



1. Introduction

Sampling is a key process in the determination of contaminants in the aquatic environment. While grab sampling is the most extended approach to collect surface waters, this sampling approach only provides a snapshot of the water pollution that may change with rain events, point discharges, etc. The TIMFIE (Time-Integrating, Micro-Flow, In-Situ Extraction) sampler is an inexpensive and low-tech device designed and optimized to collect time-proportional water samples (50 -100 mL) over one week that is currently in use to monitor pesticides in surface water by the SLU Centre for Pesticides in the Environment [1], and that can be further explored to collect time-integrated water samples in the environment for determining organic contaminant pollution.

2. Objectives

- ⇨ To adapt the TIMFIE device for the collection of ≈100 mL water samples over one day period
- ⇨ To study the performance of the one-day approach for the quantitative analysis of 64 emerging organic pollutants, including pharmaceuticals, personal care products, illicit drugs, pesticides and industrial pollutants.
- ⇨ To evaluate the collection of water samples over 24 h in the field.

3. Methodology

3.1. Optimization of the flow restrictor back-pressure for the collection of 100 mL over 24 h

Testing of various lengths and internal diameter peak tubings

3.2. Temperature-controlled (20°C) experiments to assess volume collection over 24 h:

Testing of *different water matrices* (under stirring):

Turbidity =
0 - 431 NTU
Total suspended solids (TSS) =
0 - 0.427 g/L



Figure 1: Experimental setup to assess the water collected by the TIMFIE device over 24 h

3.3. Evaluation of the extraction performance of emerging organic contaminants:

Surface water (20.63 NTU; TSS= 0.015 g/L) fortified (100 ng/L) with over 60 compounds

SPE extraction: HLB, HR-P and WAX

Analysis with target HPLC-MS/MS

$$\text{Trueness}(\%) = \left(\frac{C_{\text{measured}} - C_{\text{blank}}}{C_{\text{theoretical}}} \right) * 100, \text{ where } C \text{ is analyte concentration}$$

