

Supporting Information

Passive samplers in sewers and rivers with highly fluctuating micropollutant concentrations – better than we thought

Mutzner Lena ^{1,2}, Vermeirssen Etienne L. M³ ³, Ort Christoph ^{1*}

1 Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland.

2 Institute of Civil, Environmental and Geomatic Engineering, ETH Zürich, 8093 Zurich, Switzerland.

3 Swiss Centre for Applied Ecotoxicology Eawag-EPFL, Überlandstrasse 133, 8600 Dübendorf, Switzerland

**Corresponding author: Eawag, Swiss Federal Institute of Aquatic Science and Technology. Überlandstrasse 133, 8600 Dübendorf, Switzerland. E-mail: christoph.ort@eawag.ch*

A. Measured high resolution events in sewers and sewer overflows



Figure SI 1. Event 1: 18.05.2016. Event-based sampling directly in the sewer. Passive sampler overflowed and auto-sampling triggered at water levels above 6cm.

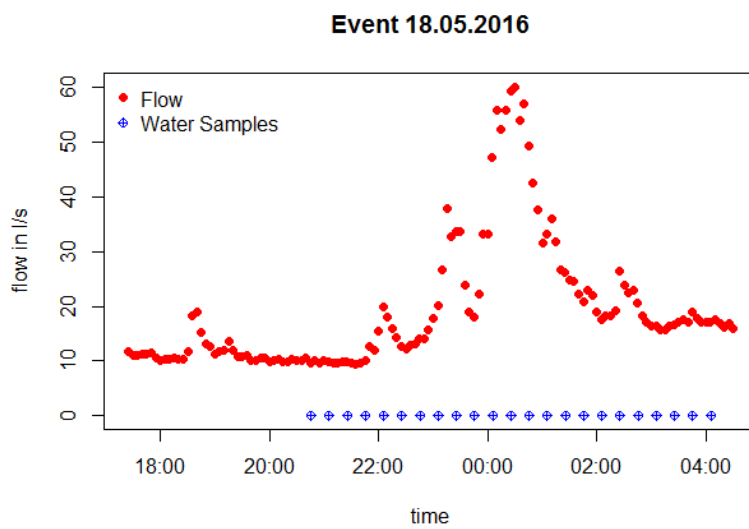


Figure SI 2. Event 1: 18.05.2016. First samples were taken before occurrence of rain event peak, hence the baseline wastewater flow was measured at the beginning of the sampled event.



Figure SI 3. Event 2: 25.04.2017. Sampling of a sewer overflow event with sampler installed at weir crust (schematic picture from a different sampled event)

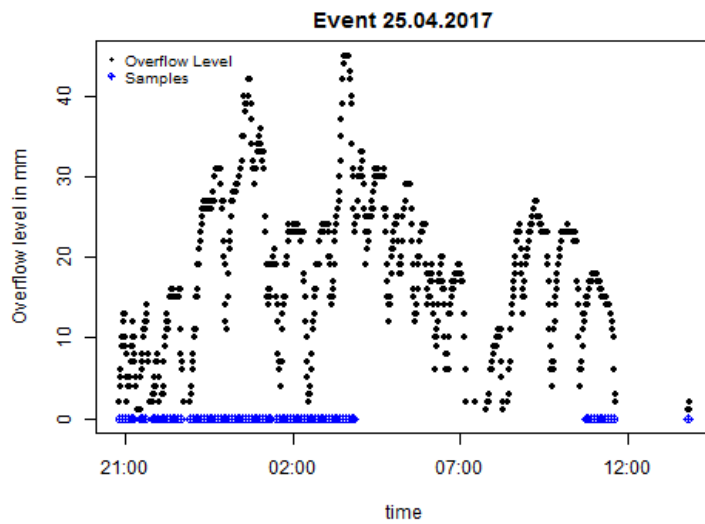


Figure SI 4. Gap in water sampling data due to malfunction of automated sampler.



Figure SI 5. Event 3: 28.06.2017. Rain-event sampling in flow channel supplied with wastewater pumped from a main sewer.



Figure SI 6. Event 3: 28.06.2017. Installation of the passive sampler setup at the flow channel wall.

