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Posted Date: 22 February 2024

doi: 10.20944/preprints202402.1266.v1

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Can Short-Term Online-Monitoring Improve the Current WFD Water Quality Assessment Regime? Systematic Resampling of High Resolution Data from Four Saxon Catchments

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Abstract: The European Union Water Framework Directive (2000/60/EC; WFD) aims to achieve a good ecological and chemical status of all bodies of surface water by 2027. The development of an integrated guidance on surface water chemical monitoring (e.g. WFD Guidance Document No. 7/19) has been transferred into national German law (Ordinance for the Protection of Surface Waters, OGewV). For the majority of compounds, this act requires a monthly sampling frequency to assess the chemical water quality status of a surface water body. To evaluate the representativeness of the sampling strategy under the OGewV, high-frequency online monitoring data is investigated under different sampling scenarios and compared with current, monthly grab sampling strategy. About 23 million data points were analyzed for this study, three chemical parameters (dissolved oxygen, nitrate-nitrogen, chloride concentration) and discharge data were selected from four catchment of different sizes ranging from 51391 km² to 84 km² (Elbe, Vereinigte Mulde, Neiße and two stations at Lockwitzbach). In this paper we proposed short-term online-monitoring (STOM) as a sampling alternative. STOM considers the placement of online sensors over a limited duration and return interval. In general we: (I) compare the results of conventional grab sampling with STOM, (II) investigate the different performance of STOM and grab sampling using discharge data as proxy for analyzing event-mobilized pollutants and (III) investigate the related uncertainties and costs of both sampling methods. Results show, that STOM outperforms grab sampling for parameters where minimum/maximum concentrations are required by law as the probability to catch a single extreme value is higher with STOM. Furthermore, parameters showing a pronounced diurnal pattern, like dissolved oxygen, are also captured considerably better. The performance of STOM showed no substantial improvements for parameters with small concentration variability, as nitrogen-nitrate The analysis of discharge events as a proxy parameter for event-mobilized pollutants proved that the probability of capturing samples during events is significantly increased by STOM.

Keywords: Online monitoring; Sampling; Water Framework Directive; Event Analysis; Water Quality; Events

1. Introduction

The European Parliament and the Council established a framework for community action in the field of water policy called Water Framework Directive (WFD) in 2000, aiming at maintaining and improving the aquatic environment. The goal of the third implementation cycle (2022-2027) is that the member states achieve a good ecological, hydro-morphological and chemical status of their water bodies by 2027. Regulations for monitoring efforts are based on article 8 and Annex V of the WFD, translated into German law, found in § 10 and Annex 10 of the Ordinance for the Protection of Surface Waters, OGewV (Oberflächengewässerverordnung). Detailed explanation for the implementation and procedures can be found in a practitioners guideline [1]. River Basin Management Plans and Programmes of Measures are required, where decisions on improving the status are based on monitoring results of water quality parameters (chemical) as well as biological and hydro-morphological (ecological) parameters in

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combination with supporting quality elements (e.g. physico-chemical parameters). This study focused on the assessment of the chemical status, for which the WFD developed a guidance for water chemical monitoring systems to support the design of a comprehensive monitoring network (Guidance No. 19, 7; [2,3]). The WFD Article 7 distinguishes the monitoring objectives as surveillance monitoring, operational monitoring and investigating monitoring respectively. Surveillance monitoring should identify the status of the water body, recognize long-term changes and provide guidance for future monitoring campaigns. Operational monitoring surveils waterbodies, which fail or are at risk of failing their environmental objective as well as to verify the effectiveness of measures. Investigative monitoring intends to identify the reason for unknown degradations of the water quality, e.g. during accidents leading to leakage or spills of pollutants.

Researchers have identified and summarized several weak points in the implementation of the WFD monitoring strategy [5–8]. In this work we focus on sampling strategies. The Annex V 1.3.4 of the WFD, suggests a sampling frequency for physico-chemical quality elements of three months, except for priority substances which should be sampled on a monthly basis. However, those intervals serve only as orientation values. The member states can adapt intervals "based on technical knowledge and expert judgement", as long as "sufficient data for a reliable assessment of the status of the relevant quality element" is provided (Annex V, 1.3.4. Frequency of monitoring, WFD). Exact values for reliability are not defined, however certain intervals are suggested by the WFD. Furthermore, "frequencies shall be chosen so as to achieve an acceptable level of confidence and precision", and the achieved confidence and precision should be stated in the river basin management plan. According to the WFD, the German OGewV defines a sampling frequency of four up to 13 times per year for physico-chemical parameters and monthly sampling for chemical parameters in rivers. To our understanding, these frequencies are mainly a compromise between the practical feasibility of the executing authorities and the vast amount of water bodies that have to be monitored. Whether current sampling regimes provide a reliable assessment of the water quality status is under discussion. According to Carstensen (2007) [9] the precision of classification depends on (1) the confidence level chosen, (2) the magnitude of random variation, and (3) the number of observations. He calculated error rates up to ± 50–70% on weekly datasets and suggested the need to use up to 500 observations for nutrients and phytoplankton measurements to characterize a water body and to ensure a precise classification. This suggests substantially higher required monitoring efforts than the ones envisaged in WFD. Previous research showed that the required minimum sampling frequency depends on sampling location [10,11], the analyte [11,12] and temporal variability [9,13–15]. Skeffington et al. (2015) [15] demonstrated the difficulties related to a reliable assessment of the five quality classes with a systematic resampling of a high temporal resolved time series where "In some cases, monthly sampling for a year could result in the same water body being assigned to three or four of the WFD classes with 95% confidence, due to random sampling effects. In the most extreme case, the same water body could have been assigned to any of the five WFD quality classes."

We want to demonstrate two applied limitations of the current sampling regime by comparing grab samples with high resolution online monitoring data:

- Limitation 1: Grab sampling is usually carried out by staff of the governmental environmental agencies, employed with regular working hours. Thereby, it is rare to have nighttime samples. Especially for parameters that have a diurnal pattern like dissolved oxygen (DO), pH or NO_3-N only daytime sampling introduces systematic errors and leads to an over- or underestimation of the true value [16]. For example, Minaudo et al. (2015) [17] showed that the diurnal amplitude for the DO concentration can be of several mg/l during summer, especially for eutrophic rivers. As DO is highest during light periods, those rivers would be categorized better than they are [11].
- Limitation 2: (Heavy) rainfall events cause discharge higher than baseflow, mobilizing particles and particle bound nutrients/pollutants within the catchment or the stream bed. Such events may cause considerable variation in the concentrations of particle-bound

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compounds. They often account for the majority of the annual load of pollutants in large and also smaller river systems [18–20]. Depending on many factors including land use, season, length of the antecedent dry weather period and others, they can reach considerable concentrations and loads in creeks and streams [21,22]. Rabiet et al. 2010 showed that more than 89% of the total load of the herbicide diuron was mobilized during storms in August 2007; Glaser et al. 2020 and Zhou et al. 2022 obtained similar results for the load mobilization of PAHs and pesticides [19,23,24]. Particle mobilizing events occur rarely and with a short duration, which reduces the probability to capture them with a monthly grab sampling regime. Skarbøvik et al. (2012) [25] analyzed the effect of sampling frequency of suspended sediments, on the load calculation and showed that weekly sampling resulted in error rates as high as 70%, monthly sampling could yield errors up to 400%. However, other studies, e.g. by Torres et al. (2022) [26] indicated that even constituents easily transported by water (such as sediments and nutrients) require more than 50 samples/year to provide a small error (< 10%, 95% confidence interval).

In comparison to research on the effect of sampling frequency focusing on a load calculation [12,27–31], the effects of frequency on regulatory parameters are underrepresented [9,11,14]. We want to address this research gap in our study and evaluate alternatives to the current sampling strategy that could reduce monitoring costs and efforts and increase information on critical ecologic conditions in streams. Therefore, we propose "short-term online-monitoring" (STOM) as compromise between the current grab sampling regime and a continuous monitoring station. According to Capodaglio and Callegari (2009) [32] online monitoring is usually defined as the unattended sampling, analysis and reporting of a parameter. It produces a sequence of data at much greater frequency than that permitted by manual (grab) sampling and it allows real-time feedback for either process control, water quality characterization for operational or regulatory purposes, and alert/alarm purposes. Unlike discharge, online monitoring for river water quality is rarely used by governmental for monitoring purposes, and mainly focus on big river catchments. Besides the costs for sensors and their maintenance, limitations in the available set of parameters are reasons for the infrequent use. We propose STOM as an alternative to grab sampling. STOM considers the installation of a continuously monitoring sensor only for defined intervals and for a limited duration. To simulate STOM, we selected four parameters (i.e. dissolved oxygen, nitrate-nitrogen, chloride and discharge) and processed highly resolved data from five monitoring stations at four watersheds of different sizes in Saxony. The parameters were chosen due to different mobilization, transport and reactivity properties. DO has a strong diurnal and seasonal pattern, Nitrate also has a pronounced seasonal amplitude mobilized from different sources, while chloride is considered as a non-reactive geogenic background signal. Discharge events were selected from the flow data and used as a proxy signal for event mobilized compounds.