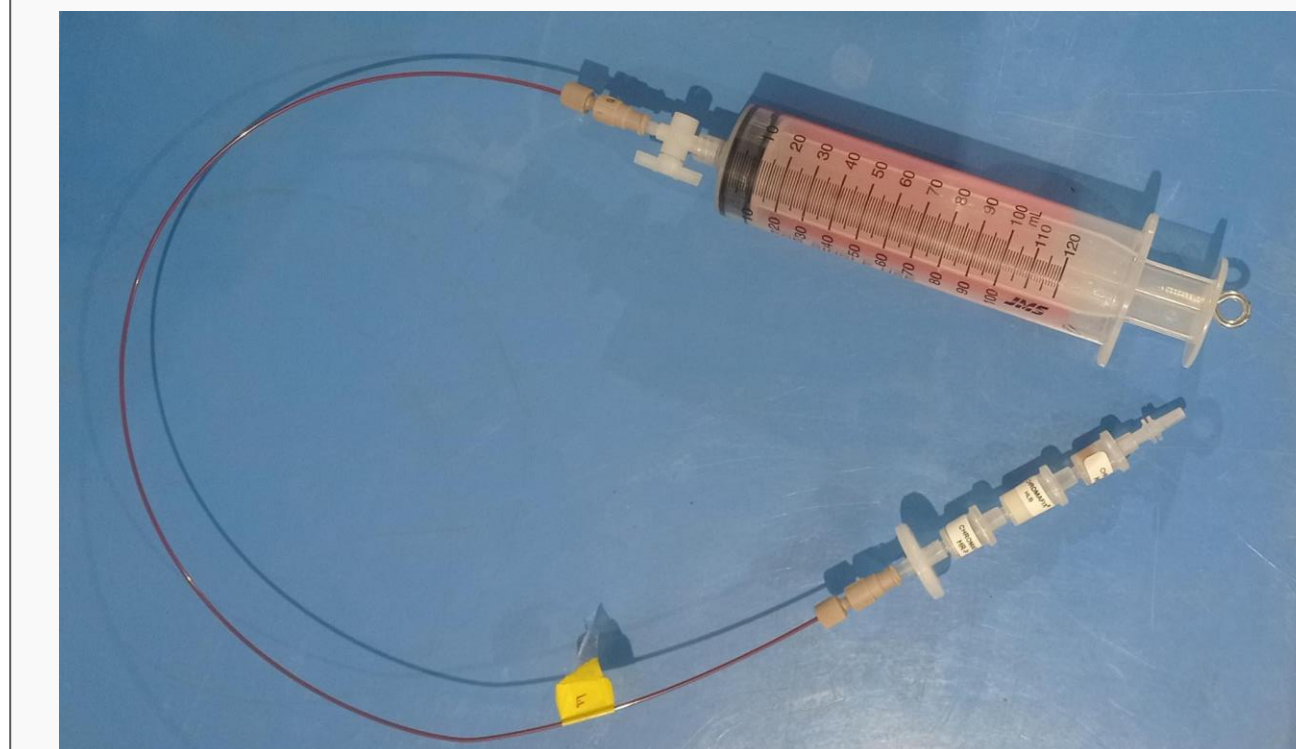


Figure 2: TIMFIE setup for in-situ 24-h SPE extraction of emerging organic pollutants

4. Results

4.1. Volume collection over 24 h in different water matrices

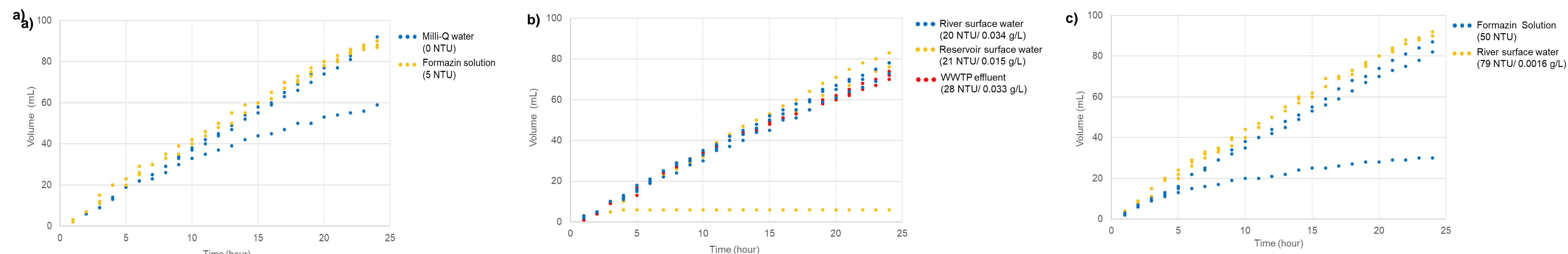


Figure 3: Volume collected by the optimized TIMFIE device over 24 h when deployed in water matrices of different turbidities and TSS: a) low (0-5 NTU), b) medium (10-28 NTU), and c) high (50-79 NTU). Flow restrictor protected with a 17 mm and 0.45 μm filter. n=3 replicates performed per matrix.

