About the Author

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Christoph Ort's main research focus is on the spatiotemporal occurrence of (micro)pollutants in raw wastewater. His findings help in setting up appropriate sampling schemes for various applications in source typing and tracking, for example, quantification of hospital effluents, influents to sewage treatment plants or transformation of pollutants in sewers.

Chapter

7

Quality assurance/ quality control in wastewater sampling

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Seasonal, weekly, daily and diurnal variations of substances in wastewater are well known to occur. However, concentrations of pollutants in wastewater can vary considerably, even within shorter time frames – that is, anywhere from seconds, when close to the source, up to minutes, in transit in sewers, influents to sewage treatment plants, combined sewer overflows or separate stormwater discharges. Such short-term variations can distort results as a consequence of inadequate sampling. To account for (un)known or (un)expected variability in wastewater, flow-weighted sampling setups with precautionary high sampling frequencies should be applied – unless objective evidence from previous experiments or expert knowledge justifies reducing the sampling frequency for this specific situation. In raw wastewater, depending on the location and substance under investigation, the required sampling frequency can be as short as 2 min to correctly capture short-term variations. If the research question, for example, requires 2-h average concentrations, samples still need to be collected at 2-min intervals, but they can be pooled over 2 h to minimize analytical effort. However, it would be careless to merely collect a grab sample every 2 h.

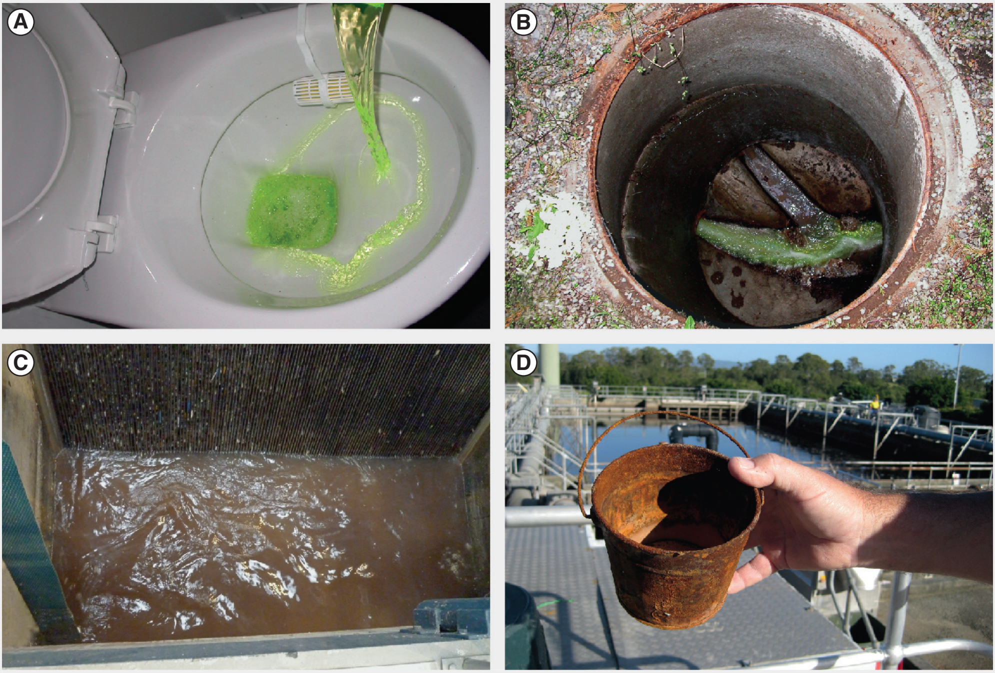
Temporal variations of pollutants in your sewer must be expected to be subject to high short-term variations (a few minutes). Inappropriate sampling may lead to artefacts exceeding the uncertainty caused by chemical analysis.

If everyone obediently followed the existing guidelines on sampling of wastewater, this chapter would be redundant. The benefit, but at the same time the challenge, is that norms and guidelines need to be of general validity to cover more than a few specific situations. This implicitly delegates the responsibility to the sampling personnel, who have to adapt these recommendations to their individual cases. Ideally, close collaboration and frequent exchange of experience and results exists between end users of data (e.g., researchers and regulatory bodies) and sampling personnel to minimize errors and to consequently maximize data quality.

"The concentration of the various determinands in a stream will vary due to random and systematic changes. The best technical solution, to determine the true values, would be to use an online automatic instrument providing continuous analyses of the determinand of interest"[1]. For many compounds of interest in real wastewater systems, no such sensors exist or they cannot be deployed and operated in hazardous environments. Therefore, for many applications (automated) sampling with subsequent analysis of the sample in a laboratory is the only practicable solution. This chapter aims to provide background information to better understand the dynamics of wastewater (in the section 'Characteristics of wastewater systems and consequences for sampling') and assisting the reader in finding optimal sampling setups for common tasks at typical sampling locations within or at interfaces with wastewater systems (in the section 'Different sampling tasks in wastewater systems'). As such, this chapter does not replace existing guidelines and does not recommend particular brands of sampling devices. The intention is to provide useful examples so that readers can better transfer and apply recommendations from guidelines to their specific situations. **Figure 7.1D** caricatures 'the amount of effort available for sampling' in the following quotation from a wastewater guideline [2]: "... samples should be taken at times which will adequately represent the quality and its variations [...] This approach contrasts with the choice of sampling frequency based on either subjective considerations or the amount of effort available for sampling and analysis." For example, for the analysis of micropollutants in wastewater, it is self-evident that expensive high-end instruments are necessary, but every fifth study used grab samples without explicit justification of why this was thought to be appropriate [3].