2. Materials and Methods

Catchments and monitoring sites

The data evaluated in this study originates from five monitoring stations in Saxony, Germany (Figure 1 and Table 1). The large (sub-) catchments of Elbe (51 387 km²), Mulde (6207 km²) and Neiße (1418 km²) are monitored by the Saxon State Operational Agency for Environment and Agriculture (BfUL), data was provided by the Saxon State Office for the Environment, Agriculture and Geology (LfULG). The same agencies are also in charge of the grab sampling program to comply with the German translation of the WFD. At Lockwitzbach (84 km²) there are two stations operated by the Chair for Urban Water Management of TU Dresden [33]. The stations are about 6 km apart from each other, one is located before the stream reaches the city of Dresden (MS6, upstream Dresden), the other shortly before the confluence with Elbe (MS4, downstream Dresden). According to the results of the latest river management plan period, all four waterbodies fail to a good chemical status, especially due to the exceedance of annual average concentration limits of total-phosphorus, Mercury, Polycyclic Aromatic

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Hydrocarbons [34].

Table 1. Station and catchment characteristics, land cover data taken from CORINE Land Cover 2012 [35], baseflow index (BFI) calculated from sub-hourly discharge data.

Station	Catchment	Drainage area [km²]	Land Cover Type (%) Settlements	Agriculture and pastures	Forest	BFI
MS6	**Lockwitzbach**	**73.3**	9.2	72.8	18.0	0.71
MS4	Lockwitzbach	84.0	18.0	67.5	14.5	0.70
Görlitz	Lausitzer Neisse	1632.7	13.0	51.0	35.0	0.81
Bad Düben	Vereinigte Mulde	6169.9	11.8	55.7	32.0	0.78
Schöna	Elbe	51391.0	6.4	54.9	37.6	0.77

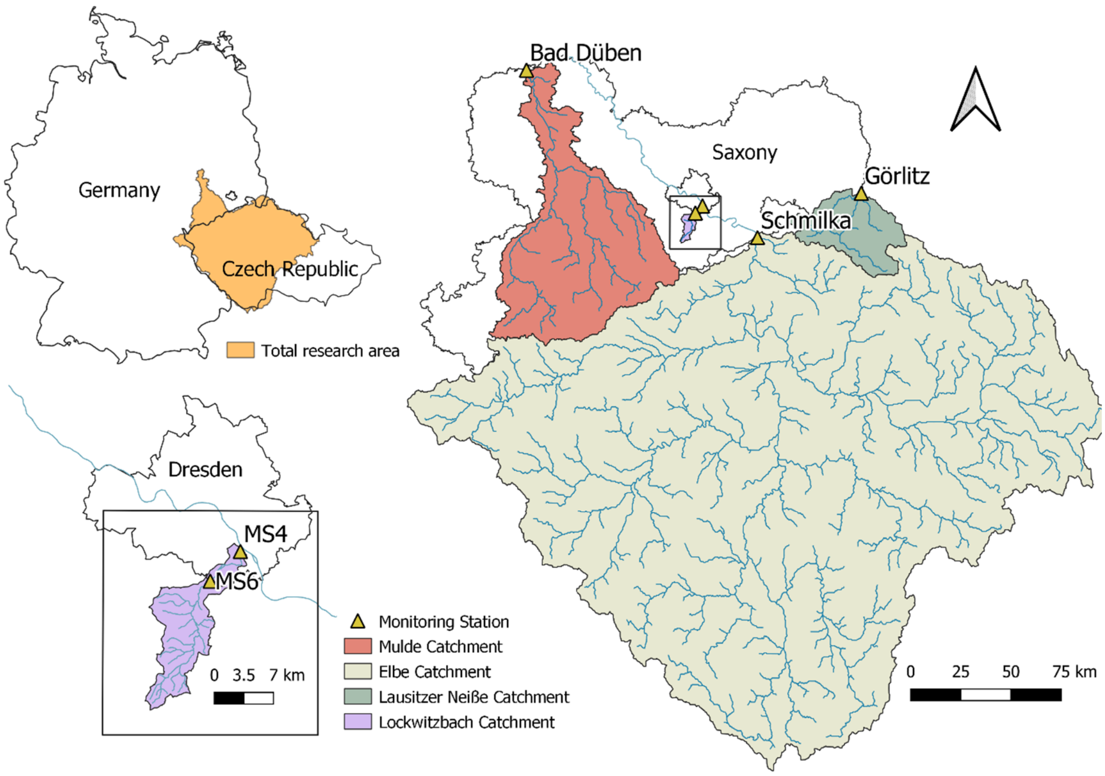

Figure 1. Catchments of the investigated streams and location of the monitoring stations.

Water quality and discharge data

The study evaluates the concentrations of nitrate-nitrogen (NO_3-N), dissolved oxygen (DO) and chloride (Cl), recorded with a temporal resolution of 10 min. nitrate-nitrogen was measured by adsorption spectrometry (Nitratax, Hach & ColorPlus 3 Nitrat, Sigrist), dissolved oxygen by luminescence (FDO 700 IQ, WTW). Chloride concentration was derived by a linear model from grab sample chloride concentration and electric conductivity using an Ordinary Least Squares approach (Appendix, Figure 10). Electric conductivity is measured by Direct Current method (TetraCon 700 IQ, WTW).

At Lockwitzbach we (Chair of Urban Water Management) measure dissolved oxygen with

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a LDO sc probe (Hach), nitrate-nitrogen was measured optically (spectro::lyser, s::can) and furthermore with an ion-selective probe (ANISE sc, Hach), which also records chloride at an interval of 10 min. For NO_3-N we mainly used the optical measurement results from the spectro::lyser and filled gaps with ANISE sc data. Mean yearly and seasonal concentrations of the five monitoring stations and their standard deviation and diurnal ranges can be found in Table 2.

Table 2. Mean concentrations, calculated from the entire dataset with standard deviation during summer (May-September) and winter (October-April) and during day and night (from 6 am to 6 pm).

	NO_3-N [mg/l]				Cl [mg/l]				O_2 [mg/l]			
	Summer		Winter		Summer		Winter		Summer		Winter	
	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night
Schmilka / Elbe	3.1±0.8	3.1±1.1	4.9±1.1	4.9±1.1	41.4±8.4	40.7±10.5	40.6±10.5	40.6±10.5	9.4±1.8	9.3±1.3	11.8±1.3	11.8±1.2
Bad Düben / Mulde	2.8±0.6	2.8±0.9	3.6±0.9	3.6±0.9	29.7±4.5	29.4±4.4	30.1±4.4.	30.5±4.4	8.3±1.8	8.5±1.5	11.7±1.6	11.7±1.6
Görlitz / Neiße	2.4±0.5	2.4±0.7	3±0.7	3±40.7	37.2±10.9	36.8±10.4	34±10.4	33.5±10.6	8.4±1.1	8.1±1.3	11.8±1.3	11.6±1.3
MS6 / Lockwitzbach	5.8±0.9	5.7±2.3	7.9±2.3	7.8±2.3	44.7±9.1	44.7±12.2	41.4±12.2	41.3±12.3	9.7±0.8	9.2±1.2	12.1±1.2	11.7±1.3
MS4 / Lockwitzbach	4.7±1.4	4.6±2.5	7.5±2.6	7.5±2.5	44.6±9.4	43.7±12.3	39.9±12.3	39.6±12.3	10.5±2.3	7.7±1.9	12.9±1.9	11.2±1.7

Discharge data was selected from flow gauges at the respectively shortest distance to the water quality stations. At Elbe, Vereinigte Mulde and Lausitzer Neiße, the BfUL operates flow gauges not further away than 7 km from the water quality stations. At Lockwitzbach flow rates were established at the monitoring sites. Monitoring periods of the water quality recordings were between five years (Lockwitzbach) to ten (Mulde) and 14 years (Elbe, Neiße). On average, seven percent of the three water quality parameters (nitrate-nitrogen, chloride and dissolved oxygen) were missing every year. The recorded discharge data is more complete with of 2% missing data per year. Highest gap was found for MS4 in 2019 with 16% of missing data. About 23 million measurement points were evaluated, the length of the datasets as well as its completeness are shown in Figure 2.

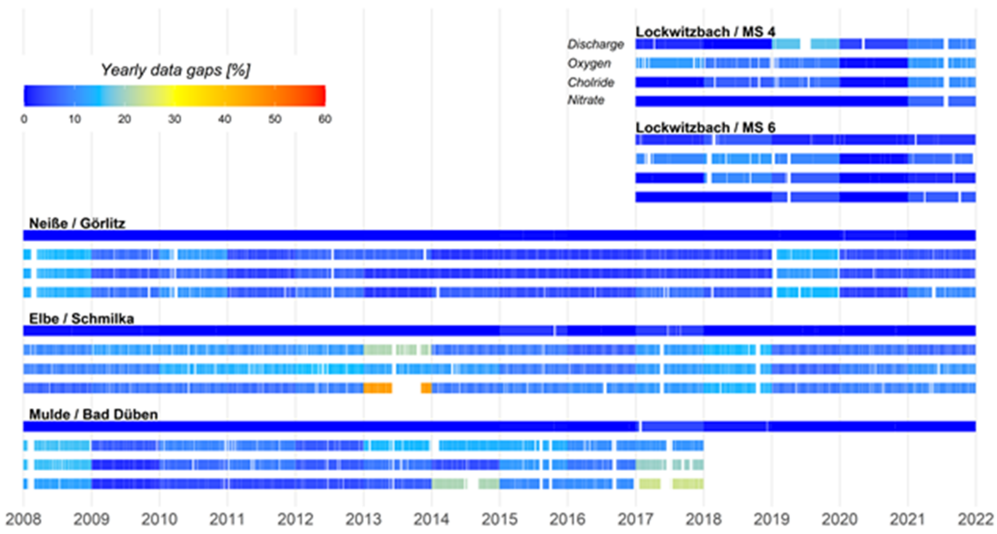

Figure 2. Data availability of the investigated parameters.