4.2. Volume collection in very-high turbidity water: effect of filter size

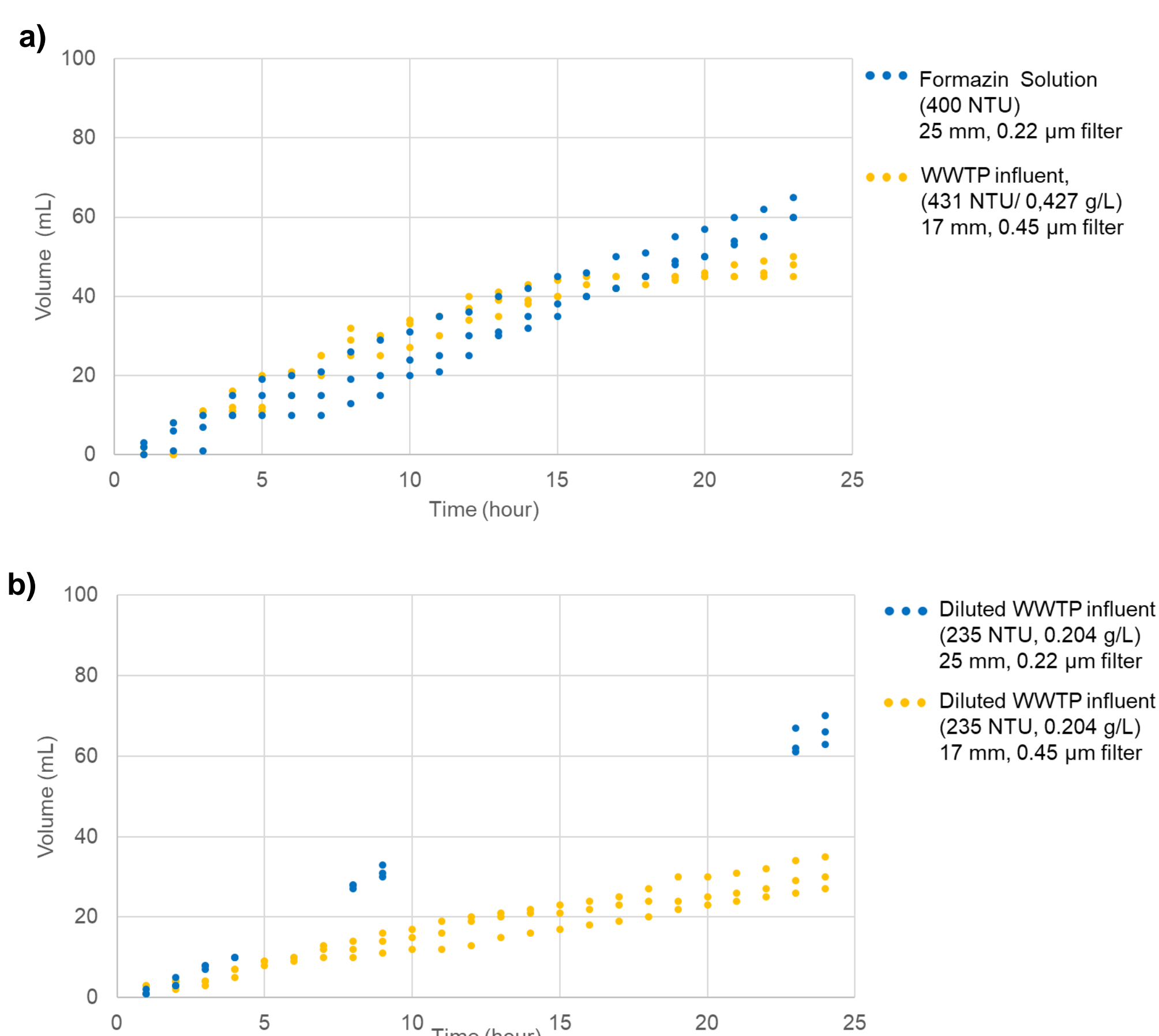


Figure 4: a) Volume collected by the optimized TIMFIE device over 24 h when deployed in high turbidity waters (a) 400-431 NTU and (b) 235 NTU.

The effect of the filter size (17 mm, 0.45 μm vs 23 mm 0.22 μm filters) used to protect the flow restrictor protected on the volume collected over 24 h is also shown. n=3 replicates performed per matrix/case.