A wide range of different sampling locations in wastewater systems, different types of wastewater and various substances under investigation

Figure 7.1. Dye-tracing of a toilet flush to assess its duration throughout the sewer network.



From the toilet **(A)** via the house connection **(B)** where a toilet flush extends over several seconds only to the inlet of the sewage treatment plant **(C)**. The effects of dispersion extend the duration of the flush at points farther downstream in the sewer system. Despite transit times of several hours in sewers, the toilet flush is not spread over hours. It may last a few minutes. Therefore, the use of inadequate sampling devices **(D)** challenges coping with high dynamics of wastewater and may lead to sampling artifacts.
(A, B & D) are courtesy of Christoph Ort (Eawag: Swiss Federal Institute of Aquatic Science and Technology).
(C) is courtesy of Christian Abegglen (Entsorgung + Recycling Zürich, Switzerland).

lead to a broad spectrum of possible or necessary sampling strategies. The exact practical implementation depends on the acceptable level of uncertainty and the timeframes that are considered. In this broad spectrum, one of the most common combinations is municipal wastewater, analyzed for dissolved substances in the liquid phase, and a 1-day period as the basic time unit. Therefore, these three aspects are the basis for this chapter and the focus is mainly on the temporal variation within 24 h to facilitate the collection of representative 24-h composite samples. Furthermore, the emphasis is on wastewater in sewer pipes since fluctuations are expected to be highest there. The reader should note that the influent to a sewage treatment plant (STP) is the 'end' of a sewer network and that dynamics before any retention tank must be assumed as high as in sewer pipes. The principles also apply to wastewater systems impacted by industrial discharges. Treated or untreated industrial wastewater is often discharged in batches, which extend over short periods only. Consequently, this can lead to high temporal variation of both water flows and pollutant concentrations. Aspects relating to spatial variations (see the section titled 'Assessing or appropriately considering spatial variations'), particulate matter, other types of sampling (i.e., passive sampling, see the section titled 'Time-weighted average concentration') or other techniques (i.e., online measurements) are not, or only briefly covered, as in-depth considerations are beyond the scope of this chapter.

Characteristics of wastewater systems & consequences for sampling

This section provides a brief overview of wastewater systems with a focus on sewers to better understand the often unknown or neglected temporal variation of wastewater flows, which impacts the choice of an adequate sampling mode, and wastewater concentrations, which impact the choice of the appropriate sampling interval. One of the most frequently encountered tasks is the determination of a daily average concentration to calculate a daily load of a substance. This requires the collection of a 24-h composite sample. The text in the next two sections was written with this task in mind. Other tasks, such as assessing diurnal variations of pollutants or sampling at the effluent of an individual building (e.g., hospital), are described in the section titled 'Different sampling tasks in wastewater systems'.

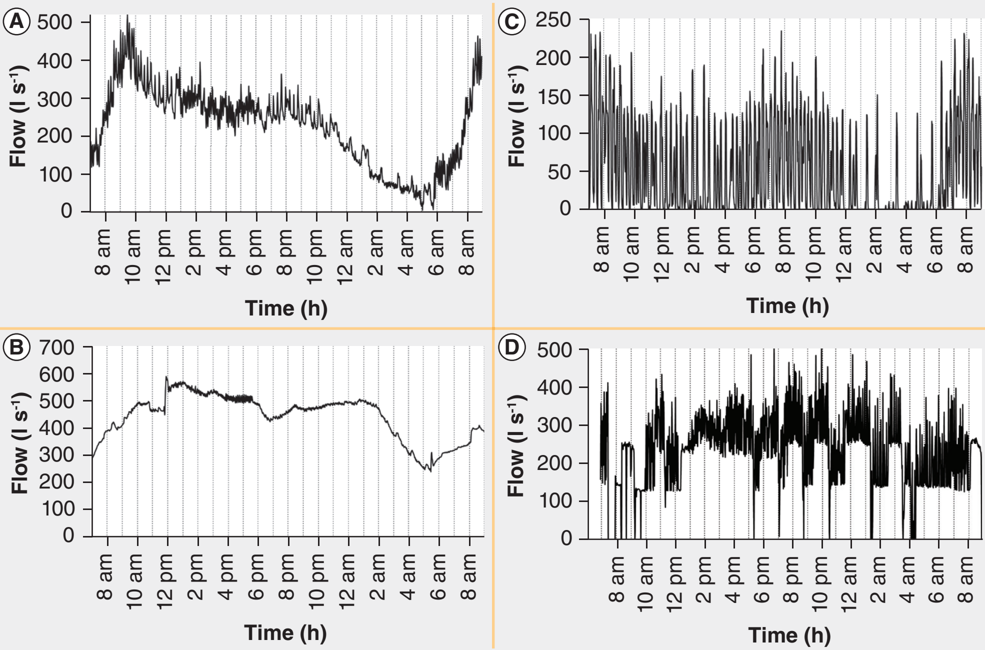
Sampling mode to address variations in wastewater flows

At the source, for municipal wastewater in households, wastewater is generated through various sanitary installations and household appliances. Individual discharges are typically intermittent and of short duration, for example, from a toilet flush **(Figure 7.1)**, dishwasher, washing machine or bath tub. Daily routine caused by habits of people, working hours and activities related to personal hygiene, including the use of toilets, implies a systematic diurnal variation of water use in households [4–8]. Consequently, this results in similar patterns of wastewater volumes, discharged into sewers, typically with a hydraulic peak in the morning. After transit in gravity-fed sewers, at the influent of STPs serving small catchments with short flow distances, this peak is still fairly pronounced. It can be followed by a plateau during the day, maybe a second smaller peak in the

Decreasing sampling intervals increases the number of samples to form a composite sample. This increases the total sample volume but not the number of samples to be analyzed.

evening and a night minimum reflecting lowest human activity related to wastewater production. In **Figure 7.2A**, the maximum/minimum ratio of flow is approximately 10, which is one of the highest observed, although it is not a very small, but fairly steep catchment with a relatively narrow flow distance distribution. In larger catchments, longer flow distances – and a wider distribution thereof – as well as extended periods of a fraction of people being awake, lead to a certain attenuation of diurnal variation.

