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# Application and Evaluation of a New Passive Sampler for Measuring Average Solute Concentrations in a Catchment Scale Water Quality Monitoring Study

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We present a field based testing, optimization, and evaluation study of the SorbiCell sampler (SC-sampler); a new passive sampling technique that measures average concentrations over longer periods of time (days to months) for various substances. We tested the SC-sampler within a catchment-scale monitoring study of NO<sub>3</sub> and P concentrations in surface water and tile drain effluent. Based on our field experiences, we optimized the flow velocity control and the sample volume capacity of the SC-samplers. The SC-samplers were capable of reproducing the NO<sub>3</sub> concentration levels and the seasonal patterns that were observed with weekly conventional grab sampling and continuous water quality measurements. Furthermore, we demonstrated that average measurements produce more consistent load estimates than “snapshot” concentrations from grab sampling. Therefore, when the purpose of a monitoring program is to estimate reliable (trends in) average concentrations or loads, the SC-samplers are a cost-effective alternative for grab sampling.

## Introduction

Surface water and groundwater pollution is a serious problem in areas with intensive agricultural land use such as The Netherlands (1, 2). Policy makers of the European Union and elsewhere in the world aim at improving water quality (e.g., ref 3). For the evaluation of action programs and pilot studies, water authorities invest heavily in the monitoring of

groundwater and surface water quality. However, interpretation of the grab sampling data from their monitoring networks is often problematic. Grab samples only provide “snapshots” of water quality at the moments of sampling, and frequencies are generally not sufficient to capture the dynamic behavior of shallow groundwater and surface water quality (4–6). Together with the uncertainties in the water quality measurements themselves (7–9), this results in large uncertainties in the estimates of loads and average concentrations. Many researchers tried to improve this by developing and testing different methods for estimating loads from discrete grab sample data. However, none of their methods clearly outperformed the others, and the accuracy of the load estimates turned out to depend mainly on the sampling frequency (10–12).

Increasing the frequencies of common sampling and laboratory analyses in regional monitoring programs is extremely laborious and expensive. Another option for increasing the measurement frequencies is the use of on-site automatic samplers and analyzers which can produce continuous water quality time series of many chemicals (4, 6). A major drawback of this equipment is the expensive purchase, maintenance, and field installation in a sheltered environment with electrical power supply.

Another strategy for dealing with short-term variability in water quality monitoring is to measure long-term average solute concentrations. Therefore, passive sampling is generally regarded as a promising emerging technique for monitoring water quality (e.g., refs 13–15). An extensive review on available passive sampling methods is given by Vrana et al. (16). Existing passive sampler techniques are based on either equilibrium or kinetic diffusion. A major shortcoming of these diffusion samplers is their poor performance under dynamic hydrological, hydrochemical, and biochemical conditions, such as varying flow velocities, temperature, and solute speciation (17, 18). In addition, kinetic passive samplers require continuous refreshment of the surrounding water, which makes the method unsuitable for application in stagnant surface waters and groundwater (19, 20).

The SorbiCell sampler (SC-sampler) is a new passive sampling technique that can measure average concentrations over longer periods of time (days–months) for various substances (21). The method is based on advective flow of water through the sampler, rather than equilibrium or kinetic diffusion. To induce the water flow through the SC-samplers, they are usually placed on reservoirs with atmospheric pressure inside. With different mounting systems, SC-samplers can be applied for sampling in groundwater wells, tile drains, and flowing or stagnant surface waters.

Although SC-samplers have been extensively tested and optimized under laboratory conditions (21), more field-based experience is needed to verify the applicability of SC-samplers for water quality monitoring. This paper presents the first large-scale field application of the SC-sampler. Furthermore, this is the first comparison between automatically recorded continuous concentrations, average concentrations from a passive sampler, and “snapshot” concentrations from common grab sampling.

The objectives of this study were (1) to test and optimize SC-samplers in a catchment-scale field study; (2) to compare the average concentration measurements with common grab sampling and continuous concentration measurements; and (3) to evaluate the applicability of SC-samplers as an alternative for grab sampling in regional water quality monitoring programs. We focused this study on the nutrient nitrate (NO<sub>3</sub>); one of the most problematic substances in

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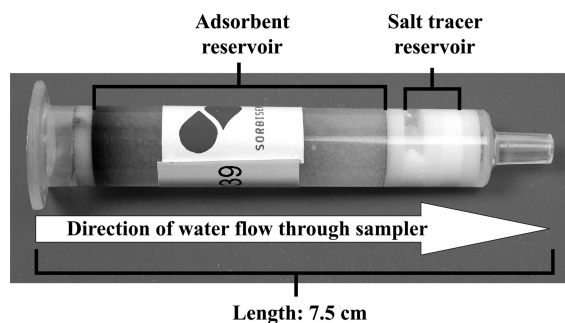


FIGURE 1. Basic components of a SorbiCell passive sampler.

surface water and groundwater. We performed our measurements in an agricultural lowland catchment in The Netherlands. Our evaluation of the SC-sampler results was based on duplicate analysis, comparison with continuous measurements and grab sample data, and comparison of load estimates based on the different types of concentration measurements.

