

Sampling of waters

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Background PFAS

- anthropogenic origin - currently, this substance includes several thousand compounds
- The best known groups of PFAS are:
 - Perfluorinated sulfonic acids (best known representative: perfluorooctane sulfonic acid (PFOS))
 - Perfluorinated carboxylic acids (best known representative: Perfluorooctanoic acid (PFOA))
- Both for the analysis in water samples according to **DIN 38407-42** and in sludge, compost and soil according to **DIN 38414-14**, the applicability of the respective method to further substances is not excluded, but must be to be checked in each individual case - ISO 21675:2019-10 a standard that provides a procedure **for up to 30 individual substances**.
- PFAS are used specifically because of their water- and lipid-repellent properties as well as their stability and durability (persistence)
- Under normal environmental conditions, no or very little abiotic or biotic degradation occurs. According to a 2019 study, PFAS from contaminated soil also accumulate in agricultural products, such as leafy vegetables and fruits, and thus enter the food chain
- many PFAS are toxic, Short-chain PFASs in particular can be taken up by plants and thus enter the food chain. All PFASs, once released into the environment, are almost impossible or very difficult to remove
- Because of their **low adsorption tendency**, short-chain PFAS are less strongly retained in the soil and thus contaminate groundwater and raw water more quickly. In contrast, long-chain representatives (e.g. perfluorooctane sulfonic acid (PFOS), or per fluorodecanoic acid (PFDA)) are usually washed out of soils relatively slowly.
- input into the environment PFOS and PFOA have also been used in the past as guide parameters for the occurrence of PFAS
 - Spreading of contaminated sewage sludge
 - Use of consumer products or during their disposal

Tabelle 1: Nach DIN-Normen analysierbare PFAS

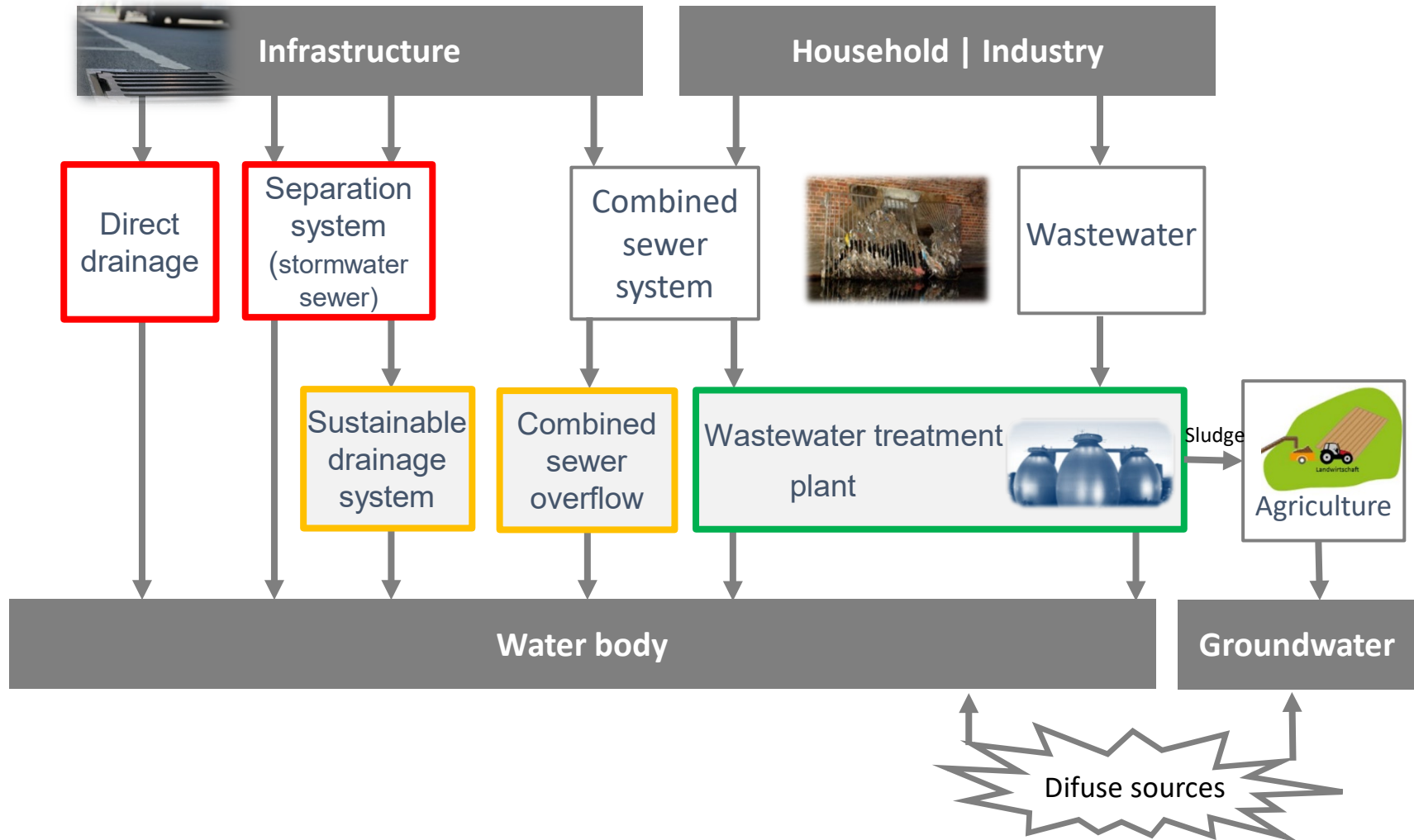
Substanz	Abkürzung	Summenformel	CAS-Nr.	Perfluorierte Kettenlänge
Perfluorbutansäure	PFBA	C ₄ HO ₂ F ₇	375-22-4	kurzkettig
Perfluorpentansäure	PFPeA	C ₅ HO ₂ F ₉	2706-90-3	
Perfluorhexansäure	PFHxA	C ₆ HO ₂ F ₁₁	307-24-4	
Perfluorheptansäure	PFHpA	C ₇ HO ₂ F ₁₃	375-85-9	
Perfluoroctansäure	PFOA	C ₈ HO ₂ F ₁₅	335-67-1	langkettig
Perfluornonansäure	PFNA	C ₉ HO ₂ F ₁₇	375-95-1	
Perfluordecansäure	PFDA	C ₁₀ HO ₂ F ₁₉	335-76-2	
Perfluorbutansulfonsäure	PFBS	C ₄ HO ₃ F ₆ S	375-73-5	kurzkettig
Perfluorhexansulfonsäure	PFHxS	C ₆ HO ₃ F ₁₀ S	355-46-4	langkettig
Perfluorheptansulfonsäure	PFHpS	C ₇ HO ₃ F ₁₂ S	357-92-8	
Perfluoroctansulfonsäure	PFOS	C ₈ HO ₃ F ₁₄ S	1763-23-1	
6:2-Fluortelomersulfonsäure	6:2 FTSA (H4PFOS)	C ₈ H ₅ O ₃ F ₁₃ S	27619-97-2	
Perfluoroctansulfonamid	PFOSA	C ₈ H ₂ F ₁₇ NO ₂ S	754-91-6	