Figure 7.2. Diurnal flow patterns in the influent of four sewage treatment plants with different drainage system layouts and designs of inlet works infrastructure.



(A) Mainly gravity-fed sewers (population ~100,000 people, 20,000 m^3 d^{-1}); the distinct peaks are caused by the intermittent operation of the fine screen, flow is measured after primary treatment. **(B)** Sewers with real time control (150,000 population equivalents, 40,000 m^3 d^{-1}); storage capacity in the sewer system is used to hold peak flows back and release wastewater at slower rate during lower flows. **(C)** Mainly pressurized sewer system (limited storage capacity in a pump sump at the inlet of the STP, whenever this is full, the water is pumped to the STP, 4000 m^3 d^{-1}). **(D)** Mainly gravity-fed sewers (30% of the wastewater volume is collected from pressurized sewers, stored in a large tank before the STP and treated during the night; this STP is operated with two sequencing batch reactors while all other STPs are flow through; population ~45,000 people; the graph shows a wet-weather situation with 20,000 m^3 d^{-1}, during dry weather the inflow volume is 10,000 m^3 d^{-1} and the influent pattern is lowered by a constant offset of approximately 120 l s^{-1}).
STP: Sewage treatment plant.
Reprinted with permission from [3] © American Chemical Society (2013).

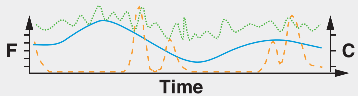
If relevant information about the hydraulic properties and the number of sources contributing to the pollutant load are not evaluated, and if preliminary investigations about dynamics cannot be carried out before the monitoring campaign, a flow-weighted sampling mode with short intervals (~5 min) should be applied.

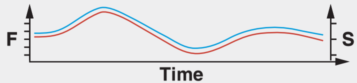
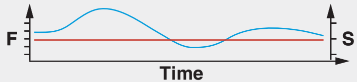
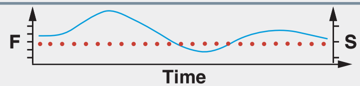
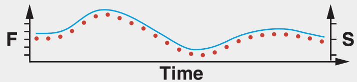
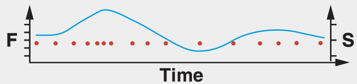
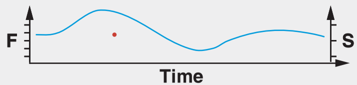
Flow control devices can level out high hydraulic peaks by using storage capacity in sewers. An example can be seen in **Figure 7.2B** with a maximum/minimum ratio of approximately 2, one of the lowest observed. Lift stations in sewer networks to transport wastewater to STPs or to feed sequencing batch reactors in STPs can lead to completely different patterns. Often, intermittently operated pumps lead to times of high flows alternating with times of no flow (infinite maximum/minimum ratio). Examples can be seen in **Figures 7.2C & 7.2D**.

Due to the characteristics described beforehand, flows in full-scale wastewater systems are usually subject to more or less pronounced variations. This also holds true for STP effluents: despite retention times of wastewater in STPs in the order of hours, hydraulic pulses can propagate through large tanks within a few minutes [9]. Consequently, a flow-dependent sampling mode is also required for effluents **(Figure 7.3)**. This implies that a flow signal must be available online to control the sampling device. For most tasks (see examples in the section titled 'Different sampling tasks in wastewater systems') flow must be measured anyway to calculate loads. Conceptually, a flow-proportional sampling mode is the best to properly weigh individual samples forming a composite sample. However, due to operational and mechanical challenges (i.e., either the diversion of a continuous flow-proportional small side stream of wastewater or accurately measuring and taking flow-dependent volumes [discrete samples]), manufacturers typically do not fabricate sampling devices that can be operated in this mode (see section titled 'Volume- versus flow-proportional sampling'). Furthermore, flow patterns, such as the one depicted in **Figure 7.2C**, may result in the following situation: whenever the timing of sampling coincided with times when wastewater in the sewer is stagnant, the sample volume at these points in time is zero, as flow in the sewer is also zero. If by coincidence the timing was bad, this can result in small sample volumes and individual samples not being taken at sufficiently short intervals to capture relevant fluctuations. As an alternative, the volume-proportional sampling mode is most often implemented. If operated at short sampling intervals (see section titled 'Sampling interval to address concentration variations in wastewater'), the volume-proportional sampling mode approximates the flow-proportional sampling mode. In addition, if the flow pattern repeatedly exhibits periods with no flow, the volume-proportional sampling mode is even superior to the flow-proportional sampling mode.

Figure 7.3. Description of different sampling modes.