## Methods

**Field Measurements.** A multiscale experimental setup was installed in the Hupsel catchment in the eastern part of The Netherlands (see Figure S1, Supporting Information) (52°03' N; 6°38' E). Water quality and discharge measurements were performed at the catchment outlet and at an experimental field from August 2007 until April 2009. A detailed description of the Hupsel catchment and of all installations and measurements is given by Van der Velde et al. (6).

We applied three methods for measuring NO<sub>3</sub> concentrations: common grab sampling, automatic continuous analysis, and average concentration measurements using SC-samplers. Weekly grab samples were collected from 4 groundwater wells and 3 tile drains at our experimental field. Surface water was sampled weekly at 2 locations: the Hupsel stream at the catchment outlet and the artificial ditch draining the experimental field (Figure S1). The samples were transported and stored at 4 °C and analyzed within 48 h, using IC (ion chromatography) and ICP-MS (mass spectrometry). For the continuous NO<sub>3</sub> analysis at the catchment outlet, we used a Hydriion-10 multi parameter probe (Hydriion BV Wageningen, The Netherlands).

Average NO<sub>3</sub> concentrations for installation periods of approximately 1 month were measured using SC-samplers. The basic components of the samplers are shown in Figure 1. As water passes the sampler, NO<sub>3</sub> is captured by an adsorbent. Simultaneously, a tracer salt with a known solubility (calcium-citrate) is leached from the downstream side of the sampler. The volume of water that passed through the sampler during the installation period is estimated from the mass reduction of this tracer. Together with the mass of adsorbed solute, this gives an average solute concentration for the installation period. A detailed description of the SC-sampler and results of the laboratory testing have been published by De Jonge and Rothenberg (21).

We installed SC-samplers at 23 tile drain outlets and 13 surface water locations throughout the Hupsel catchment (Figure S2). We replaced all SC-samplers monthly, with the exception of the last sampling round, when an installation period of 3 months was tested. A detailed description of the SC-sampler field installation methods and laboratory analysis procedures is given in the Supporting Information (pages S3–S4).

**Duplicate Analysis.** The first part of the evaluation of the SC-sampler results in this study was based on duplicate analysis. Several locations were equipped with double mounting systems, which allowed for the installation duplicate SC-samplers. We analyzed a total amount of 64

duplicate pairs from June 2008 to April 2009. The average absolute differences between the duplicate pairs in measured NO<sub>3</sub> concentrations were calculated as follows:

$$D_{\text{avg}} = \frac{|d1_1 - d2_1| + |d1_2 - d2_2| + \dots + |d1_n - d2_n|}{n} \quad (1)$$

where  $D_{\text{avg}}$  is the average absolute difference,  $d1_i - d2_i$  is the difference between the two measured NO<sub>3</sub> concentrations of the  $i$ th duplicate pair, and  $n$  is the number of duplicate pairs.

Based on the duplicate measurements we also deduced the standard deviation of SC-sampler measurements ( $S$ ). Because the average difference between the duplicate pairs approximates to zero, we can estimate the standard deviation following:

$$S = \sqrt{\frac{(d1_1 - d2_1)^2 + (d1_2 - d2_2)^2 + \dots + (d1_n - d2_n)^2}{2n}} \quad (2)$$

Subsequently, relative standard deviations were also derived by dividing the standard deviations by the average measured concentrations. These relative standard deviations give a measure for the precision of the SC-samplers, which is insensitive for the absolute concentration values.

**Load Estimates.** The second part of the evaluation of the SC-sampler results was based on load estimates using the three types of concentration measurements. We used the NO<sub>3</sub> measurements of February 12 to May 21, 2008 because no major technical failures interrupted the continuous water quality and discharge measurements in this period.

The load estimate using the continuous NO<sub>3</sub> concentrations was straightforward, following:

$$L_p = \sum C_i \cdot Q_i \cdot \Delta t_i \quad (3)$$

where  $L_p$  is the estimated load over period  $p$ ,  $\Delta t_i$  equals  $t_i - t_{i-1}$  and represents the semicontinuous measurement interval (10 min), and  $C_i$  and  $Q_i$  are the concentration and discharge at  $t_i$ .

