectives

- Development of **a transportable automated sampling and measurement platform** to capture micropollutant temporal dynamics
- Automated sampling of **raw wastewater and surface water**
- **High-resolution mass spectrometry** to capture a broad compound spectrum and to enable non-target analysis
- High **temporal resolution** (20 min measurement frequency)
- **Unsupervised** measurement for **extended periods** (up to 1 week)

Challenges

- Particulate matter: avoid **clogging** etc.
- **Robustness:** long unattended operation, error tolerance

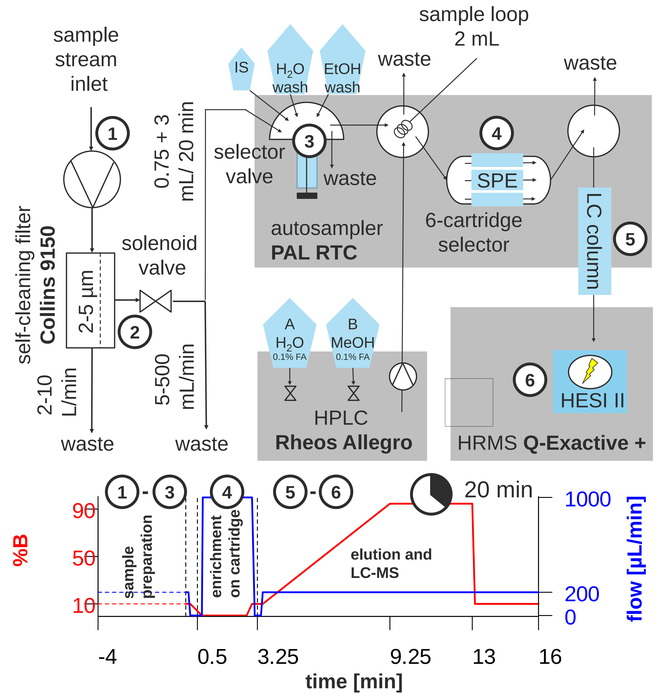
Development set-up

- Small-scale experimental **wastewater treatment plant** (200 pers. eq.), influent is sampled after sand trap

sample filtration → sample preparation → chromato-graphy → mass spectrometry → data processing → evaluation → visualization

METHOD

Setup using online SPE – LC – HRMS



Sample preparation:

- Pre-rinse inlet (solenoid ON 30 sec)
- Wash syringe with sample (3 mL)
- Load internal standard to the loop
- Dilute sample (0.75 mL) and load loop

After enrichment:

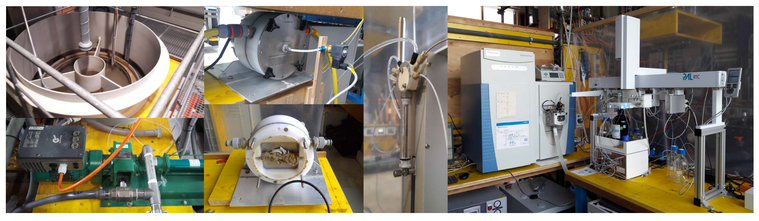
- Wash loop and sample inlet
- Post-rinse inlet (solenoid ON 90 sec)

Materials:

- SPE: XBridge 10 µm, 2.0 x 10 mm (Waters)
- LC: XBridge 3.5 µm, 2.1 x 50 mm (Waters)

Mass spectrometry:

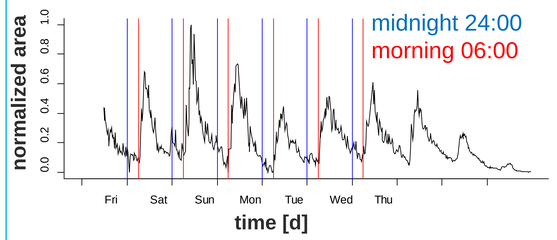
- Polarity switching
- MS1 – top 3/top2 ddMS2
- MS1 – 2x2-window DIA



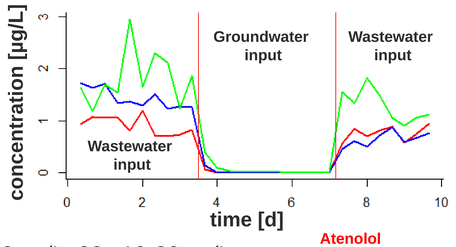
RESULTS

System evaluation

Time series: Candesartan (antihypertensive drug)



System response time



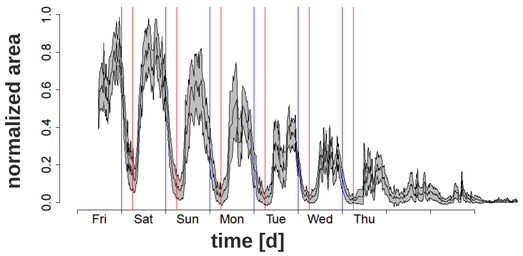
- **LOQs** for 59 micropollutants in wastewater: 19x <10 ng/L, 20x 10-20 ng/L
- **Carryover** mostly <1%, for individual compounds up to 10%
- MS **sensitivity loss** (spray clogging) **after ca. 1 week** of continuous operation
- **Bypass/filter** operation **max. 1 week** between servicing

Non-target feature extraction

600 raw files (1 week)

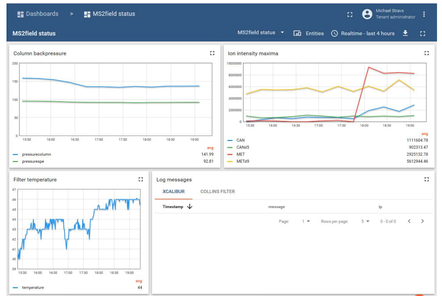
pre-processing → spectral analysis → clustering

90'000 profiles in 500 clusters



1 cluster with 228 periodic features
+ 50 other periodic clusters

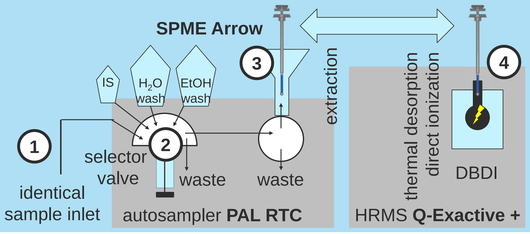
Online live monitoring



- **Sensor input** for instrument health
- Automated **data evaluation** after each sample
- **MQTT** dashboard allows various data sources and easy visualization

OUTLOOK

In development: SPME – DBDI – HRMS



Deployment in air-conditioned trailer

- Field studies in sewers and rivers

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