Conceptual example



	Sampling mode	Short description		Specific equipment†	Flow meter‡
Continuous	Flow proportional	Divert a side stream, proportional to the flow in the sewer		Pump with speed control (proportional to external flow signal)§	Yes
Continuous	Constant	Divert a constant side stream from the sewer		Pump	No
Discrete	Time proportional	Take a constant sample volume at constant time intervals		Standard auto-sampler	No
Discrete	Flow proportional	Make sample volume proportional to the flow in the sewer taking them at constant time intervals		Auto-sampler with adjustable sampling volume¶ (proportional to external flow signal)	Yes
Discrete	Volume proportional	Take a constant sample volume at variable time intervals, after a certain volume of wastewater has passed the sampling point		Auto-sampler totaling an external flow signal up to a predefined volume and then triggering a sample#	Yes
Discrete	Grab sample	Take one (or a number of) grab sample		Scoop, no power supply	No

†Indicates the type of equipment that is required besides sampling bottles, suction hose and power supply.

‡Is a flow meter required for taking samples (external flow signal)? To calculate environmental loads from sampled (average) concentrations, it always needs a flow meter.

§Ideally a robust peristaltic pump with fine increments to accurately control speed with external flow signal. Linearity of pump speeds and performance (suction and pressure height) need to be checked for conditions that apply in the field.

¶Sampling volume of individual samples needs to be checked for linearity over the entire range of discharge in the sewer.

#Check variation of individual sample size.

F: Flow in sewer; S: Sampling volume.

There may be a few exceptions where flow is controlled and constant (e.g., in pilot-scale plants or laboratory experiments). In these cases, the flow- and volume-proportional sampling mode are equivalent to a time-proportional sampling mode. However, unexpected flow variations can occur in most applications and a flow- or volume-proportional sampling mode helps to appropriately account for such variations. If flow variations are not considered during the sampling process, the average concentration may be systematically over- or under-estimated [10,11]. Without knowing the concentration variations at high temporal resolution (i.e., at the scale of minutes), it is difficult to quantify this potential bias. A method on how to estimate the maximum bias in practical applications is suggested in the section titled 'Difference between time- & flow-weighted average concentration when flow rates vary'.

Sampling interval to address concentration variations in wastewater

As described in the previous paragraph and **Figure 7.1**, wastewater volumes intermittently discharged at the source are often of limited duration: for municipal wastewater, think of a toilet flush (5–10 s), pumping wastewater out of a dishwasher or a washing machine (30 s–2 min), water from a shower or bath tub (3–5 min) or a sink (10 s–1 min). Furthermore, each of these wastewater pulses contains different groups of substances. Toilet flushes, for example, can contain excreted pharmaceutical residues and different toilet flushes are likely to contain different pharmaceutical residues since different people or patients take different medications. Cumulated at the influent of a STP, the grayish, brownish wastewater may appear to us as a continuous and homogeneous stream; however, in reality it is a patch-work of thousands of different wastewater pulses each being more or less different. The number of pulses containing the substance of interest determines how variable the concentration pattern is over time. It is clear that a substance contained in a small number of wastewater pulses typically leads to higher variability than a substance that is contained in a large number of wastewater pulses. Small numbers must be expected either in small wastewater systems or in bigger systems in which only a small fraction of the population is taking and excreting a certain medicament. The variability of a concentration profile over time determines the required sampling interval to not exceed an acceptable level of uncertainty associated with the average concentration in a pooled sample. For many substances, it is not trivial to estimate the number of wastewater pulses they are contained in.

> Close to a source (e.g., effluent of a hospital) flow and concentration variations are much higher than at influents of sewage treatment plants. Concentration variations are further attenuated through sewage treatment plants and besides influent loads mainly depend on operational conditions.

For a model-based optimization of your sampling setup, which is one of three approaches further described below, you need to know the relevant number of wastewater pulses (e.g., number of toilet flushes containing the substance of interest) before sampling to determine the adequate sampling interval. However, if you knew the number of wastewater pulses, you probably also knew relatively well which amount of this substance was discharged and you would not have to take and measure the sample. Furthermore, the same samples may be analyzed for many different compounds originating from many or few wastewater pulses only. Therefore, the substance contained in the smallest number of wastewater pulses determines the required (shortest) sampling interval. The readers should note that individual wastewater pulses are a challenge for sampling due to their short temporal extension at the influent of a STP not due to the low concentration as a result of dilution. The latter challenges chemical analysis (detection of a substance, see the section titled 'Proof presence of a substance in a sewer system'), but not sampling.

Not only toilet flushes or wastewater volumes discharged into sewers through other household appliances can be considered as wastewater pulses. In sewer networks that are not purely gravity fed, the situation is more complex. From subcatchments at elevations lower than the STP, the wastewater is collected in pump sumps. From there, lift stations pump the wastewater in rising mains to higher levels: either pressurized from the lift station to the STP or only over short distances from where the wastewater again flows via gravity towards the STP. Often pumps are operated intermittently. The pump sump fills up and, once a certain level is reached, the pump starts and empties it. This volume is much bigger than an individual toilet flush but may still be a very small fraction of the total influent to a STP. If relevant amounts of the substance of interest are contained mainly in the wastewater volume from such pump events, the number and duration of pumping cycles determine the required sampling interval. This also holds true for industrial discharges that are often released in batches.

Most sewer networks consist of both gravity-fed and pressurized pipes. Despite sharing some common characteristics, each combination of investigated substance and sewer network may be a more or less unique situation. Therefore, three different approaches exist to identify the appropriate sampling interval, which are briefly described below.

Model-based approach

This approach makes use of *a priori* knowledge on the system and substances under investigation. A procedure to perform a model-based determination of the adequate sampling frequency is described in detail in [3,11]. It requires the collection of a minimum of data on catchment characteristics, wastewater production and consumption or sales data of substances under investigation. Usually, these data need to be obtained from experts operating the wastewater systems. A questionnaire to assist you in the collection of relevant data for your catchment can be found in the supplementary material of [12]. The software package to calculate different scenarios and determine the appropriate sampling frequency or retrospectively estimating the sampling uncertainty is available online [101].