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The importance of the investigated parameters as well as the thresholds for the classification for a waterbody are stated in §5 and §6 OGewV referring to the appendices 3,4,7 and 8. Dissolved oxygen and chloride are considered as physico-chemical components. These parameters serve as supporting parameters for defining the ecological status of a waterbody, while the biological and chemical components are the main criteria. Based on the river type the threshold concentrations for the mean annual minimum dissolved oxygen concentration varies between 9 mg/l (Lockwitzbach) and 8 mg/l for all other investigated streams to reach a very good status; for a good status 8 / 7 mg/l are required. The annual mean of the chloride concentration needs to be equal or below 50 mg/l for a very good status and below 200 mg/l for a good status at all river types. The mean annual nitrate concentration threshold is given in Appendix 8 with 50 mg/l NO_3 (11.3 mg/l NO_3-N). The parameter is among 46 compounds that are used to define the chemical status. If one of them is exceeding the environmental quality standard the waterbody fails a good status.

The "real or reference concentrations" were calculated according to the guidelines of the OGewV, which states different ways to calculated the concentrations for classification: The yearly mean value of nitrogen-nitrate is required, similarly the arithmetic mean value for chloride should be taken, however for chloride a series of three consecutive years can be used for the calculation for a mean value. The same applies for dissolved oxygen, but with the mean of a window of three consecutive yearly minimum values. This allows to reduce the effect of outliers on the water quality status. For simplification, we omitted this rule addressing the three-year-window except for the DO concentrations at Lockwitzbach / MS4, where we observed close to zero DO concentration in two years, respectively 2018 / 2020. In 2018 there was a severe CSO event that lead to close to zero DO concentration that lasted for about half an hour. On six days in August 2020 discharge in Lockwitzbach dropped to almost zero and we observed anoxic condition during night hours.

Modelling of the sampling strategies

With the previously described data was systematically subsampled to evaluate the following sampling strategies:

Modelling of grab sampling

The OGewV requires quarterly to monthly grab samples for determining physico-chemical parameters and monthly sampling for priority compounds of the OGewV listed in appendix 8. Based on this and the information on sampling routine by the LfULG we decided to randomly sample the time series with a frequency of once every month, on working days and between 9 am and 5 pm.

Modelling of short-term online-monitoring - STOM

In contrast to grab sampling, STOM obtains continuous monitoring data in defined, limited intervals and for limited durations. The duration of the STOM application was selected between one and 21 days (the term *sensor application duration* is used for this dimension in the following). For application intervals the limits were set from once per month to once every six months (the term *return interval* is used for this dimension in the following). For these time series we applied the previous explained regulations according to the OGewV guidelines. We varied the two parameters (application duration & return interval) and obtained a 6x21 matrix for every year and parameter at a monitoring station.

Modelling of sampling during events

To find out, weather STOM or grab sampling was carried out during a high discharge event, we had to carry out an event selection. Therefore, a base flow time series was calculated by a graphical method, based on the work of Gustard et al. (1992) [37] and events were subsequentially selected by flow being 10% higher than the calculated baseflow. In general there are many different approaches to identify base flow (for an overview on base flow calculation e.g. [38]). We used a graphical method as for the event selection since it provides a precise in time selection of events.

Gustard et al. (1992) developed his method for daily resolution discharge data, however we applied it to data with a high temporal resolution (5 and 15 mins). Therefore, we varied the window widths used to calculate the daily mean values in way that events with a duration below one day could be also separated from baseflow. That was of higher importance for smaller catchments, where event durations are considerably shorter than in bigger watersheds like Elbe. Hence, depending on the size of the catchment, we used shorter windows widths to calculate the mean values: between four and 24 hours in hydrological summer and 12-36 hours in hydrological winter, instead of one day window. The following procedure is similar to Gustard et al. (1992) who calculated the local minima of five-day non-overlapping consecutive periods and identified subsequently turning points by restricting increases by gradient filtering with the previously calculated, higher resolved minima-time series. These turning points are connected by linear interpolation, they form a base flow hydrograph. To identify events, we split the time series into hydrological winter and summer. We defined thresholds of different parameter sets considering: 1) events having a discharge 10% higher than base flow; 2) minimum duration and 3) minimum discharge difference between event minimum and maximum (e.g. Figure 3).

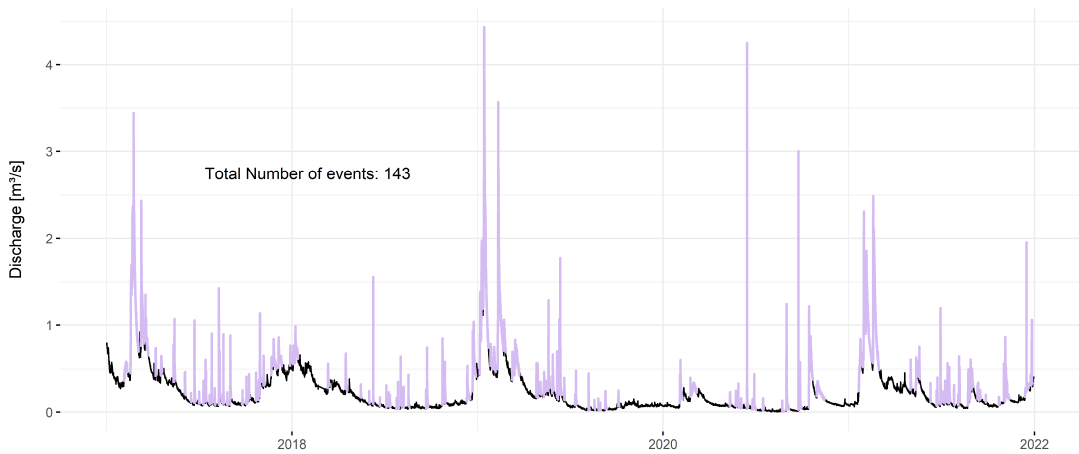

Figure 3. Results of event detection algorithm at Lockwitzbach - MS6.

To compare STOM and grab sampling strategies we simulated 500 sampling realizations and calculated the reference concentration according to the OGewV guideline. The Performance is then defined as the logarithmic quotient of the sampling accuracy of STOM and grab sampling. The sampling accuracy was calculated using the absolute difference between the "real concentration" and the model results of STOM and grab sampling (compare formula in Figure 4). We log transformed the values to indicate whether STOM or grab sampling was yielded better results, e.g. Negative Performance indicates that grab sampling achieves results closer to the "real concentration" than STOM. To identify an unambiguous threshold for the parameter settings that lead to a surpass of the performance of STOM over grab sampling a model was fitted to the data and used to identify the point where the Performance it close to zero (indicating a similar result of STOM and grab sampling). For the model a linear relation between Performance and application duration was identified, for return interval and Performance the values followed a logarithmical trend, regression was done using the least square method and yielded a mean coefficient of determination (R^2) of 0.9.

For the discharge signal we used the number of samples that were taken during an event and compared this with the amount of total detected events every year. All calculations were carried out with R, functions and scripts can be found on github (see credentials) [39].

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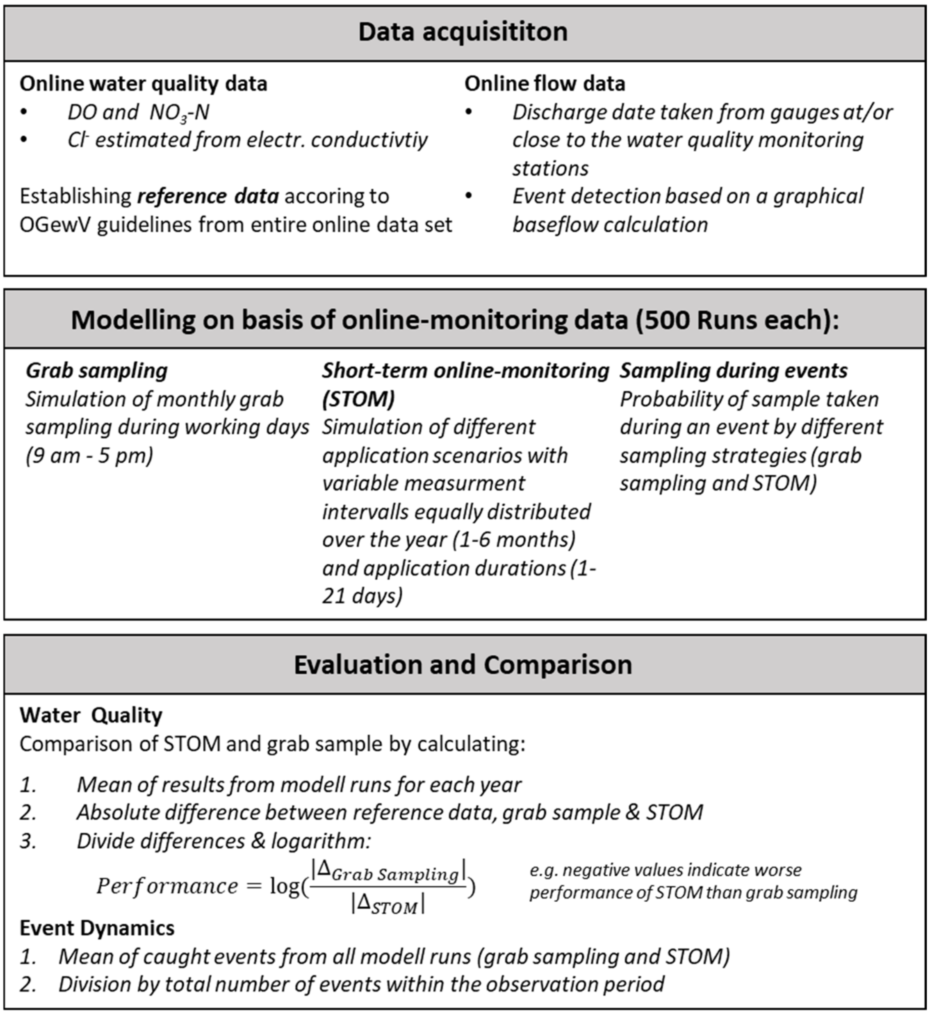

Figure 4. Overview of schemes for comparing different sampling approaches.