B. Characterization of concentration fluctuations

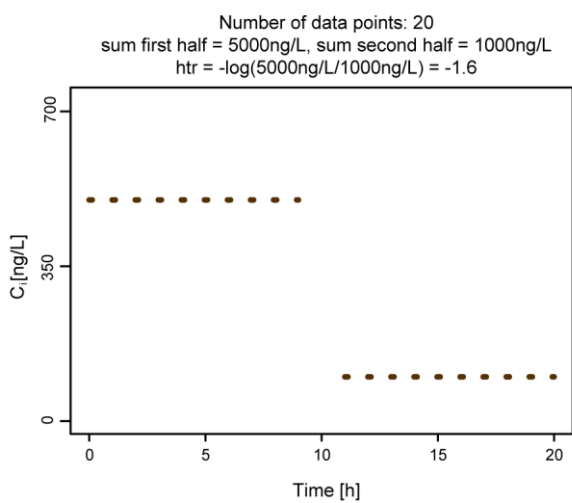


Figure SI 7. Schematic example for calculation of the half time ratio (htr) used to determine the position of the peak. A negative htr means in the beginning.

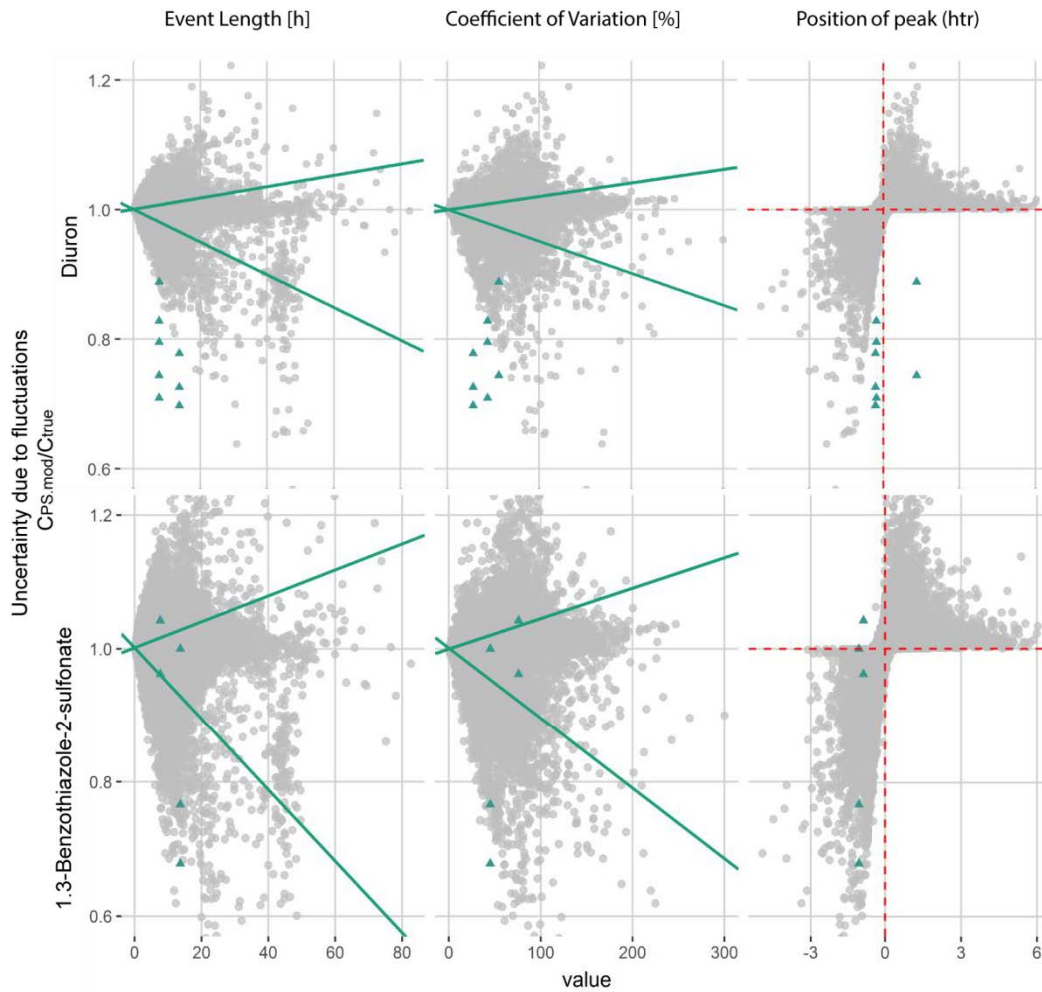


Figure SI 8. Predicted deviation of $C_{M,PS,mod}$ to C_{true} for the modelled event-based sampling of sewer overflows (half-transparent black point): Event Length [h], Coefficient of Variation (CV in %), Half-time ratio (htr). 10% and 90% quantile regression are shown by the green solid lines, red dashed line shows htr = 0 and no deviation = 1. Triangles represent replicate $C_{M,PS,meas}$ vs. $C_{CS,meas}$ of the three events, only value within visible range.

The effect of the position of the peak can be detailed by looking at three exemplary events with an identical event length of five hours. These three events result in distinctively different deviations of $C_{M,PS,mod}$ from C_{true} of 33% (Figure SI 9 A), 183% (Figure SI 9 B) as well as no deviation (Figure SI 9 C).