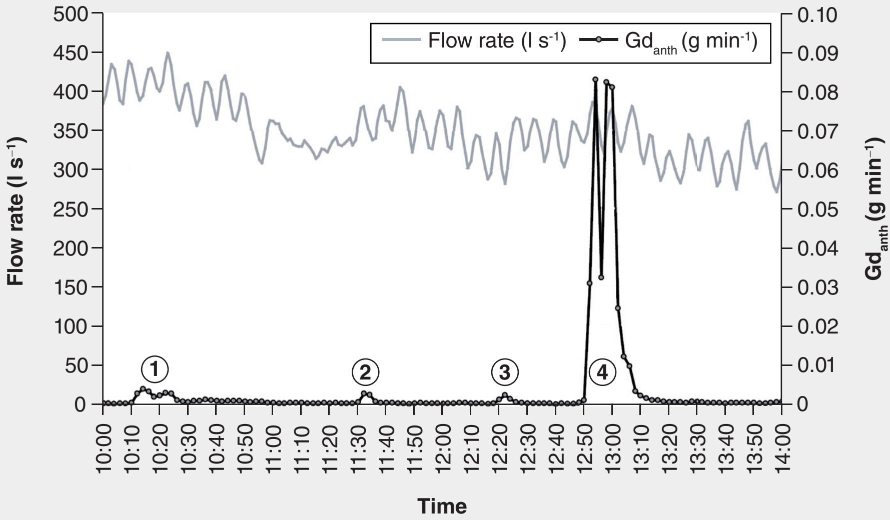
Experimental approach

As outlined in the guidance on the design of wastewater sampling programs by the International Organization for Standardization, "The times and frequencies of sampling in any programme can be properly decided only after detailed preliminary work, in which a high sampling frequency is necessary" [2]. In sewers (i.e., from the effluent of a household or any other building downstream to the influent of a STP), the concentrations and loads are expected to be highly variable. From previous investigations, 'a high sampling frequency' in 'detailed preliminary work' implies sampling intervals of 2 min or even less. This depends on the initial pulse duration at the point of discharge, flow distances and effects of dispersion [13,14]. An example is charted in **Figure 7.4**. To cover a few hours, this approach requires the collection of hundreds of samples, which all need to be analyzed individually. A few hours may or may not be representative for the variation throughout an entire day or on another day. Therefore, this approach is only applied in very specific situations in which time series must be obtained at high temporal resolution for a meaningful statistical evaluation of short-term variations. For all other situations, samples may be collected at such short intervals but can be pooled over time periods relevant for the research question to minimize analytical effort (average concentration).

Be-on-the-safe-side approach

If both previously described approaches imply too much work, there is this third approach. It suggests applying precautionary short sampling intervals of 5 min to a maximum of 10 min. This will allow properly accounting for most variations that can occur at the influent of a STP. It is based on a number of previously observed time series obtained with the experimental approach and results simulated with the model-based approach for different substances in different sewer networks [3,11,15].

Figure 7.4. Investigating short-term variability of wastewater constituents in the influent of a sewage treatment plant serving approximately 100,000 people: anthropogenic gadolinium as an example.



These data are taken from 28 October 2009. Circles: loads of Gd_{anth}; (grab samples at 2-min time intervals) before the fine screen. Gray line: flow rate, measured online in the effluent of the primary clarifier, slowly decreases from over 400–300 l s^{-1} over the sampling period. Short-term variations of the flow rate (~10%) are caused by the periodic cleaning of the fine screen. Therefore, these oscillations do not occur in the influent where samples were collected. The time shift of the flow signal was estimated to be less than 5 min and did not affect the sampling in the sewer and evaluation of gadolinium loads. Four distinct peaks were observed: peaks **(1–3)** contain only small amounts of Gd_{anth} and most probably originate from a patient that was treated on the day before, while the substantially bigger peak **(4)** is certainly related to a patient that was treated only a few hours before (fast pharmacokinetics).

Gd_{anth}: Anthropogenic gadolinium.

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Different sampling tasks in wastewater systems

The previous section was focused on explaining the origin of inherent variations in flows and concentrations of wastewater at the source, where wastewater is produced, how it is collected and transported to STPs. In this section, the focus is on specific tasks that researchers, operators or regulators may frequently face **(Table 7.1)**. These are concrete combinations of specific sampling locations and research or project goals. In the subsequent sections, the most critical points are highlighted and suggestions are made on how to avoid pitfalls. In general, challenges are relatively small if only the presence or absence of a compound need to be assessed. However, as soon as a more accurate quantification is desired,

Table 7.1. Possible sampling tasks within wastewater systems and degree of challenge related to this task.