Uncertainty of sampling strategies

Similarly to the Performance-comparison, we analyzed the uncertainty of both sampling strategies by their relative standard deviation. The modelling results of both STOM and grab sampling for every station and parameter were used. Therefore, we took the average of the yearly standard deviations divided by the yearly mean concentration. The comparison was carried out by the quotient of the relative standard deviations of STOM and grab sampling. A value greater than one indicates that conventional sampling has a smaller standard deviation, whereas a value below one indicates the opposite. In a similar way to the pervious comparison of the results from STOM grab sampling a log-linear regression was fitted to identify the turning point where the quotient is below one.

Cost Calculation

In order to show how STOM behaves from an economic perspective, we performed a rough cost estimation. As an example, we used the previously analyzed water quality parameters at the five monitoring sites. We met the following assumptions to estimate yearly monitoring costs:

Grab sampling:

- Grab sampling is assumed to be carried out 12 times per year
- 8 € per sample for the analysis of NO_3-N and Cl, O_2 is measured on site with a hand-held for 642 € per year (4500 € over seven years depreciation period)
- Driving costs of 4.5 € per site and 240 € personnel costs per sampling day (8 hours with an hourly wage of 30€)

STOM:

- Intervals for STOM are varying on the different application scenarios
- Multi Parameter Probe (15 000 €) with a depreciation period of seven years (2143 €/year). Number of sensors is depending on return intervals and duration of sensor application.
- Driving and personnel costs based on the values of grab sampling but multiplied by two, since the sensor needs to be installed and picked up.

3. Results

Water quality parameters

For a general overview of the comparison between STOM and grab sampling, the mean of all yearly Performances (according to Figure 4) were calculated and concluded as a heat map. Results for single years can be found in the supporting material. The parameters were chosen from the 6 x 21 matrix (1-6 months return interval and 1-21 days of sensor application duration) and selected to favor a lower interval of return interval over the duration of the sensor application. For example, if a similar Performance of zero was achieved for either a 3 month return interval and 20 days of sensor application or for 2 month return interval and 2 days of sensor application the first parameter set was chosen (as a longer application is easier feasibly than a regular installation of the sensor). The predicted intercepts, or break even points, where STOM becomes more accurate than grab sampling, are marked in the following graphs with a black frame. Differences between empirical (number in the box) and fitted intercepts of the Performance index are caused by deviation between the mixed linear regression model and resampling data. The results of the five monitoring stations are sorted by parameter and catchment area:

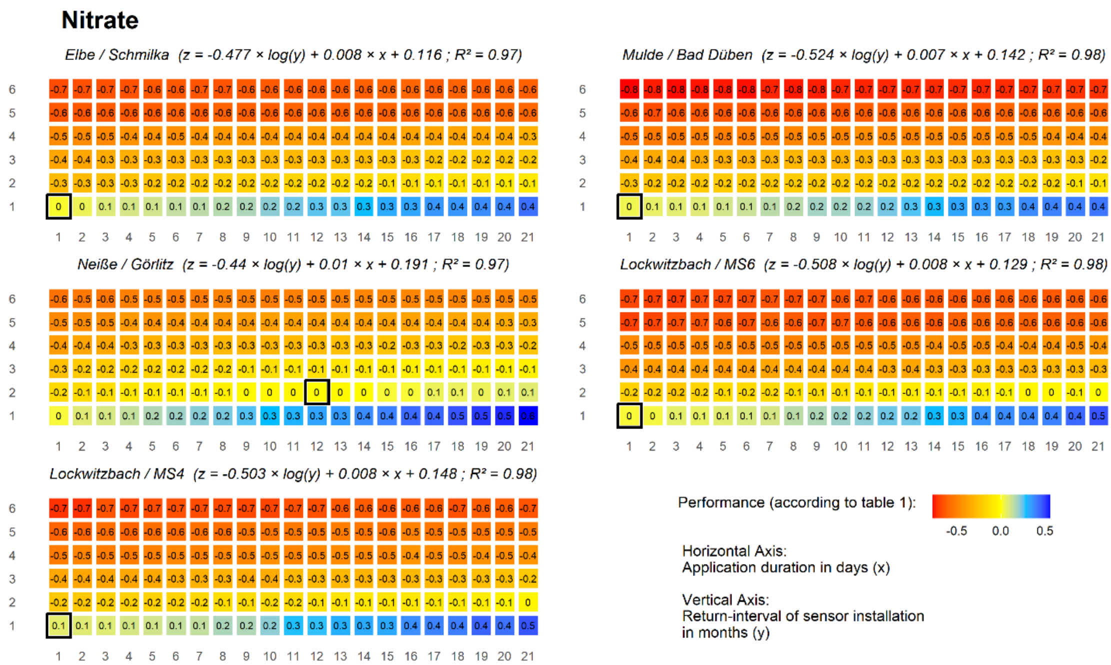

Figure 5. Comparison of STOM and grab sampling for nitrogen-nitrate, values were calculated according to *Figure 4*, break even points from regression model are highlighted with black frames.

For nitrogen-nitrate monthly grab sampling lead to 3.0% mean absolute deviation or assessment error from the complete data set. Mean grab sampling errors were similar among all catchments ranging from 2.5 to 3.5%, with a tendency to get reduced by increasing watershed size.

As Figure 5 concludes, STOM outperformed grab sampling at similar duration-interval combinations in all catchments. Return intervals were monthly or bi-monthly, whereas a duration of one day sufficed in four out of five catchments. For all catchments, the resampling-

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based Performance yielded similar or better Performance with monthly one-day STOM.

The coefficient for STOM sampling duration were extracted from the mixed linear regression model and ranged from 0.007 to 0.01, with lowest value at Mulde river and highest at Neiße river, the two intermediate size rivers in the study. This indicates a systematic improvement of the relative STOM Performance with increasing sampling duration. Notably, the Performance improvement is more pronounced at shorter return intervals. The coefficient of log-transformed sampling interval ranged from -0.44 to -0.52, again with Mulde (lowest) and Neiße (highest) defining the range. Hence, for Mulde river STOM Performance appeared more sensitive to return interval while for Neiße sampling duration was more decisive.

Results of STOM for single years did also not exceed a return period of two months, only in 2013 Neiße STOM showed the best outcome, that is indicated by the earliest break-even point among all stations with a return interval of three months and an application duration of 15 days.

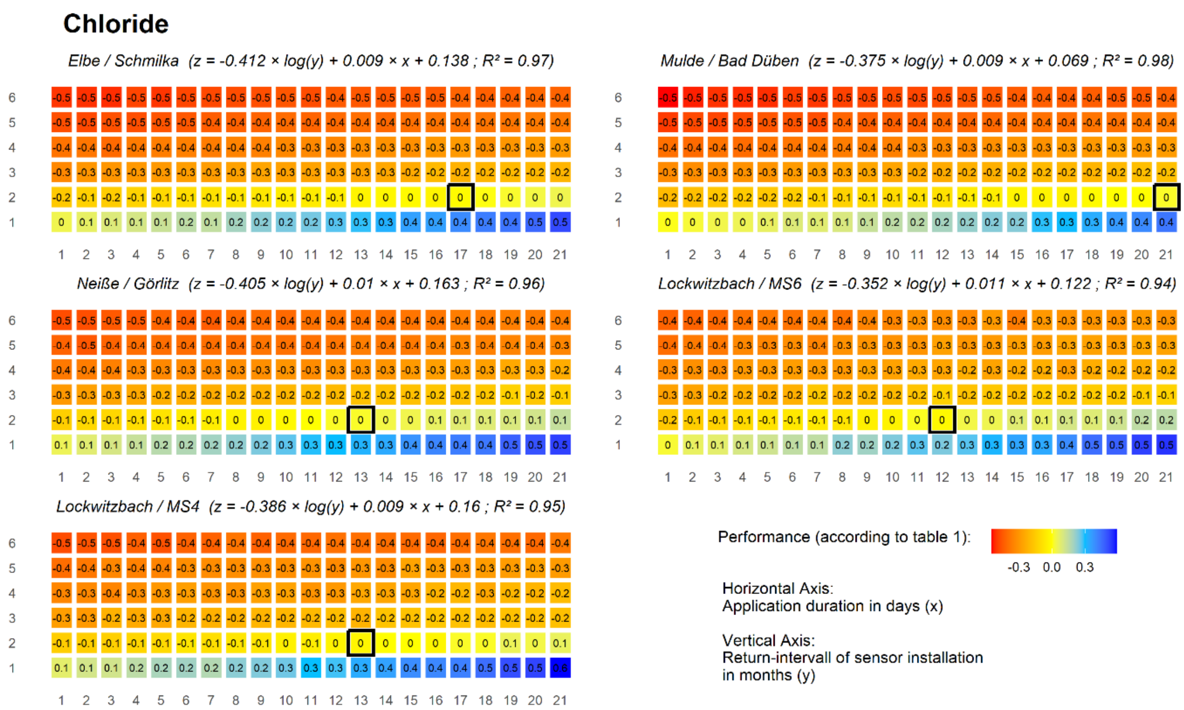

Figure 6. Comparison of STOM and grab sampling for chloride, values were calculated according to *Figure 4*, break even points from regression model are highlighted with black frames.