Stoffname		GFS µg/l	GOW µg/l	BBodSchV 01.08.2023 µg/l
Perfluorbutansäure	PFBA	10		10
Perfluorpentansäure,	PFPeA		3,0	
Perfluorhexansäure,	PFHxA	6,0		6,0
Perfluorheptansäure,	PFHpA		0,3	
Perfluoroktansäure,	PFOA	0,1		0,1
Perfluornonansäure,	PFNA	0,06		0,06
Perfluordecansäure,	PFDA		0,1	
Perfluorbutansulfonsäure,	PFBS	6,0		6,0
Perfluorhexansulfonsäure,	PFHxS	0,1		0,1
Perfluorheptansulfonsäure,	PFHpS		0,3	
Perfluoroktansulfonsäure	PFOS	0,1		0,1
6:2-Fluortelomersulfonsäure	6:2 FTSA H4PFOS		0,1	
Perfluoroctansulfonamid	PFOSA		0,1	
Weitere PFAS mit R1-(CF ₂) n-R2, mit n>3			0,1	

Basis for the derivation of evaluation standards

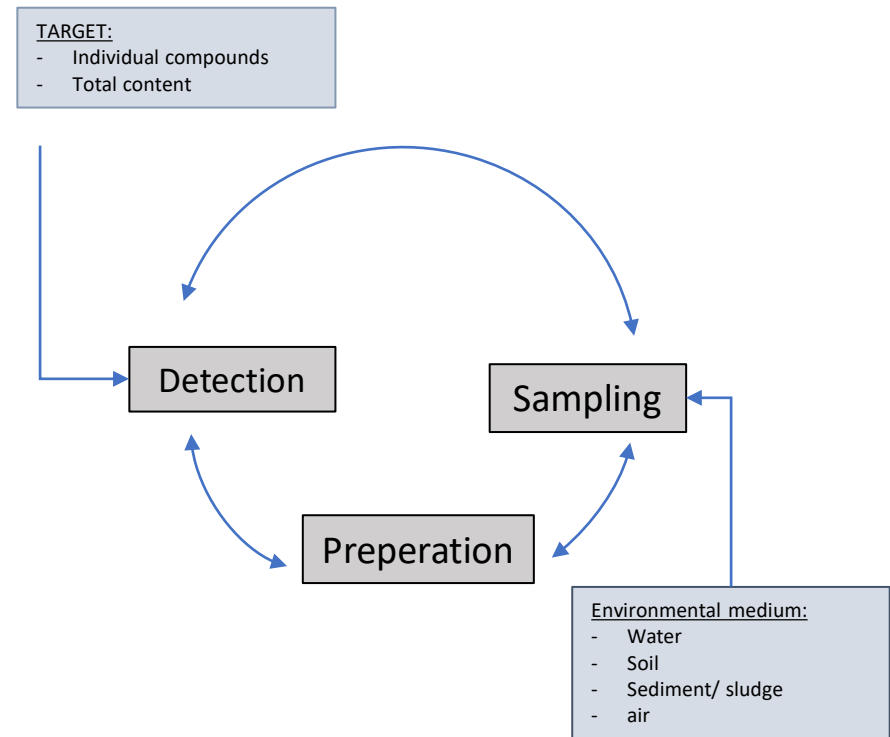
- The de minimis thresholds for PFASs are consistently based on human toxicological effects
 - Tolerable **Daily Intake** - 28.6 nanograms per kilogram body weight per day (ng/kg bw*d) each for PFOA and PFOS
 - **Directive (EU 2020/2184)** of 16.12.2020 lists representatives from the PFAS group as pollutants for the first time - For the 20 listed individual compounds, a sum value of 0.1 µg/l is applied or alternatively 0.5 µg/l, if the entire PFAS group is covered
 - In Germany 13 PFASs designated (by LAWA) as a priority for groundwater - seven GFS values are also derived as guide values according to the **Drinking Water Ordinance**
 - In the German **Federal Soil Protection and Contaminated Sites Ordinance** (BBodSchV), which was amended in 2021, these GFS values were adopted as test values for the impact pathway soil-groundwater
 - The **European Food Safety Authority** (EFSA) recommends TDI of four compounds (PFOA, PFOS, perfluorohexanesulfonic acid [PFHxS], and perfluorononanoic acid [PFNA]) at 4.4 ng/kg bw - for the first time, the aspect of mixed toxicity was also taken into account
 - the environmental quality standard for PFOS introduced via the **Surface Water Ordinance** (OGewV) is still based on the outdated EFSA value of 2008
 - **Stockholm POP** (Persistent Organic Pollutants) Convention: PFOS and PFOA were added due to their widespread distribution
 - In addition, under **REACH**, several PFAS are already classified as Substances of Very High Concern (SVHC) - European Chemicals Agency (ECHA): Environmental authorities of five European countries have proposed to ban PFAS in the EU

Emission pathways from the urban infrastructure into the aquatic environment



Sampling: definition

- Sampling is the process of taking a representative partial quantity from a body of water (or sludge or sediment) [ISO 5667-1] and is the first partial step of any analytical investigation
- Thus, sampling is of particular importance, since errors in sampling, sample division, preservation or transport cannot be corrected in the further analytical course
- In order to provide the laboratory with a task-oriented sample with a representative composition for the subsequent investigations, *intensive structured planning* as well as *quality control measures* for the collection and handling of water samples must be observed in addition to the *technology* and the *apparatus* to be used



Structure legal basis

- Standards are embedded in legal regulations (e.g. EU Water Framework Directive) and serve to implement environmental law
- State of the art defined by standards
- Standardized regulations are generally proven in practice
- Standardization Sampling:
ISO TC 147 SC 6
- Adoption of international standards by CEN (then valid in all member states)



Legal basis - Standardization

- Basic standards:
 - Sampling program
 - Sampling technique
 - Sample preservation
 - Sample pretreatment
- Water type specific standards