Sampling tasks		Read section titled	Task
1	Taking a grab sample (also known as spot sample), because buying/operating an automated sampling device is not affordable	Grab sample	S
2	Adapt an existing analytical method to quantify a substance in a real wastewater matrix	Sample to adapt an analytical method	S
3	Obtain a time-weighted average concentration	Time-weighted average concentration	M
4	Estimate the potential sampling error when flow rate varies but samples can only be collected in a time-weighted mode	Difference between time- & flow-weighted average concentration when flow rates vary	M
5	Apply a volume-proportional sampling mode since the sampling device does not support flow-proportional sampling to obtain a 24-h composite sample	Volume- versus flow-proportional sampling	M
6	Apply a continuous flow-proportional sampling mode to obtain a 24-h composite sample	Continuous, flow-proportional sampling	XL
7	Proof the presence of substance in a sewer system (including influent of STP)	Proof presence of a substance in a sewer system	L
8	Quantify the load of a substance at the effluent of a building (e.g., hospital, industry or prison)	Quantify the load of a substance in the effluent of a building	XL
9	Quantify the load of a substance at the influent of a STP	Quantify the load of a substance in the influent to a STP	M
10	Quantify the removal of a substance in a STP	Quantify the removal of a substance through a STP	XL
11	Quantify the load of a substance in a combined sewer overflow or a separate stormwater discharge	Quantify the load of a substance in a combined sewer overflow or separate stormwater discharge/quantify the load of a substance in the effluent of a building	XL
12	Compute mass balances to assess removal in my pilot scale treatment plant	Setup a sampling scheme around a pilot-scale treatment plant	M
13	Assess diurnal variations of substances	Assess diurnal variations of pollutants	L
14	Assess or appropriately consider spatial variation	Assessing or appropriately considering spatial variations	S–XL

L: Large; M: Medium; S: Small; STP: Sewage treatment plant; XL: Extra large.

it becomes more demanding because information on flow is required. While at the influent of a STP a flow meter is typically available, the experimenters may have to install and maintain a portable flow meter themselves upstream in sewer systems (e.g., effluent of a building or combined sewer overflow). Furthermore, representatively sampling for particulate matter (suspended solids) adds another layer of complexity compared with sampling for dissolved compounds.

Grab sample

Grab (or spot) samples are typically collected manually once per day and considered as convenience sampling [16]. Conclusions drawn from the concentrations determined in a grab sample may only be valid for the very limited point in time at which the sample was taken. Generally, the grab sample does not represent an average concentration over an extended period and extrapolations on either daily or longer periods are very uncertain. Therefore, one-time grab samples are typically not suitable to reliably determine full-scale mass fluxes or identify processes over extended periods. However, if the system under investigation is such that perfect mixing over time (i.e., an extended period) can be guaranteed, a grab sample may be appropriate. Furthermore, in the case of the sampling tasks 2 and 12 (sections titled 'Sample to adapt an analytical method' and 'Setup a sampling scheme around a pilot-scale treatment plant'), grab sampling may be a valid alternative to automated (composite) sampling.

Sample to adapt an analytical method

The development and validation of an analytical method in real wastewater requires assessing the accuracy in real samples – that is, trueness (avoiding or correcting systematic errors) and precision (random errors). As this is often achieved with spiking real wastewater with known amounts of the substance(s) of interest, a few spot samples as described in the section titled 'Grab sample' may be adequate. The reader should note that the wastewater matrix may change over time (e.g., day and night, dry weather and rain events) or may be different in different locations. This may require testing different samples. The evaluation of full-scale mass fluxes is, as outlined in the section titled 'Grab sample', only valid for the snap shots in time when samples were collected.

Time-weighted average concentration

There is an inherent difference between determining an average concentration for the calculation of a mass flux (which must be flow weigthed) or an exposure assessment. To assess the average concentration that an aquatic organism is exposed to requires the determination of a time-weighted average concentration and, therefore, time-proportional samples are appropriate. Time-weighted concentrations can also be obtained with passive samplers. This is a sampling technique for its own and more details can be found in [17–19]. However, in (un)treated wastewater, exposure to aquatic organisms must rarely be assessed and samples are most often collected to quantify an average concentration for the calculation of mass fluxes, for example, which mass originates from a hospital or which mass flows into or out of a STP. Guidance on how to estimate the error when calculating a mass load from a time-weighted average concentration obtained from a stream with variable discharge can be found in the next section.

Difference between time- & flow-weighted average concentration when flow rates vary

If an average concentration for the calculation of a mass flux should be determined over a period of time with variable flow rates, samples must be collected in a flow- or volume-proportional sampling mode. If instead only a time-weighted mode can be applied, a systematic error may result depending on the extent of flow variations and depending on how the concentration profile correlates with the flow pattern. In brief, the difference can only be determined if both flow and concentration variations are known at high temporal resolution. Typically, only flow is measured at a high temporal resolution (i.e., at intervals of 1–5 min). To assess the magnitude of systematic errors we therefore assume that the concentration pattern is directly correlated with the flow pattern. This scenario can be easily calculated based on measured flow variations according to **Table 7.2**.

In the example outlined in **Table 7.2**, two time steps are considered with different flows and positively correlated concentrations (in the column titled 'System under investigation'). In the columns titled 'Time-weighted sampling' and 'Flow-weighted sampling', individual sample volumes and mass loads are computed for the corresponding sampling mode. Total volumes and total mass loads are calculated in the columns titled 'Time-weighted average concentration' and 'Flow-weighted average concentration' for both sampling modes. If concentrations are positively correlated, the mass fluxes are systematically underestimated due to the overweighting of low concentrations at low flows. In the example in **Table 7.2**, this is a factor of 0.6 (5.5/9.2). If the concentrations were negatively correlated, the systematic error would be an overestimation, for the flow variations in the example, it would be a factor of 3 (5.5/1.8). The potential systematic error in your system can easily be calculated. You will need flow measurements at high temporal resolution (i.e., 1–5 min) being representative for the period you would like to make the estimation and to assume a concentration profile, for example, directly correlated with flow or any other scenario.