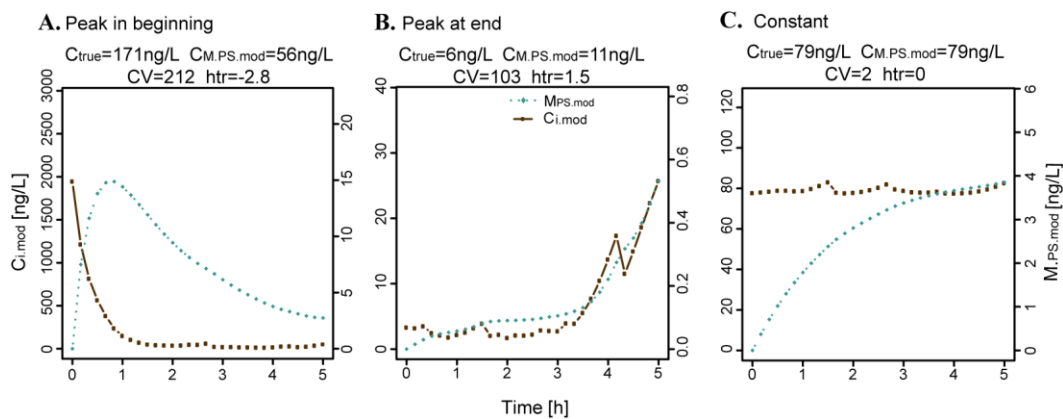


Figure SI 9. Exemplary modelled peaks – extreme case with very low K_{SW} of 150 and typical average R_s of 0.03L/h. Equal event length but different position of peaks (htr) and coefficient of variation (CV). The predicted deviation from the true TWA concentration (Dev) is stated on top of the figures (A-C). A peak in the beginning

(A) leads to underestimation due to desorption, a peak in the end (B) to an overestimation, a constantly varying pattern (C) with almost zero slope, however leads to a very small deviation from the true TWA concentration.

C. Chemical analysis

Event 1 and 2

Table SI 1. HPLC gradient used for the chromatographic separation on an Atlantis T3 column. FA: formic acid.

| Time [min] | H ₂ O + 0.1% FA [%] | MeOH + 0.1 % FA [%] | Flow [μL/min] |
|------------|--------------------------------|---------------------|---------------|
| 0.0 | 95 | 5 | 300 |
| 1.5 | 95 | 5 | 300 |
| 17.5 | 5 | 95 | 300 |
| 25.0 | 5 | 95 | 300 |
| 25.5 | 95 | 5 | 300 |
| 29.5 | 95 | 5 | 300 |

Table SI 2. Settings for the QExactive mass spectrometer

| Parameter | positive | negative |
|-----------------------------|--------------------|--------------------|
| <i>ESI settings</i> | | |
| Spray voltage | 4000 V | 3000 V |
| Capillary temperature | 350 °C | 350 °C |
| S-Lens RF voltage | 50 V | 50 V |
| Probe Heater Temp | 40°C | 40°C |
| Sheath Gas Flow (Arb) | 40 | 40 |
| Aux Gas Flow (Arb) | 10 | 10 |
| Spare Gas Flow (Arb) | 0 | 0 |
| <i>Orbitrap settings</i> | | |
| MS1 | | |
| Scan range (m/z) | 100 - 1000 | 100 - 1000 |
| Mass resolution (m/z 200) | 70,000 | 70,000 |
| Automatic Gain Control | 5e5 | 5e5 |
| Max Injection time | 100 ms | 100 ms |
| MS2 | | |
| Mass resolution (m/z 200) | 17,500 | 17,500 |
| Automatic Gain Control | 1e5 | 1e5 |
| Max Injection time | 80 ms | 80 ms |
| Acquisition type | data-dependent | data-dependent |
| Data- dependent loop count | 1 | 1 |
| Isolation window (m/z) | 1 | 1 |
| Collision energy normalized | compound-optimized | compound-optimized |
| Dynamic exclusion | 2 s | 2 s |

Arb: arbitrary units

ms: milli seconds

s: seconds

Event 3

Table SI 3. HPLC gradient used for the chromatographic separation on an Acquity UPLC HSS T3 column. FA: formic acid.

| Time [min] | H ₂ O + 0.1% FA [%] | MeOH + 0.1 % FA [%] | Flow [μL/min] |
|------------|--------------------------------|---------------------|---------------|
| 0.0 | 100 | 0 | 500 |
| 18.5 | 5 | 95 | 500 |
| 22.0 | 5 | 95 | 500 |
| 22.5 | 100 | 0 | 500 |