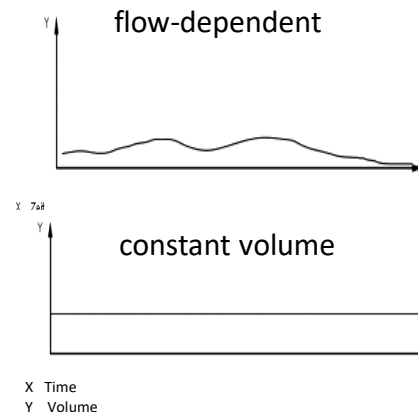
Title	International standard
Guidance on the preparation of sampling programs and sampling techniques	ISO 5667-1*
Instructions for preservation and handling of water samples	ISO 5667-3*
Sampling from standing waters	ISO 5667-4
Sampling of raw water and drinking water	ISO 5667-5
Sampling from flowing waters	ISO 5667-6
Sampling of cooling water for industrial use	ISO 5667-7
Sampling from the sea	ISO 5667-9
Waste water sampling	ISO 5667-10
Sampling from groundwater aquifers	ISO 5667-11
Sampling of sediments	ISO 5667-12
Instructions for sampling sludge from WWTP and water treatment plants	ISO 5667-13
Guidance for quality assurance and quality control in the collection and handling of environmentally relevant water samples	ISO 5667-14*
Instructions for sampling and performing biological test procedures	ISO 5667-16
Guidance for sampling marine sediments	ISO 5667-19
Instructions for sampling aquatic benthic macro-invertebrates with the hand net	ISO 7828
Sampling devices for quantitative detection of benthic macro-invertebrates on stony substrates in shallow freshwater	ISO 8265
Sampling of macro-invertebrates in deep waters	ISO 9391
Guidance for quantitative sampling and sample processing of marine soft-bottom macrofauna	ISO 16665
Sampling for microbiological analyses	ISO 19458

Sampling types

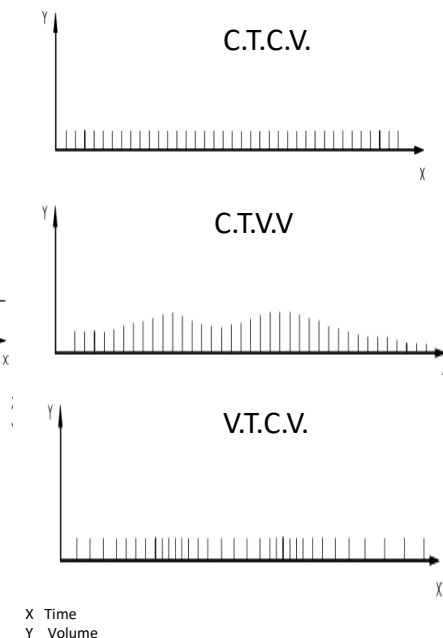
- Manual or automatic sampling
- Continuous or periodic sampling
 - Periodic sampling with fixed time intervals (time-dependent) or sampling with constant time and constant volume
 - Periodic sampling with fixed flow intervals (volume dependent) or sampling with constant time & variable volume
 - Sampling of equal sample volumes with a time frequency proportional to the flow rate or sampling with variable time and constant volume
- Fluctuations (dynamically changing concentration peaks)
- Passive sampling is not recommended

[ISO 5667-1:2023]

continuous sampling



periodic sampling

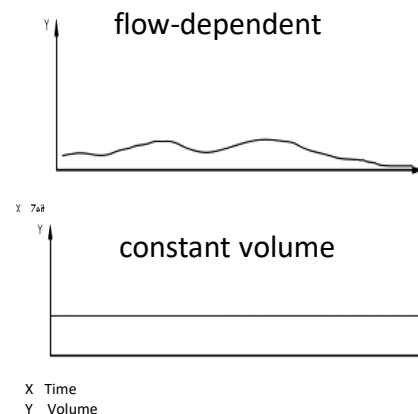


Sampling types

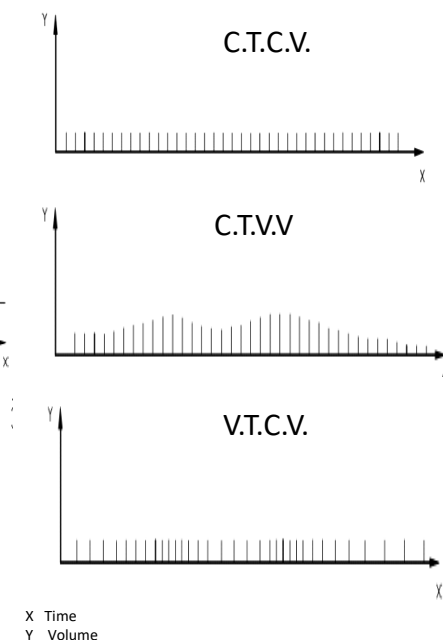
- Spot/individual sample
 - one or more individual samples taken immediately after each other and combined to assess a momentary condition
- Mixed sample
 - two or more samples taken individually or continuously and mixed in a suitable, known ratio to determine from the mixture the average value of a desired characteristic
- *Qualified sample*
 - consisting of at least five samples taken and mixed in a period of not more than 2 h at intervals of not less than 2 min*
- Depth profile sample
- Area profile sample