The overall mean values for chloride did exhibit similar patterns as nitrogen-nitrate. Monthly grab sampling lead to 3.6% mean absolute deviation or assessment error from the complete data set. While the smallest catchment (Lockwitzbach, Neiße) showed the highest mean absolute errors (4.2% & 4.3%) the error margin got reduced towards bigger rivers to 3.5% at Mulde and 2.0% at Elbe.

For all catchments a return-intervals of two months provided better Performance of STOM than grab sampling. Application durations at the break-even point, ranged between 12 to 21 days (Figure 6). Combinations of monthly one-day sampling or bi-monthly 15-day sampling always outperformed grab sampling.

The coefficient for STOM sampling duration ranged from 0.009 to 0.011, with lowest value at Mulde river and highest at Lockwitzbach / MS6 river. Indicating a slightly stronger improvement of the relative STOM Performance with increasing sampling duration, as compared to nitrate results. The coefficient of log-transformed sampling interval ranged from -0.35 at Lockwitzbach / MS6 to -0.41 at Elbe, this corresponds to the smallest and largest catchments in the study. Hence, for chloride sampling, return-interval is more decisive in large than in small catchments, despite larger summer-winter differences at Lockwitzbach (compare

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Table 2).

STOM showed the best Performance compared to grab sampling among all stations and all years with a return interval of three months and 17 days in 2014 at the monitoring station in Görlitz (Neiße) and at MS6 (2018). However, the worst scenarios were found at Elbe/Schmilka for several years with a similar Performance than nitrogen-nitrate (one month return interval and one day of application) in 2014, 2015, 2016, 2017, 2018, 2020 and in Mulde/Bad Düben in 2009, 2013, 2014, 2016 and 2017.

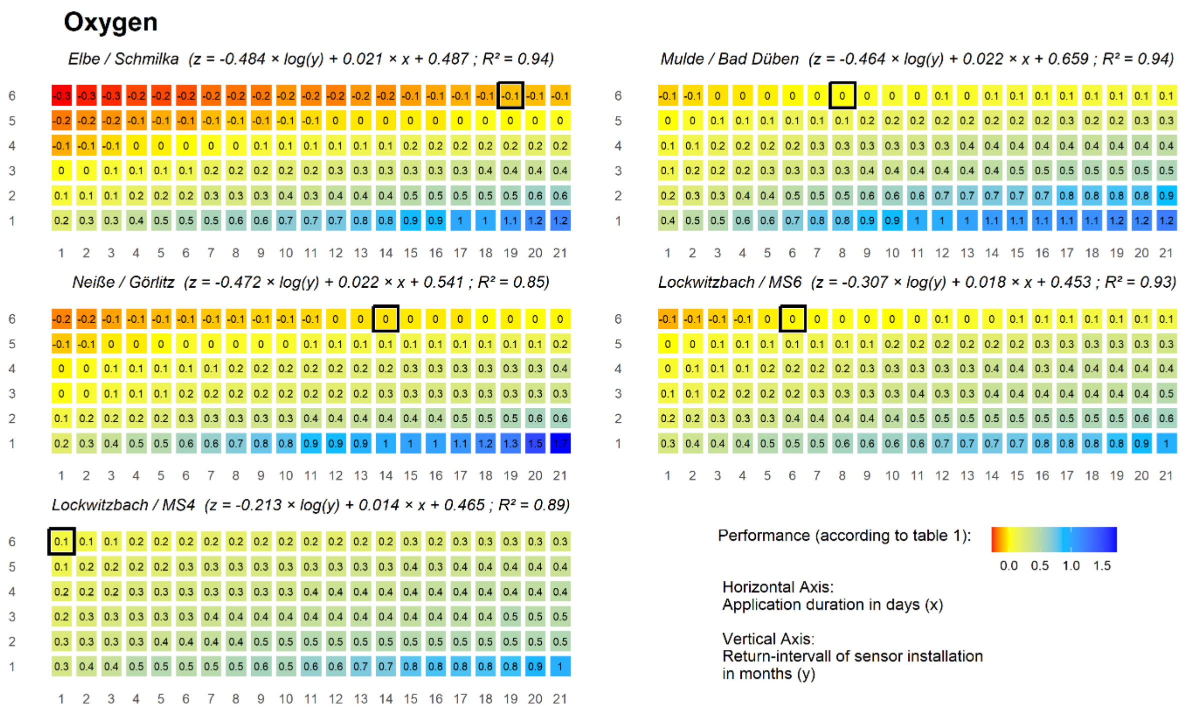

Figure 7. Comparison of STOM and grab sampling for dissolved oxygen, values were calculated according to *Figure 4*, break even points from regression model are highlighted with black frames.

Monthly grab sampling lead to 80.4% mean absolute deviation or assessment error from the complete data set. Lockwitzbach showed both, the highest and smallest mean absolute errors (MS6: 20% & 246%). No effect of catchment size on the error could be identified, the Neiße in Görlitz showed an error of 42.6%, the Elbe in Schmilka 31.2% and at Mulde in Bad Düben 61.8%.

DO sampling Performance underlines the potential of STOM, for all catchments a return-interval of half a year was sufficient with an application duration between 1 to 19 days, depending on the stream, to be as good as monthly grab sampling (Figure 7). In all cases a STOM regime of 3-monthly sampling during one day or five-monthly sampling during twelve days outperforms monthly grab sampling.

The coefficient for STOM sampling duration ranged from 0.014 to 0.022, with lowest value at Lockwitzbach / MS 6 and very similar values at the larger water bodies. Hence, of all three water constituents, dissolved oxygen sampling accuracy benefits most from longer STOM sampling duration. The higher coefficients at both Lockwitzbach stations coincide with more pronounced day-night differences there. The coefficients of log-transformed sampling interval ranged from -0.21 at Lockwitzbach / MS4 to -0.48 at Elbe, suggesting that oxygen sampling at the larger rivers benefits more from a reduced return-interval than sampling at the smaller stream.

For several years the rarest option (six month return interval and one day of monitoring) were reached at Mulde/Bad Düben (2018) and MS4 (2018,2019,2020). For Elbe/Schmilka and Neiße/Görlitz five months return intervals and 18/21 days of sensor application were the worst Performances in 2009 and 2012 respectively. According to the OGewV, the yearly minimum DO concentrations or the mean of max. three consecutive yearly minima need to be selected for the classification. Results from STOM with frequent return intervals and long application duration frequently detected the "real" yearly minimum value according to the OGewV regulation. These values were omitted for the calculation of the presented mean values, as well as in the uncertainty assessment, since they would yield "infinite" Performance (Δ_{STOM} = 0, division by zero, see Figure 4).

Sampling during events

On average, the Lockwitzbach catchment shows the highest yearly number of events and as well as the highest standard deviation between the years (28.6 ±8 events at MS4, 27.8 ±9 at MS6), followed by Neiße and Mulde (18.2 ±7 and 10 ±4). A mean of 7.4 ±2 events per year was calculated for Elbe. Summarizing the duration of all events per year at Lockwitzbach resulted in 81.4 ±19 and 83.6 ±22 (MS6/MS4) days on average. At Elbe and Mulde these values were higher with 109.3 ±41 and 105.8 ±44 days. Neiße has the shortest event duration of 70 ±32 days per annum. Results of the simulation show, that taking a grab sample once per month during an event is very unlikely, for all monitoring stations an average probability of 0.3% was calculated (Elbe: 0.52%, Mulde: 0.51%, Neiße: 0.21% and 0.03/0,1% for Lockwitzbach MS6/MS4). A relation between the yearly event duration or the number of events per year and an increase in probability of an event-grab sampling could not be found. Contrary to that, the results of the simulation using STOM show, that the probability to take a sample during an event is significantly higher (Figure 8). Under the most labor-intensive setting (monitoring every month for 21 days), about 52±2% at MS6 to 92±13% at Elbe (long lasting events at Elbe lead to multiple detections during one event) of yearly events were caught over all monitored years (75±13% Mulde, 55±7% at Neiße and 53±4% at MS4).