4.3. In-situ extraction of emerging organic contaminants

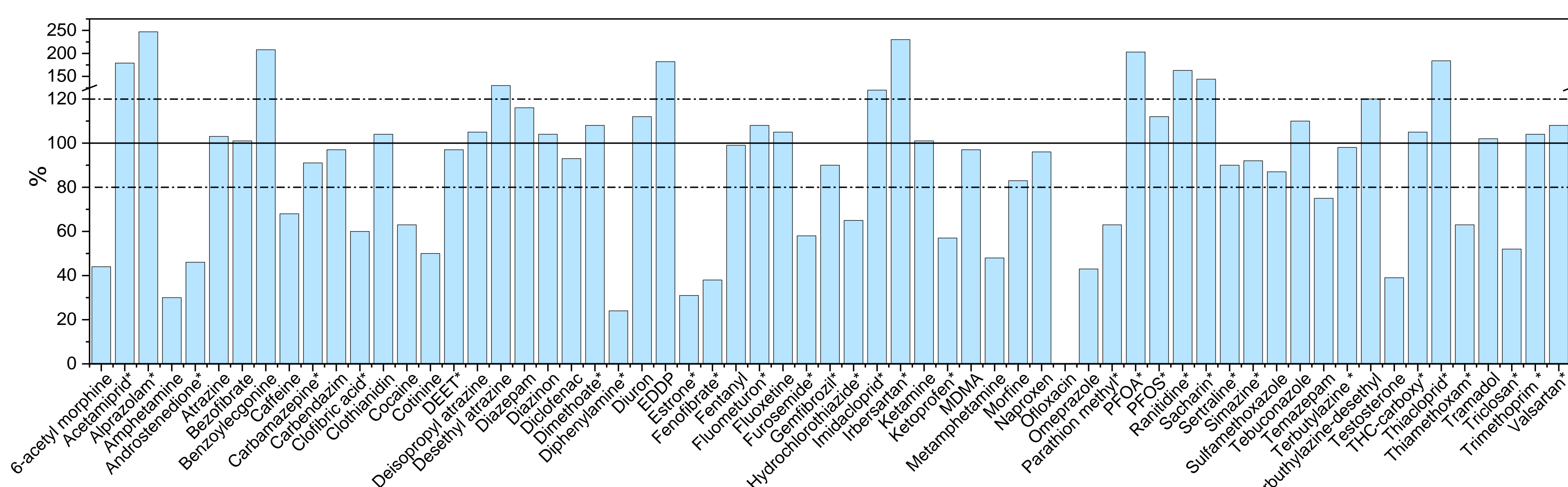


Figure 5: Trueness of the target analytes after 24-h TIMFIE in-situ extraction and HPLC-MS/MS analysis (average of n=2 samples). * Compounds for which an isotopically labelled analogue was not available for quantification