[ISO 5667-1:2023]

continuous sampling



periodic sampling



Sampling challenge

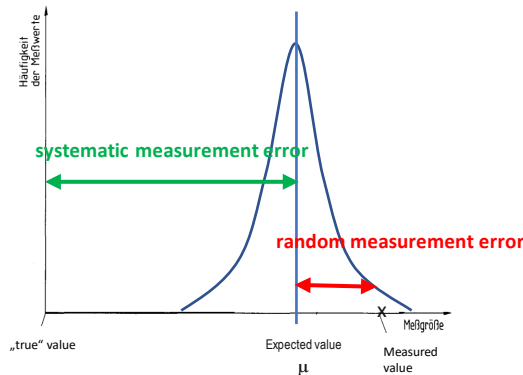
- by sensitive and selective single substance analysis, the total load can be significantly underestimated
 - further error due to measurement inaccuracy
 - we need extended substance spectrum for the analysis
- Heterogeneous distribution (dissolved and particle-bound) -> Sampling over the entire water column necessary/ problems in recording, among other things, inflow conditions.
 - Aging processes and environmental influences affect properties and composition
- PFASs are ubiquitously distributed - risk of contamination - observe equipment and working conditions during sampling and in the laboratory (PPE, parts carrying medium)
 - Zero samples/blank values
 - Multiple determination
- Documentation
 - Determine influence and characterization of ecosystem/compartment
 - Accompanying parameters

Quality assurance

- Quality assurance serves to avoid errors and quantifies the quality of the generated data
- Quality assurance includes an evaluation of the entire sampling procedure with regard to its suitability for the respective test objective and determination of the measurement uncertainty specific references ISO 5667-14 and DIN EN ISO/IEC 17025
- Recommendation from ISO 5667-14: The scope of quality and control measures should be at least **2 % of the total analytical effort**
 - Repeat tests for accuracy and precision determination (recovery rates)
 - Field blank samples to identify sources of contamination
 - Use of spiked samples to assess sample stability during transport and storage
 - Verification of cleaning of sampling equipment and sample containers

Uncertainty of measurement

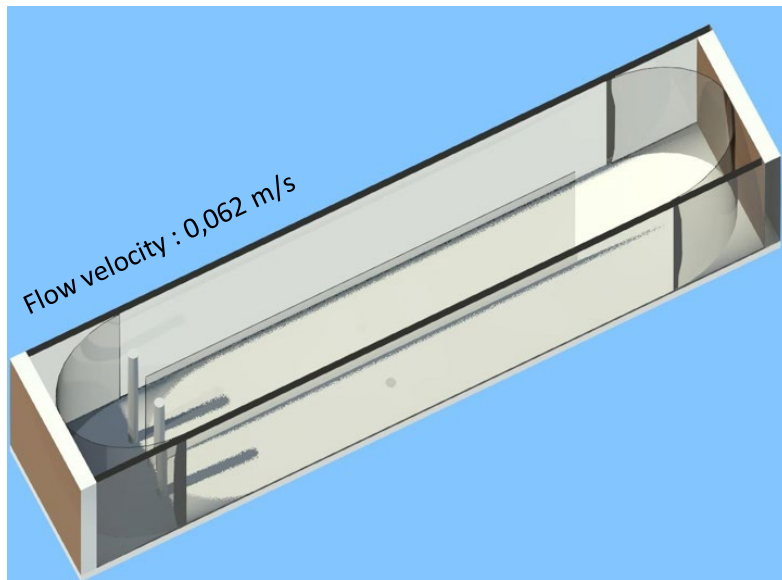
- | Measured value = estimated value of a measurand
- | If measurements under seemingly identical conditions are repeated infinitely often, a distribution of the measurement results around an expected value (away from the *true value*) results



- | due to a multitude of uncontrolled influences, the measurement results show an unpredictable scatter = **random measurement error**
- | Shift of the center of the distribution (mean) from the true value = **systematic measurement error**
- | Measurement result (x) is always subject to uncertainties from the entire measurement process - must definitely be taken into account when interpreting the results
- | Estimation of measurement uncertainty by means of U-value determination according to *ISO 11352:2013* (based on validation and control data)
 - Performance parameters: Accuracy and precision

Uncertainty of measurement

Systematic examination on the test stand



centrifugal pump



peristaltic pump

Systematic investigation of different influencing variables under constant conditions (e.g. turbulent/laminar flow, test substance density/size/shape, sampling positioning)

8 repetitions

Water+plastic mixture -> Gravimetric analysis
Angepasste Soll-Konzentration

Illustration of floating, suspended and sedimentable substances for the determination of a common error variable (generally valid).