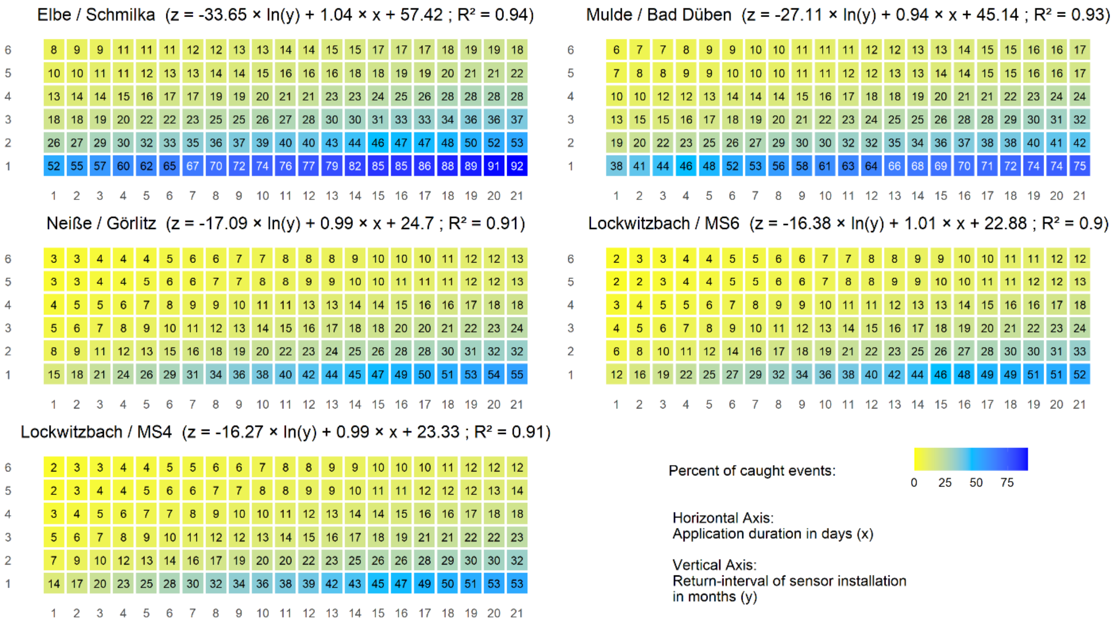

Figure 8. Average percentage of events caught per year with STOM at the gauges at/close to the monitoring stations.

Uncertainty of the sampling strategies

The application duration and the return interval for the break-even point of the quotients of the relative standard deviation do not coincide with the previously gained results from the Performance comparison (Figure9, Figure 10, Figure 11). In general, a shorter return interval and a longer application duration decrease the relative standard deviation in all cases. Nitrate-nitrogen reaches a smaller quotient of standard deviation earlier at all monitoring stations (than

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in Performance comparison), chloride slightly later. Dissolved oxygen, that had a high Performance, requires shorter measurement intervals to reach an equal standard deviation than grab sampling.

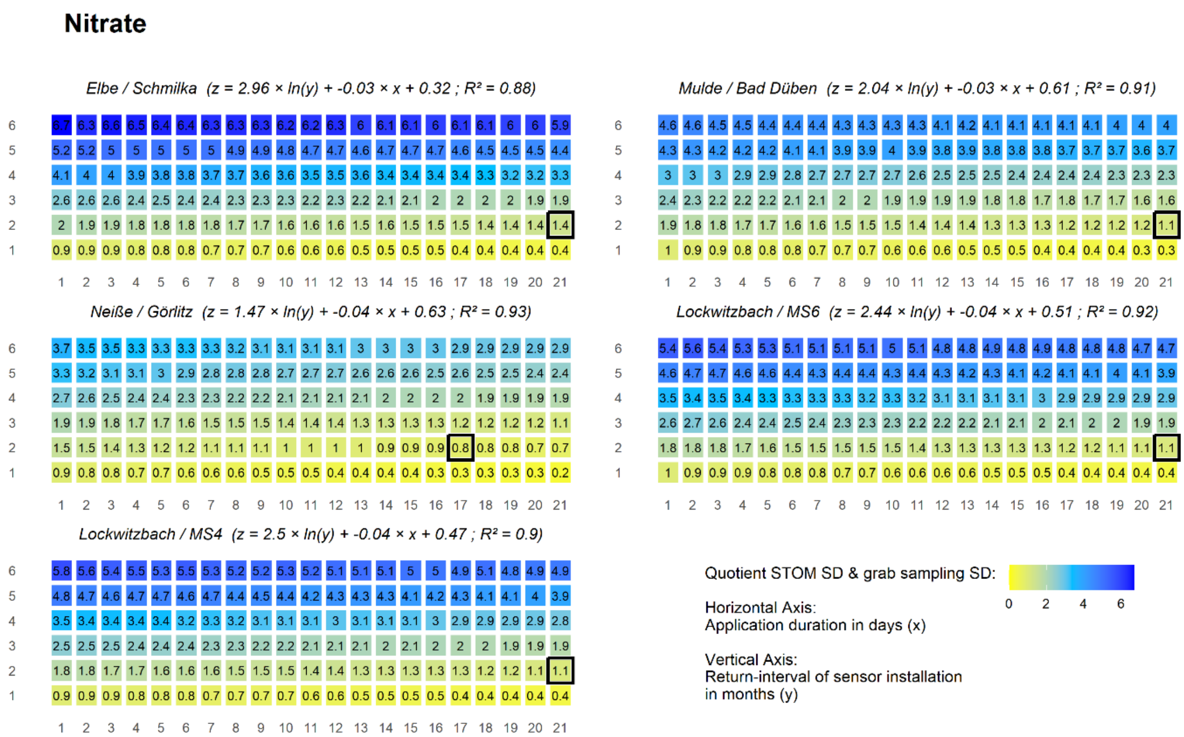

Figure 9. Quotient between the relative standard deviation of STOM and grab sampling for NO_3-N, similar standard deviations between both sampling strategies are highlighted with black frames.

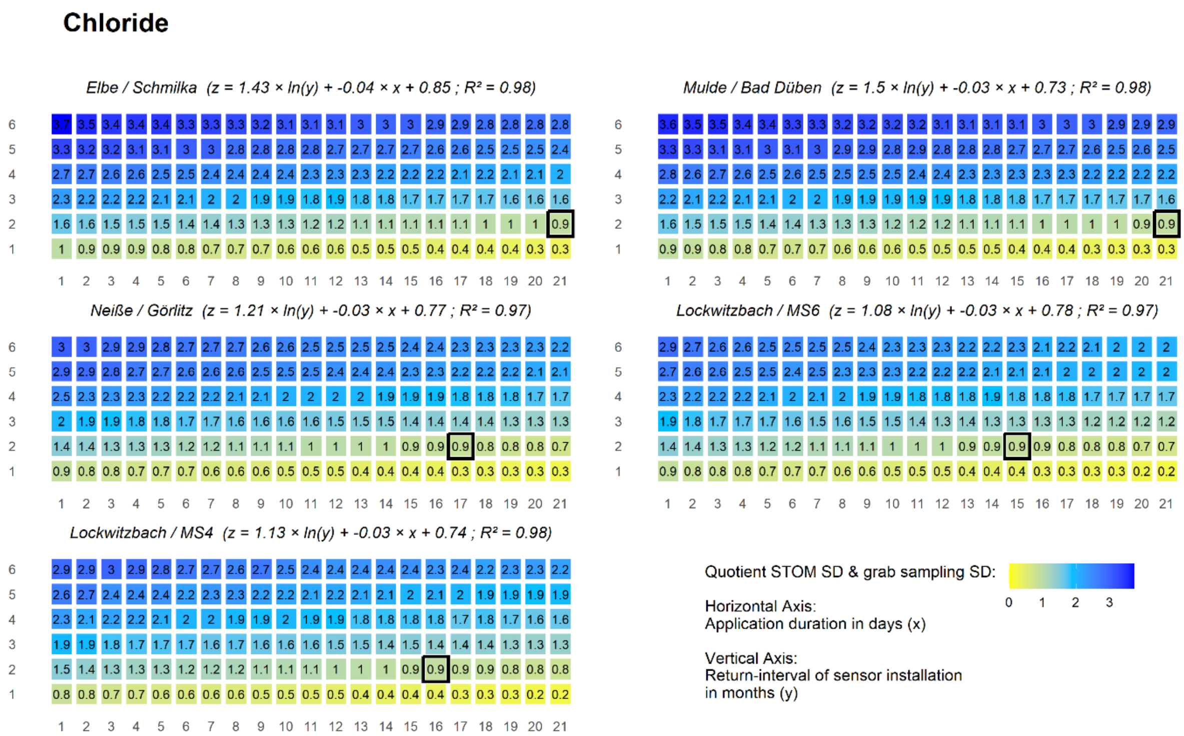

Figure 10. Quotient between the relative standard deviation of STOM and grab sampling for chloride, similar standard deviations between both sampling strategies are highlighted with black frames.