4.4. Volume collection (and extraction) after field deployment of 24-h TIMFIE devices

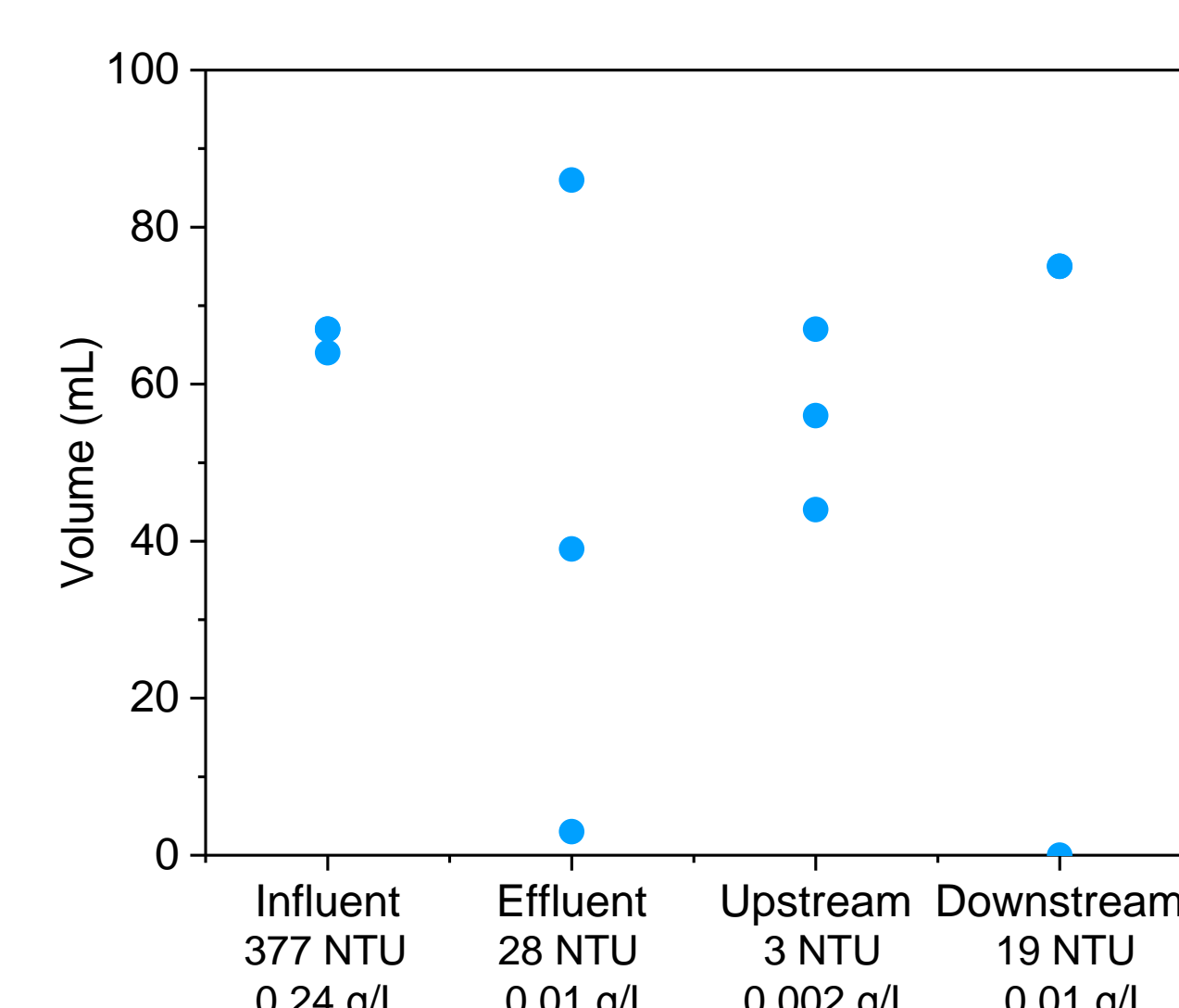


Figure 6: Volume of water collected and extracted in the field

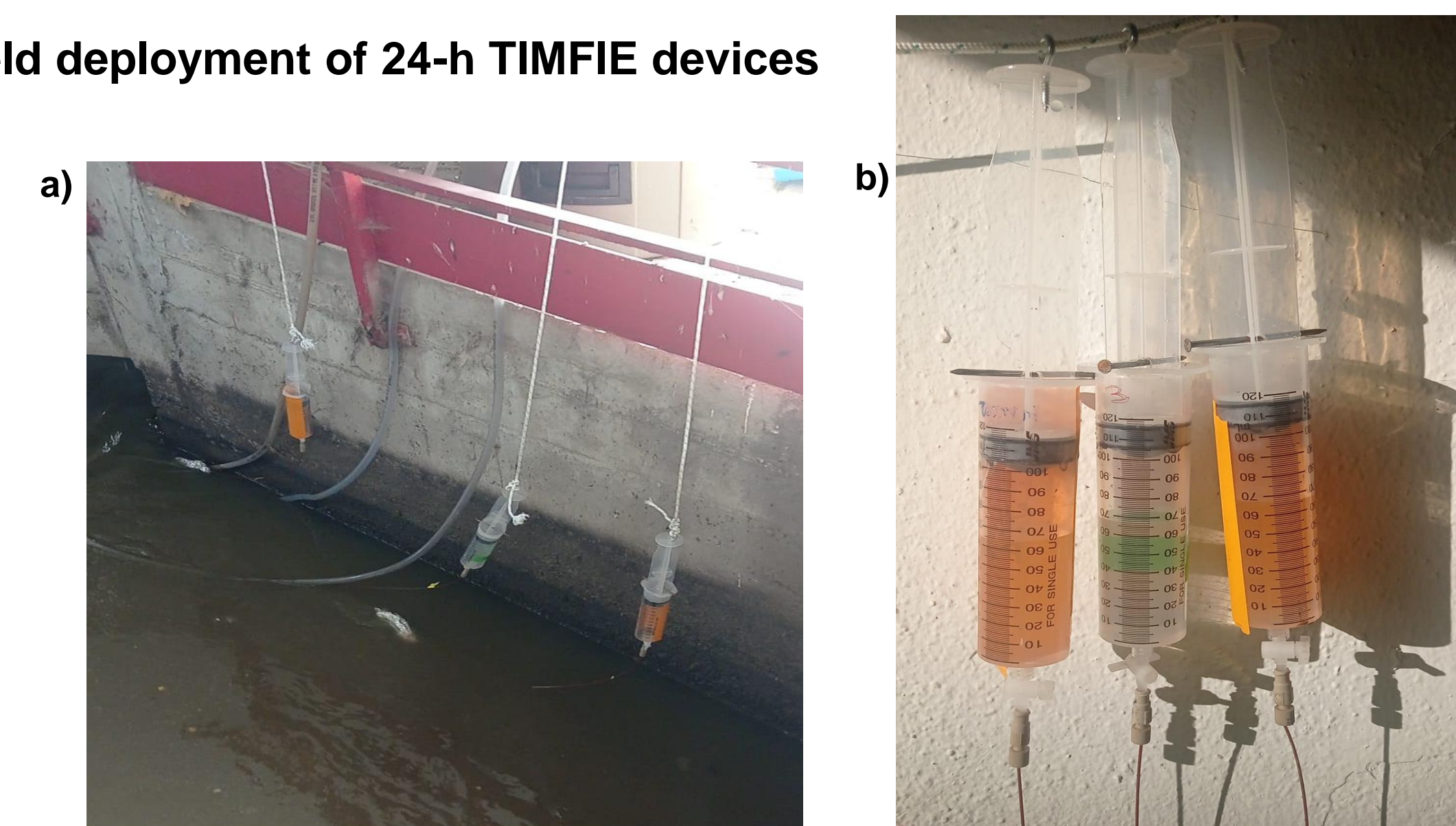


Figure 7: a) TIMFIE devices positioned in influent wastewater. b) Volume of influent wastewater collected after 22 h.

5. CONCLUSIONS

- ⇨ A TIMFIE approach for time-integrated sampling of water and the simultaneous extraction of organic contaminants was optimized.
- ⇨ Volume collection is reduced in high-turbidity waters. Increasing the diameter of the filter disk and reducing its pore size contributes to protect the flow restrictor and improves TIMFIE performance. This was confirmed in the field experiments with influent wastewater (377 NTU, 65 mL on average)
- ⇨ Method to add IS addition after sample collection needs to be improved for its proper adsorption on the SPE column and improve method trueness.
- ⇨ Deployment of TIMFIE in the field showed good performance if highly turbulent areas (effluent samples) are avoided. Despite only 16% of the devices deployed (2 out of 12) did not work, the use of triplicate TIMFIES for sample collection is recommended.

REF: [1] Jonsson et al. *Environ Sci Technol* 53 (1): 279. <http://dx.doi.org/10.1021/acs.est.8b02966>

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