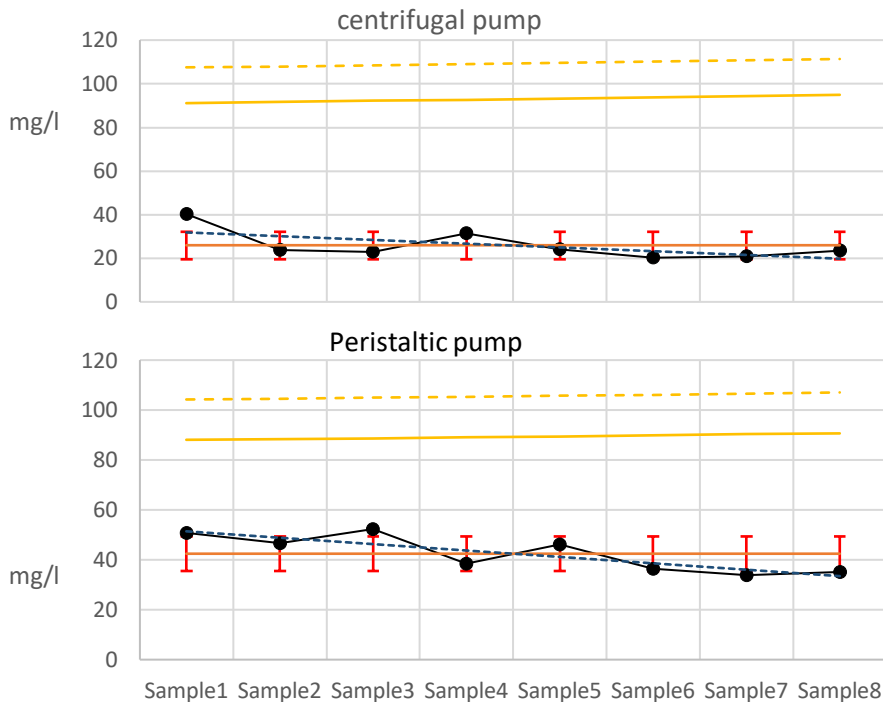
PS -flour:
 $d_{50} = 298 \mu\text{m}$
 $\rho_{PS} = 1,05 \text{ g/cm}^3$

PE-flour:
 $d_{50} = 145 \mu\text{m}$
 $\rho_{PE} = 0,98 \text{ g/cm}^3$

Rubber flour K 002:
 $d_{50} = 125 \mu\text{m}$
 $\rho_{RM} = \text{ca. } 1,17 \text{ g/cm}^3$

Recovery PE (floating substance)

1/3 below water surface (according to ISO 5667-10)



» centrifugal pump

» Accuracy : 28 % (47 %)
» Precision : 25 % (19 %)

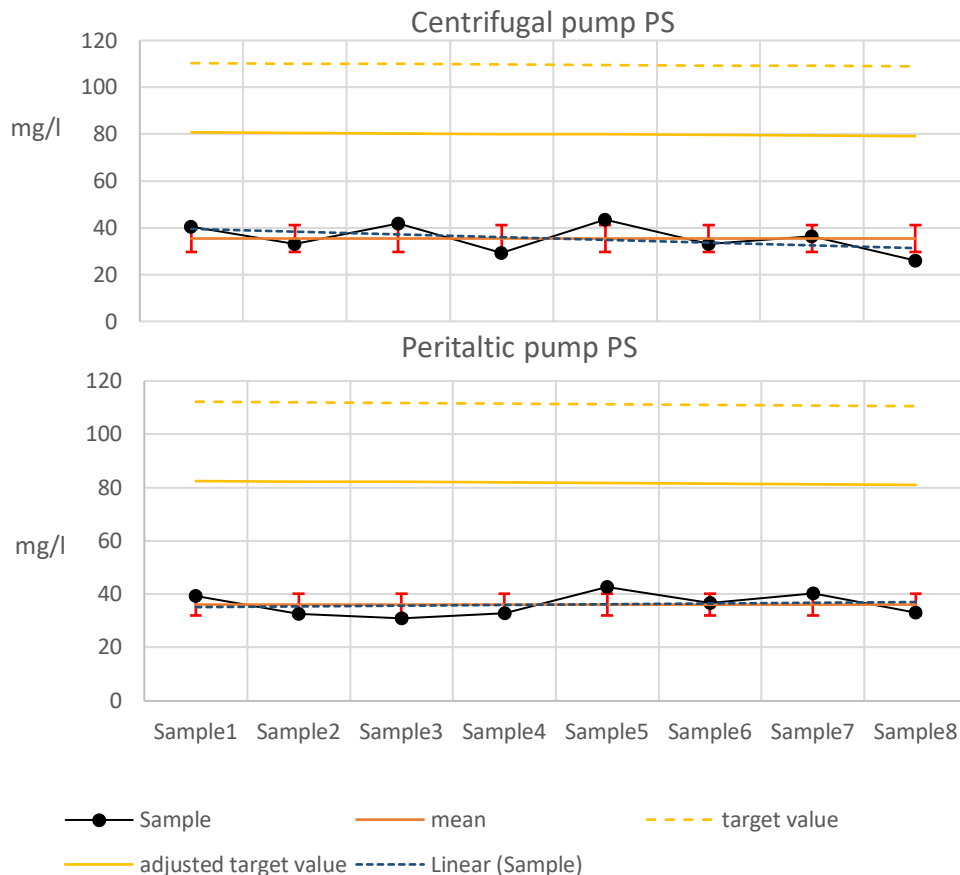
» Peristaltic pump:

» Accuracy : 48 % (44 %)
» Precision : 16 % (32 %)

—●— Sample
— Mean
- - - target value
— adjusted target value
- - - Linear (Sample)

Recovery PS (suspended particulate matter)

1/3 below water surface (according to ISO 5667-10)



» centrifugal pump

» Accuracy : 44 % (59 %)
 » Precision : 16 % (6 %)

» Peristaltic pump:

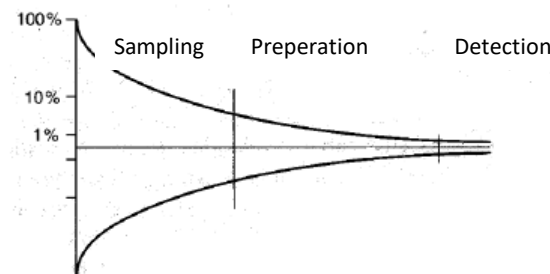
» Accuracy : 44 % (71 %)
 » Precision : 11 % (13 %)

Uncertainty of measurement

- Calculation of the measurement uncertainty from all analytical sub-processes according to the error propagation law.

$$\sigma_{Gesamt}^2 = \sigma_{\text{Sampling}}^2 + \sigma_{\text{Preparation}}^2 + \sigma_{\text{Detection}}^2$$

- Due to the low variances in the measurement technique, the main source of error is in the sampling process



Aus: Cammann, Instrumentelle Analytische Chemie (2001)

Uncertainty of measurement Microplastics

U Sampling	= ± 67 - 87 %
U Field sample preparation	= ± 4 %
U preparation in lab	= ± 31 %
U Detection	= ± 20 %

U Analysis, PE	= ± 85 %
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Investigation sampling

systematic effects

- Mixing - This will reduce the segregation?
- increase the size of the sample - increasing the sample size will give a better representation of the whole target

Random effects are easier to quantify and can be minimized. They are mainly caused by variations in the composition of the sample in space or in time, variations that may be either cyclic or non-cyclic.

- reducing random effects is to increase the number of samples taken, which in turn will lead to a smaller standard deviation of the mean result.

PFAS sampling notes

- Sampling with comparison measurement and duplicate determination
- For investigations near the source of the pollutant, it is recommended to analyze for the summary parameters AOF or TOP assay in addition to the single substance analysis.
- The waste water specific sum parameters COD and TOC are not meaningful for PFAS
- in dried samples PFAS concentrations in the eluate can be up to approx. 10 times higher than in field-fresh samples - A drying step therefore leads to better comparability of the results

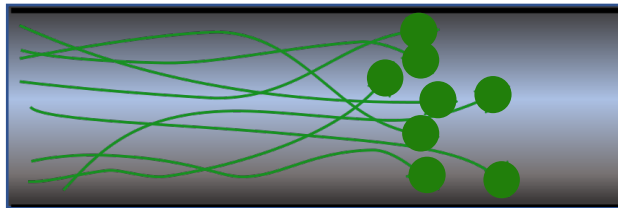
Thank you for your attention!

Significant influencing variables when taking samples from flowing media

Streamlines in laminar flow



Streamlines in turbulent flow



Description of the prevailing conditions during sampling.

» Result of a flow is mass transport

» **Description of the flow:**

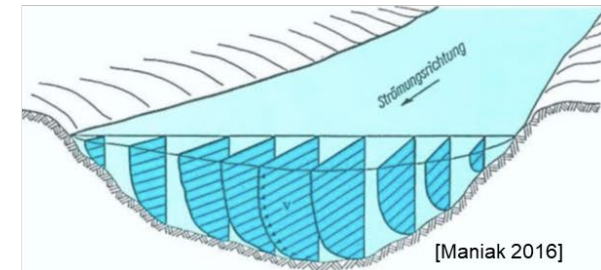
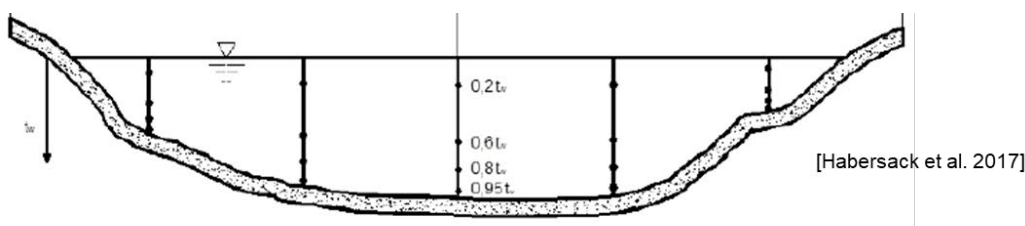
Reynolds-number $Re = \frac{vD}{\nu}$