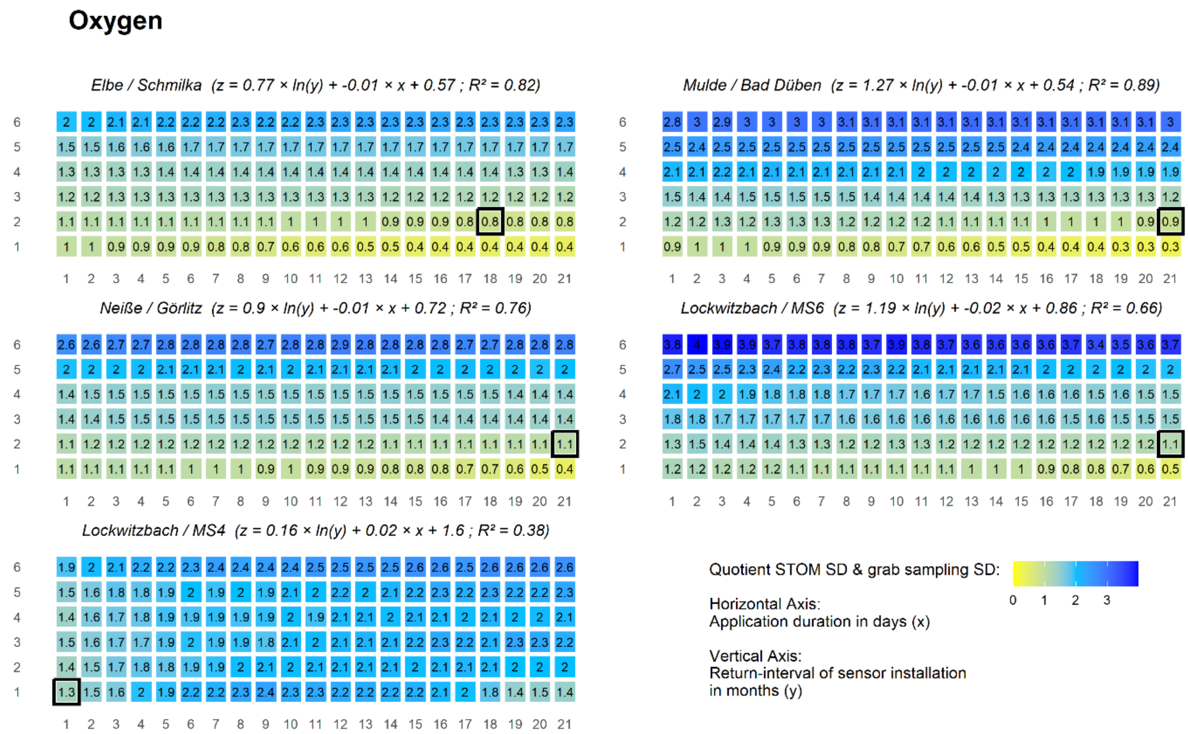

Figure 11. Quotient between the relative standard deviation of STOM and grab sampling dissolved oxygen, similar standard deviations between both sampling strategies are highlighted with black frames.

Cost calculation

According to the chosen assumptions, one year of grab sampling costs about 3673 € for the three investigated parameters at the five monitoring sites. Costs for STOM vary between 14 439 and 3121 €, the highest prices are occurring with highest return intervals and the longest sensor application durations. Especially for long application durations, more multi parameters sensors would be necessary to fit to the monitoring framework, leading to exponentially rising costs. A matrix with the yearly monitoring costs for STOM can be found in the appendix (Table 2)

4. Discussion

Water Quality Parameters

Estimation of chloride concentration

We were using a linear regression model to calculate the chloride concentration from the electrical conductivity. The obtained regression equations revealed similar parameters (Appendix: Figure 10) between the catchments and were in accordance with values reported in literature [40,41]. Other studies found, that the linear relation between electrical conductivity and chloride are different for lower concentrations, due to a change in the composition of solutes and their effect on the electrical conductivity of water. To overcome this issue Perera et al. (2009) [42] used a second linear regression for this specific value range. Our dataset did not show evidence for such a breaking point, most probable because of the lack of grab sample data with low conductivity/chloride concentrations.

Performance of STOM in comparison to grab sampling

We defined, that grab sampling happens during workdays from 9 am to 5 pm to be close to regular working hours. Increasing this time frame further by including the weekend did not lead to significant improvements, on average the break-even point between grab sampling and STOM got extended by half a day of sensor application. If grab sampling would take place during the whole day (24 h), nitrogen-nitrate and chloride will not show significant improvements as well

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but the monitoring of DO will be considerably better. This resulted in a prolongation of the break-even point with STOM by an average amount of five days at all monitoring stations, ranging from two days in Schmilka to nine days at MS4. The graphs similar to Figure 5, Figure 6 and Figure 7 for those cases can be found in the appendix.

Our results revealed that the catchment size has no influence on the Performance between STOM and grab sampling (according to Figure 4), only for dissolved oxygen a slight tendency for a better performance at small catchments could be suspected. The interval of application, e.g. if the sensor is placed once every month or every second month, has a significantly higher influence on the performance of STOM than the duration of the sensor application. The relation between an increase in Performance and the duration of the sensor application can be well represented with a linear function. In contrast, the relation between the Performance and the return interval follows a logarithmical trend, indicating a nonlinear Performance-improvement with a shorter return interval. These findings are underlined with the factors of the regression functions (see Figure 5, Figure 6 and Figure 7), which are consistently higher for the return interval. Probably longer return intervals do not represent seasonal and inter-seasonal changes of rivers sufficiently enough and cannot be compensated by longer sensor application time. The variability of the relative standard deviation seems to be independent of the catchment size and water quality parameter. The shown Performance is more variable between parameters and watersheds mainly because we calculated the mean of the yearly values durations, which had a high variability as well as a small sample size of 14, 10 and 5 years.

However, the analyzed parameters showed noticeable variations among each other. Especially for DO, STOM leads to a considerable improvement of monitoring accuracy The diurnal pattern of the dissolved oxygen concentration, controlled by photosynthesis and respiration in the aquatic ecosystem, appears to get well recorded by STOM. Unlike for nitrate and chloride, the OGewV defines the minimum DO concentration as threshold, which is also more likely to be caught during longer application periods of continuous monitoring than by a grab sample. Other researchers identified this fact before, like Halliday et al. (2015) [13]), who recommend to establish specific sampling time windows for certain WFD parameters or to use online sensors, stating that first experiences were already made in England at a number of sites [43].

The small difference between grab sampling and STOM for nitrogen-nitrate and chloride can be explained by the comparable low variability of both parameters that are mainly affected by seasonal changes or by dilution during rain events. Fluctuations in nitrate concentration and the effect of rainfall characteristic of were studied by Winter et al. (2022) [44] on six sub-catchments of the Bode River, who found strong drivers in event magnitude and seasonality which are controlling the relevant flow paths of nitrate within the land-to-stream connection. Even though some publications mentioned that diurnal patterns were detected for nitrate, our dataset did not show those trends or only marginal amplitudes were visible [27,45,46]. Vilmin et al. (2018) [11] showed that with a grab sampling frequency of 25 days per year a good representation of the mean nitrate concentration of the Seine in Paris can be achieved. Bieroza et al. (2014) [27] stated a weekly and monthly sampling as adequate for their investigated agricultural catchment in Sweden

Studies on the importance of sampling frequency for chloride concentration assessment are rare. Harmeson and Barcelona (1981) [47] mention, that the average deviation of monthly samples was found to be acceptable for chloride in Ilinois' watersheds. Generally, several papers reported linkage between the chloride concentration and discharge, e.g. a dilution of chloride by elevated streamflow and vice versa [48]. Especially from the northern hemisphere there are manifold studies focusing on the additional input of salt during the winter months by road salt applications [41,49,50]. By using a yearly mean value for classification instead a maximum value, the OGewV rather neglects these spikes from road salt application. Reports in literature warn about several adverse effects of increasing salinization in water bodies [51–53]. Only at Lockwitzbach peaks above 200 mg/l for some hours were measured during winter, they are below acute toxicity defined by CEQG (2011) or US EPA (1988) [54,55]).

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The two monitoring stations at Lockwitzbach (MS6 & MS4) also allow us to investigate the influence of the sampling location on the classification in small streams. For chloride there is a small difference between the monitoring stations recognizable with 3% on average over all years relative to the mean concentration at MS6. Nitrate shows a slight reduction of 9% between the stations, probably by increased nitrate uptake and denitrification during the summer months. If a mean value would also be the rule for Oxygen according to OGewV, like for nitrate and chloride, there would be hardly any difference cognizable (0.5%) between the two stations. However, the rules for dissolved oxygen calculation are set by using the yearly minima for classification, leading to a mean reduction of 63% between the two monitoring stations. The decrease between the two monitoring station arises by pronounced day patterns of dissolved oxygen at MS4, reaching considerable low concentration in the summer nights. Changes in the catchment characteristics is leading to these results: The stream flows from a rather rural area (MS6) through the city of Dresden. The station MS4 is located at the outlet of this urban section shortly before the confluence with Elbe river. Within this urban section, the waterbody is lacking natural shading by trees and bushes. The cross-section is comparably broad with shallow water levels that expose high surface area to sunlight. According to the official information provided by LfULG, one sampling location is used for the chemical classification of Lockwitzbach (https://www.umwelt.sachsen.de/datenportal-ida-4626.html, Accessed 29.07.2023). This point is located close to MS6 and would not indicate these large differences. Choosing sampling locations based on an analysis of catchment land use types within the catchment would help to overcome such underestimations and reveal potential for improvement measures in the watershed.