Volume- versus flow-proportional sampling

In a system with variable flow rates, the flow-proportional mode is usually the best choice to determine an average concentration for applications requiring the calculation of mass fluxes (in contrast to time-weighted average concentration, see the section titled 'Time-weighted average concentration'). However, most manufacturers do not produce or sell only small numbers of devices that can be operated in a truly flow-proportional mode **(Figure 7.3)**. The reasons are: the challenge to accurately measure sample volumes proportional to the flow; and the technical implementation to operate such a device in harsh wastewater environments over extended periods without clogging, breaking or too much maintenance. If increments of volume for the volume-proportional mode are selected such that time intervals during the lowest flows are not exceeding 10 min, the volume proportional mode is a valid compromise to the flow-proportional mode in most applications **(Figure 7.3)**. In cases with repeated or extended periods of no flow, the volume-proportional sampling mode may even be superior to the flow-proportional mode (see the section titled 'Sampling mode to address variations in wastewater flows').

Continuous, flow-proportional sampling

Conceptually, this is the most robust sampling mode, as it provides a continuous side stream properly weighted to the full-scale flow and not missing any (un)expected short events [20]. Statistically, this infinite number of samples per

Table 7.2. Example on how to calculate the maximum difference/error between time- and flow-weighted average concentration based on known flow variations and assumed concentration pattern.

Time steps	System under investigation		Time-weighted sampling (20 ml independent of flow)		Flow-weighted sampling (20 ml per 1 l/s)	
	Measured F (l/s)	*C assuming C ∞ F (µg/l)*	*Sample volume (V_T = 20 ml), ml*	*Mass of substance ($M_T = V_T \cdot C$), ng*	*Sample volume (V_F = 20 ml/l/s·F), ml*	*Mass of substance ($M_F = V_F \cdot C$), ng*
dt1	1	1	20	20	20	20
dt2	10	10	20	200	200	2000
			Time-weighted average concentration $= \Sigma M_T/\Sigma V_T$ (220 ng/40 ml) 5.5 [µg/l]		Flow-weighted average concentration $= \Sigma M_F/\Sigma V_F$ (2020 ng/220 ml) 9.2 [µg/l]	

C: Concentration; F: Flow; M: Mass of substance; V: Sample volume.
See main text for more details. This calculation can easily be implemented in a Microsoft Excel (Microsoft, WA, USA) spreadsheet.

time unit is not a sample, but representing the entire stream. However, the application in (raw) wastewater is not trivial: to avoid the collection of large volumes of water, a small sampling hose must be used. Depending on site-specific characteristics, it can be difficult to avoid clogging of the sampling hose. Furthermore, due to relatively long retention times in the sampling hose and high ratios of surface (sampling hose) to water volume, biofilm may grow inside the sampling hose, which potentially alters concentrations during sampling. Therefore, this sampling mode requires almost daily maintenance: exchanging or cleaning the sampling hose to avoid the growth of biofilm and checking for clogging, among others. In addition, due to the low velocity in the sampling hose, this sampling mode is not suitable to representatively sample for particulate matter.

Prove presence of a substance in a sewer system

If a substance can be detected analytically in a sample, this is proof of presence of this substance in the (sewer) system under investigation – if contamination of the sample can be excluded. However, if the substance cannot be detected, this is no proof of absence for two reasons: first, the substance may have been present, but below the limit of detection; second, it may have been present at times that were not sampled. To overcome these problems, two somewhat laborious solutions exist. First, in order to not miss any short events, either sampling intervals typically shorter than 10 min are required (see the section titled 'Sampling interval to address concentration variations in wastewater'), or, alternatively, a continuous sampling mode. If only presence or absence of a substance needs to be assessed, the latter must not be flow-proportional. Second, if the substance of interest was present over a short period of time above the limit of quantification, it may be diluted in a composite sample and not detectable anymore. The only solution then is to analyze shorter time intervals [21]. This implies that a larger number of samples must be analyzed.

Quantify the load of a substance in the effluent of a building

This is probably one of the most challenging tasks, mainly for the following reasons: access can be difficult; a portable power supply may be required; typically there is a lack of flow measurements; and there are extremely short pulse durations (e.g., toilet flush) and high dynamics of concentrations in wastewater. Since flows and concentrations are highly variable (see the section titled 'Sampling interval to address concentration variations in wastewater') – unless there is a retention tank in the building leading to substantial attenuation and a known/

controllable flow pattern – flow must be measured for the collection of samples already. It is not sufficient to collect time-weighted samples (see the section titled 'Difference between time- & flow-weighted average concentration when flow rates vary') and multiply the average concentration with total flow (either measured or estimated from drinking water consumption making certain assumption on losses and shift of time from usage to discharge). Finally, if a flow meter can be installed and properly operated after careful calibration, the challenge will be to collect samples at time intervals as short as a toilet flush (i.e., seconds to minutes). Tracer experiments with a fluorescent dye in toilet flushes demonstrated that 90% of the mass passed the monitoring station outside the building within less than 1 min [13].

Quantify the load of a substance in the influent to a STP

The advantages onsite a STP are that flow measurements and sampling devices are typically available in an environment protected from vandalism. Nonetheless, it may be necessary to use precautionary short sampling intervals (see the section titled 'Sampling interval to address concentration variations in wastewater') or consider sampling after the primary clarifier. A tank like a primary clarifier can attenuate short-term variations. However, it needs to be noted, that primary clarifiers remove a substantial fraction of particulate matter. In addition, depending on the layout of the STP and sampling points, there may be internal recirculation streams that need to be accounted for (see next section).