» In turbulent flow, mixing due to transverse movements

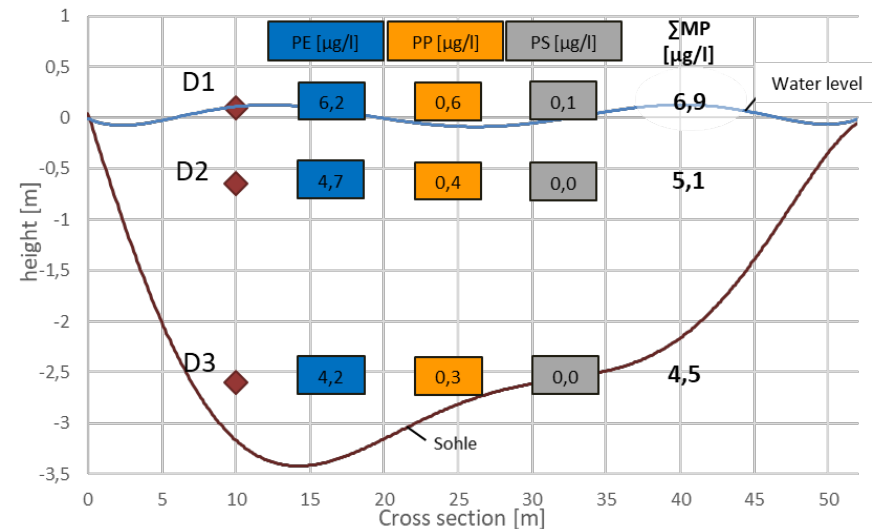
» Effective transport shear force τ (bedload - suspended sediment transport)

Receiving Water

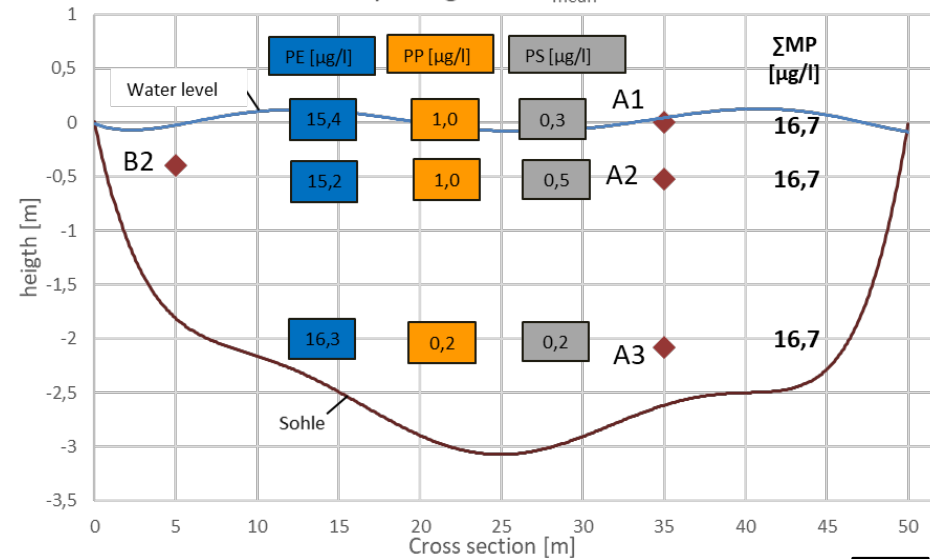
Site Spree (Berlin)



Site Roentgen Bridge - MP_{mean}



Site Gotzkowsky Bridge – MP_{mean}



Maniak, U. (2010): Hydrologie und Wasserwirtschaft: Eine Einführung für Ingenieure. 6th edition. Heidelberg: Springer-Verlag. ISBN: 978-3-662-22018-4

Habersack, H.; Haimann, M.; Kerschbaumsteiner, W.; Lalk, P. (2017): Schwebstoffe im Fließgewässer. Leitfaden zur Erfassung des Schwebstofftransportes – 2nd edition, <http://www.bmlfuw.gv.at/>