STOM and event sampling

The catchment size seems to have an effect on the standard deviation of the number of yearly events, showing higher variability of number of yearly events at smaller catchments. Unlike to the investigated water quality parameters, there is a clear tendency for bigger catchments to show a higher probability to catch a sample during an event using STOM sampling. Comparing the regression equations from the previous Performance calculation, it becomes obvious, that the application duration has a higher importance for event monitoring while for water quality parameters the return interval had a more pronounced impact.

The simulation showed that there is no clear positive correlation at all catchments between the number of sampled events by STOM and their duration or the number of yearly events. Even under long exposure and regular installation of sensors only Neiße showed a correlation for both and Elbe only for the event duration. Already mentioned in the previous chapter, datasets for Lockwitzbach are considerably shorter than the ones of Elbe, Vereinigte Mulde and Lausitzer Neiße and not suitable for a meaningful statistical analysis.

The German Working Group of the Federal States and the Government on Water Issues ([1], recommends 12 samples per year for compounds that show a strong variance in their concentration or that are introduced on basis of special occasions or sampling during the period of usage. The results of the simulated grab sampling strategies for event monitoring shows, that it is not possible to reliably monitor pollutants that are mobilized during rain events by taking a sample once per month. These high flow periods are of further importance if particle bound pollutants are considered as they mainly get transported during and especially at the beginning of these events (chemodynamic transport or first flush phenomena [56]). Often the $\log K_{OW}$ (octanol/water partitioning coefficient, a measure for hydrophobicity) is used for estimating sorption coefficients of compounds to soil or sediments [57]. There are 46 compounds that are used to classify the chemical status of a waterbody in Appendix 8 of the OGewV by using a maximum mean concentration. For 30 out of those 46 compounds a maximum allowable concentration is assigned, which is not allowed to be exceeded in any sample taken. A literature research on the $\log K_{OW}$ values showed that only nitrate has a value below one, indicating high solubility in water The rest is above one and has a higher probability to be attached to particles.

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Since these relevant compounds are supposed to be measured in the unfiltered sample - except for the heavy metals: cadmium, lead, mercury and nickel – high solid concentrations during rain events are of most ecological concern according to the chemical classification of OGewV. Their environmental concentration is highly likely to be underestimated with the current monitoring strategy. Furthermore, if most of the mobilized sediments get transported in the beginning of an event, the probability for catching representative grab samples becomes even smaller. To overcome this issue within the framework of the current grab sampling regime, special event sampling programs are necessary. Usually automated samplers or sediment collectors like centrifuges that are triggered during a discharge event. They are used to improve the accuracy of the standard monitoring program. To operate and maintain such an extended program for all streams is unrealistic in many ways – mainly by the amount of required personnel for handling samplers and required capacity for the analysis of samples Furthermore there are several sources of errors to be taken into account by auto samplers like limited sampling volume and degradation processes [58].

STOM for modelling

Recent publications show the benefit of using different river models for the status assessment of water bodies, parameter, sampling frequency and location [11,59–61]. We want to emphasis the value of data generated by STOM for further improvement of the model quality especially in the calibration and validation process. Among many studies, e.g. [30] showed the benefits of model predictions of sediment and nutrient loads using high-frequency data and more frequent sampling as a calibration source in an flashy Finnish watershed for several parameters by improvements in KGE. Nafees Ahmad et al. (2011) [62] who showed that monthly samples lead to a considerable underestimation of SWAT model results for sediment and nitrogen loads during high precipitation events in comparison to a high resolved time series. However, other studies found that nitrate measurement frequency (daily to fortnightly) do not "*have a significant effect on the total uncertainty of nitrate predictions, because the combination of model structural error and measurement errors were much higher relative to parametric prediction uncertainty*" [60].

Cost Calculation

According to our assumption for sampling, personnel and travelling expense we found that STOM is cheaper than grab sampling after a return interval of four months, irrespective of the application duration. STOM costs are mainly affected by the rising costs for additional sensors, which are most demanded for frequent and long lasting monitoring campaigns. However, this is an example with simple assumptions to demonstrate the related costs for both approaches. Conventional sampling regimes consist of a higher number of sampling sites and analytes, leading to a more complex relation of personnel and travelling costs. The grab sampling regime for operation monitoring in Saxony observes about 2240 monitoring sites, the analysis covers about 420 compounds (120 industrial chemicals, 190 agricultural chemical or pesticides, 80 pharmaceuticals and 30 metals [34]).

Considering the very limited number of parameters that we can measured online with affordable probes, STOM would not be able to replace completely grab sampling. However, we consider that STOM can be smartly combined to extend the value of the gathered water quality information to deepen our understanding of hydrological and chemical dynamics of rivers [63,64]. Looking at the WFD-types of sampling an application of STOM aside of operational monitoring seems promising. It can be used for investigative monitoring, which is usually done less frequent but with more effort [6]. Among other examples, the federal state of Saarland in Germany is doing investigative monitoring by using online monitoring over a certain time span for „at-risk"-waterbodies successfully for several years to identify and evaluate contributions of point sources and diffuse pollution, crosscheck the efficiency of measures to improve ecosystem quality and capturing eutrophication state of a waterbody (www.gewaesser-

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monitoring.de/en/, [65,66]).

5. Conclusions

After comparing the simulated STOM and grab sampling strategies, results showed how STOM would fundamentally improve the current approach for monitoring parameters with a pronounced diurnal pattern (such as DO), especially when maximum and minimum concentrations are requested by regulations or laws. For example, in case of DO, placing and picking up a sensor once every three months instead of grab sampling every month can be an alternative for gaining more information with less frequent sampling. This is a clear benefit of STOM, since it takes advantages of continuous monitoring to improve the understanding of contaminant transport patterns. . However, for chloride and nitrogen-nitrate we do not see big improvements compared to a monthly grab sampling regime, because of their low variability and the usage of mean concentrations for the assessment by the OGewV.

Furthermore, using discharge and high discharge events as a surrogate signal to analyze event-mobilized pollutants, the STOM sampling strategy would increase the probability of capturing pollution spikes by several orders of magnitude. We found evidence, that these results are dependent on the catchment size in contrast to the Performance-comparison of the three water quality parameters, where the results could not be directly linked to the size of the watershed area and appear rather similar among all catchments. Taking into consideration that grab sampling fails for monitoring event-mobilized pollutants it becomes obvious that sampling strategies need to be adapted, which has been highlighted by many researchers already [19,67,68]. Especially for those compounds, a faster development of online-sensors would be desirable [5]. For several WFD-relevant parameters, technologies are available but still far away from field application [69–72]. Alternative monitoring technologies and approaches can also help to close this gap and efforts to implement them as standard tools for river monitoring should be made. In this context, we proposed STOM as an alternative showing its potential to analyze the chemical and ecological status of a surface water body.

Our research at the Lockwitzbach catchment, including the analyzes of two monitoring points upstream and downstream an urban area, shows some of the challenges for monitoring small streams and to assess their ecological quality. For example, the results from this watershed showed that OGewV dissolved oxygen classification can be very variable within a short river section depending on land use changes within the catchment. Looking at the event dynamics, our data revealed that Lockwitzbach has a flashy hydrograph with a high number of events and a considerable short duration in the summer months. This makes it further difficult for planning and executing monitoring campaigns for event mobilized pollutants. This challenge can be better addressed using STOM as a sampling strategy instead of grab sampling, since it demonstrated a higher probability to depict event dynamics.

In order to further evaluate the benefits of STOM, future studies can include selecting other proxy-parameters that can be easily measured with a high temporal resolution. Additionally, comparing STOM with passive sampling for the estimation of mean concentrations might provide insights about the potential of using less resource intensive sampling approaches.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org.

Author Contributions: Conceptualization, J.B.; methodology, J.B. and X.C.; software J.B. and X.C..; validation, J.B. and B.H.; formal analysis, J.B.; investigation, J.B.; resources, J.B.; data curation, J.B. and X.C.; writing—original draft preparation, J.B.; writing—review and editing, J.B. and B.H.; visualization, J.B.; supervision, B.H. and P.K..; project administration, J.B. and B.H.; funding acquisition, P.K. All authors have read and agreed to the published version of the manuscript." Please turn to the CRediT taxonomy for the term explanation. Authorship must be limited to those who have contributed substantially to the work reported.

Funding: This research was funded by Helmholz-Wasser Netzwerk, Teilprojekt Urbanes Wasserressourcenmanagement and by the DFG founded project Urban Resistom, grant number KR 2337/17-1.

Data Availability Statement: The discharge data sets used in the present study are publicly available at the

 doi:10.20944/preprints202402.1266.v1

Saxonian State Agency for the Environment, Agriculture and Geology (SLULG): https://www.umwelt.sachsen.de/umwelt/infosysteme/hwims/portal/web/download-von-messwerten, Data from Lockwtizbach can be requested from the author. Scripts for the STOM approach and the graphics are available on github: https://github.com/Jakobbenisch/STOM

Acknowledgments: We thank the Helmholtz-Centre for Environmental Research for funding personnel and monitoring at Lockwitzbach. Further thanks to Reinhard Pohl, Susanne Heise and Dr. Sascha Goldstein from BfUL for sharing data and operating and maintaining the monitoring station at Schmilka, Bad Düben and Görlitz. Special thanks for supporting the maintainence of the Lockwitzbach monitoring network to Stephan Becker and Marvin Dropp.

Conflicts of Interest: The authors declare no conflicts of interest.

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