Table SI 4. Settings for the Agilent G6495A mass spectrometer

| Parameter | positive | negative |
|-----------------------------|--------------------|--------------------|
| <i>ESI settings</i> | | |
| Gas Temp | 250 °C | 250 °C |
| Gas Flow | 15 l/min | 15 l/min |
| Nebulizer | 25 psi | 25 psi |
| Sheath Gas Heater | 380 °C | 380 °C |
| Sheath Gas Flow | 12 l/min | 12 l/min |
| Capillary | 3500 V | 3000 V |
| <i>QQQ settings</i> | | |
| Cycle time | 650 ms | 650 ms |
| Acquisition type | DynamicMRM | DynamicMRM |
| MRM Repeats | 3 | 3 |
| Collision energy normalized | compound-optimized | compound-optimized |

Table SI 5. Acquisition Method on Agilent G6495A triple quad mass spectrometer

| Cpd Name | ISTD | Prec Ion | MS1 Res | Prod Ion | MS2 Res | Frag (V) | CE (V) | Ret Time (min) | Polarity |
|-----------------------------------|------|----------|---------|----------|---------|----------|--------|----------------|----------|
| 1,3-Benzothiazole-2-sulfonic acid | No | 216 | Unit | 134.1 | Unit | 380 | 16 | 8.98 | Pos |
| 1,3-Benzothiazole-2-sulfonic acid | No | 216 | Unit | 90.1 | Unit | 380 | 20 | 8.98 | Pos |
| Benzotriazole-D4 | Yes | 124.08 | Unit | 96.1 | Unit | 380 | 18 | 9.37 | Pos |
| Benzotriazole-D4 | Yes | 124.08 | Unit | 69.1 | Unit | 380 | 26 | 9.37 | Pos |
| Diclofenac | No | 296.03 | Unit | 249.9 | Unit | 380 | 10 | 17.6 | Pos |
| Diclofenac | No | 296.03 | Unit | 214.1 | Unit | 380 | 30 | 17.6 | Pos |
| Diclofenac | No | 296 | Unit | 215 | Unit | 380 | 20 | 17.6 | Pos |
| Diclofenac-D4 | Yes | 300.05 | Unit | 254 | Unit | 380 | 10 | 17.64 | Pos |
| Diclofenac-D4 | Yes | 300.05 | Unit | 219.1 | Unit | 380 | 20 | 17.64 | Pos |
| Diclofenac-D4 | Yes | 300.05 | Unit | 218 | Unit | 380 | 34 | 17.64 | Pos |
| Diuron | No | 233.03 | Unit | 72.2 | Unit | 380 | 28 | 15.35 | Pos |
| Diuron | No | 233.03 | Unit | 46.3 | Unit | 380 | 20 | 15.35 | Pos |

| | | | | | | | | | |
|----------------|-----|--------|------|-------|------|-----|----|------|-----|
| Diuron-D6 | Yes | 239.06 | Unit | 78.1 | Unit | 380 | 40 | 15.3 | Pos |
| Diuron-D6 | Yes | 239.06 | Unit | 52.4 | Unit | 380 | 20 | 15.3 | Pos |
| Metolachlor | No | 284.14 | Unit | 252.1 | Unit | 380 | 12 | 17.5 | Pos |
| Metolachlor | No | 284.14 | Unit | 176.2 | Unit | 380 | 28 | 17.5 | Pos |
| Metolachlor-D6 | Yes | 290.18 | Unit | 258.2 | Unit | 380 | 16 | 17.5 | Pos |
| Metolachlor-D6 | Yes | 290.18 | Unit | 182.2 | Unit | 380 | 28 | 17.5 | Pos |

Table SI 6. Relative recoveries and LOQs for the different measurement series

| Used mass spectrometer & injection/enrichment mode | Thermo Scientific QExactive Plus, direct injection* | | Thermo Scientific QExactive Plus, coupled with online-SPE | | Agilent 6495 TQ, direct injection | |
|--|---|-------------------------|---|-----------------------|-----------------------------------|-----------------------|
| | Rel. recovery [%] | LOQ [$\mu\text{g/L}$] | Rel. recovery [%] | LOQ [ng/L] | Rel. recovery [%] | LOQ [ng/L] |
| 1,3-Benzothiazole-2-sulfonic acid | 130-202 | 1-2 | 158 | 8 | 130 | 13 |
| Diclofenac | 94-116 | 0.7-1 | 105 | 2 | 102 | 1 |
| Diuron | 101-119 | 0.6-2 | 102 | 2 | 114 | 1.9 |
| Metolachlor | 115-128 | 0.6-1 | 100 | 1.8 | 112 | 5.3 |

*Three measurement series were conducted with this setup, therefore a range of relative recovery and LOQ values is given