Quantify the removal of a substance through a STP

Depending on the required level of accuracy, different sampling strategies should be applied [22]. For a complete assessment of mass fluxes, both liquid and solid samples must be obtained from various locations in the treatment train. The STP layout should be discussed with STP operators to sample at appropriate locations (e.g., using the routine sampling equipment of the STP or installing additional sampling devices to be able to close mass balances). It is recommended to consider the hydraulic residence time distribution [23] or to pool samples over significantly longer time frames (i.e., more than 24 h), either by physically pooling individual 24-h composite samples volume proportionally over several days, or by appropriate statistical averaging after analyses. If dynamics should be assessed for a more detailed understanding of the treatment process and/or the modeling thereof, aspects outlined in the section titled 'Assess diurnal variations of pollutants' should be considered.

Quantify the load of a substance in a combined sewer overflow or separate stormwater discharge

The predictability of the occurrence and duration of stormwater-related events, the extreme dynamics and instrumentally equipping the corresponding sites with appropriate devices make sampling for stormwater and combined sewer overflows one of the most challenging sampling tasks. Therefore, the reader is referred to Chapter 5, in which the most important task-specific aspects are covered and described in depth.

Set up a sampling scheme around a pilot-scale treatment plant

In contrast to full-scale systems, certain variables in a pilot-scale treatment plant can be controlled by the experimenter (e.g., flow rates). Although this does not make sampling a trivial task, it facilitates certain aspects. One of the most important aspects is to have a realistic idea of timescales that are relevant for the transformation and removal processes under investigation. Grab samples at suitable time intervals may be a good choice for batch experiments. In larger flow-through plants, composite sampling should be considered depending on the expected variability and mixing over time. Furthermore, reactor volume and design should be taken into account to define the appropriate sampling location(s) in a compartment.

Assess diurnal variations of pollutants

Historically, for most applications covered in the section titled 'Different sampling tasks in wastewater systems', samples over 24 h are the most common ones. This is mainly for practical reasons (i.e., limited storage volume and the need for preserving samples). To assess annual, seasonal or weekly variations, the averaging or analysis of daily samples is adequate. A higher temporal resolution is needed for more detailed evaluations of sources and dynamics. As a consequence, composite samples are often considered inappropriate as they only provide average concentrations. So what should you do if you, for example, want to assess diurnal variations at a temporal resolution of 1 h? In view of the expected high dynamics described in the section titled 'Sampling interval to address concentration variations in wastewater', you should certainly not collect a grab sample every hour. Instead, you should collect composite samples over 1 h. It should be noted that the required sampling interval for a composite sample shorter than 24 h is shorter than that for a 24-h composite sample, if the same accuracy should be achieved [15]. In summary, the length of the composite sample duration is determined by your research question (e.g., 1 or 2 h for assessing diurnal variations), and the appropriate sampling interval to collect individual samples forming a composite sample in a representative manner, is a function of the prevailing short-term variation and composite sample duration [13].

Assessing or appropriately considering spatial variations

Spatial variations may occur or be relevant at completely different scales. They can be of interest at large geographic scales (i.e., between two different STPs in different cities) or within the cross section of a sewer at a given location (e.g., when sampling for particulate matter). The latter is mainly of interest if concentrations or loads of particulate matter *per se* are of interest or substances that are associated with particulate matter. It then depends furthermore on the particle sizes and the distribution thereof (e.g., [24]). For dissolved compounds, it is a reasonable assumption that they are well mixed due to turbulences in sewer systems. However, if two trunk sewers are combined at the influent of a STP, the mixing of dissolved compounds also depends on the geometry and hydraulics of the confluent (mixing length; **Figure 7.5**). In larger structures within STPs (e.g., primary clarifier or activated sludge tanks), or in wetlands, mixing of the influent, short cut flows or dead volumes must be considered for a proper assessment [25–34].

Figure 7.5. Confluent of two trunk sewers at the influent of a sewage treatment plant.

These two streams may not be completely mixed until after the primary clarifier. The difference between the left and right is visually apparent, as the right sewer also collects wastewater from an abattoir, not only municipal wastewater. Without the temporarily reddish color, this may not have been noted although the concentrations of different compounds may in fact have been very different left and right. Photograph is courtesy of Christian Abegglen (Entsorgung + Recycling Zürich, Switzerland).

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Summary.

- The effort that needs to be invested into sampling for wastewater depends on the desired accuracy related to the goal (fit-for-purpose). As outlined with numerous examples, this effort can range from very small to extremely high.
- Wastewater variations of flow and concentration in full-scale systems are not under the control of the experimenter. Therefore, these variations must be either assessed before the monitoring campaign or a sophisticated sampling system must be used, which can account for any (unexpected) flow and concentration variations.
- Calculating mass fluxes requires measuring both average concentrations and total wastewater volumes over the timespan relevant for your research question. Furthermore, flow measurements must be available in real time during sampling to control a flow- or volume-proportional sampling mode. This is necessary to obtain unbiased average concentrations when flow is varying considerably within the relevant time span (e.g., systematic diurnal variations).
- Quantifying sampling uncertainty with a sampling proficiency test is typically more demanding than trying to reduce it to a minimum by applying a flow-weighted sampling mode operated at precautionary short sampling intervals.
- Flow-through tanks, in which wastewater is well mixed, lead to an attenuation of concentration variations but will not affect hydraulic peaks. During dry weather such tanks are usually not in operation in sewer systems. Hence, the intermittently discharged water packets at the source (e.g., toilet flush) will still be of relative short duration at the influent of a sewage treatment plant. Only in the effluent of tanks in the sewage treatment plant will these variations be attenuated allowing longer sampling intervals to be appropriate.

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