The loads based on the average SC-sampler concentrations were estimated by multiplying the average concentrations by the average discharge volumes for the same period:

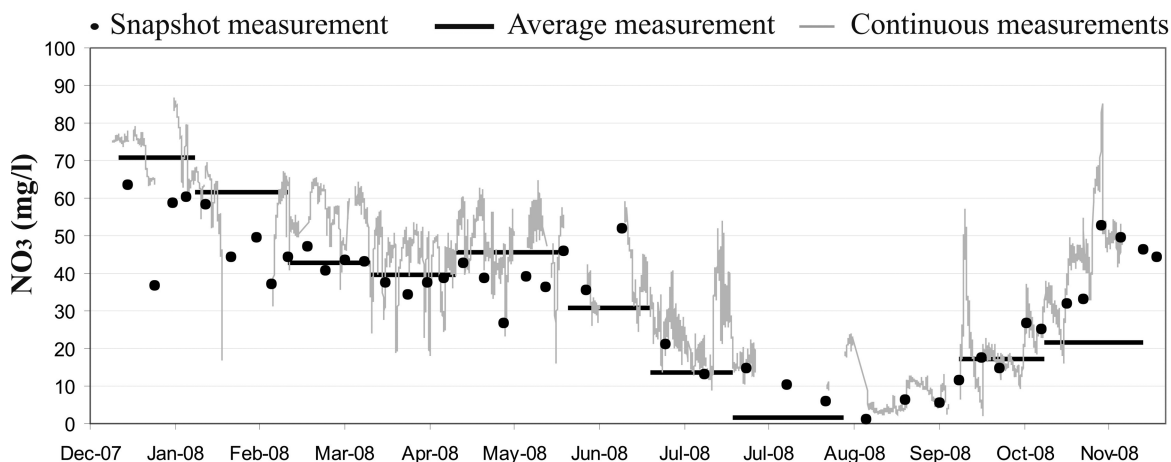
$$L_{si} = C_{si} \cdot Q_{si} \cdot \Delta t_{si} \quad (4)$$

where  $L_{si}$  is the estimated load over SC-sampler installation period  $si$ ,  $\Delta t_{si}$  is the installation period duration,  $C_{si}$  is the SC-sampler average concentration, and  $Q_{si}$  is the average discharge at the catchment outlet over installation period  $si$ .

For load estimates based on discrete grab sample data, many methods have been described in literature. However, several researchers reported that none of these methods clearly outperforms the others in all cases (e.g., refs 10–12). Therefore, we applied a simple stepwise interpolation between our weekly concentration measurements (22). In other words, the grab sample NO<sub>3</sub> concentrations were assumed to be representative for the period around which the sample was collected. The load estimate for these periods is similar to eq 4:

$$L_{gs} = C_{gs} \cdot Q_{gs} \cdot \Delta t_{gs} \quad (5)$$

where  $L_{gs}$  is the load estimate for the period around the moment of sampling,  $C_{gs}$  is the measured “snapshot” concentration,  $Q_{gs}$  is the average discharge for the period around the sampling, and  $\Delta t_{gs}$  is the time interval represented



**FIGURE 2.** Graph with the three types of  $\text{NO}_3$  concentration measurements that were applied at the catchment outlet: grab sample snapshot measurements, SC-sampler average concentration measurements, and continuous measurements.

by the grab sample measurement. This time interval depends on the sampling frequency.

For the comparison of load estimates, we used the 1-month SC-sampler installation periods ( $s_i$ ) as the common time intervals. The amount of grab samples per installation period defines how many  $L_{gs}$  values (eq 5) are summed to represent the common time interval  $s_i$ . For the load estimate from the continuous data (eq 3) the period  $p$  equaled installation period  $s_i$ .

One of the aims of this study was to compare SC-sampler measurements to continuous measurements and grab sampling data. Structural differences between the different measurement techniques may result in differences between the load estimates that are based on the different concentration data types. Another possible source of deviations is the bias introduced by using average concentrations and discharges. This averaging bias is proportional to the covariance between the continuous concentration and discharge time series (23, 24). When we combine the load estimate eqs 3 and 4 for a period  $p$  equal to SC-sampler installation period  $s_i$ , and include the covariance ( $\text{COV}[C_p, Q_i]$ ), we obtain:

$$L_{p,s_i} = \sum C_i \cdot Q_i \cdot \Delta t_i = C_{s_i} \cdot Q_{s_i} \cdot \Delta t_{s_i} + \text{COV}[C_p, Q_i] \cdot \Delta t_{s_i} \quad (6)$$

We can eliminate the structural difference between the measurement methods and isolate the effect of the averaging bias by subsampling hypothetical data sets of snapshot measurements and SC-sampler-like average  $\text{NO}_3$  concentrations from the continuous data set. We calculated hypothetical SC-sampler-like average concentrations by averaging the continuous concentration data for each SC-sampler installation period. To represent grab sampling with different time intervals, we subsampled three hypothetical data sets with one, two, and four snapshots for each SC-sampler installation period. Loads were calculated using the subsampled SC-sampler-like concentrations (eq 4) and the concentrations from the stepwise interpolation between the subsampled snapshot samples (eq 5).

A major source of uncertainty associated with snapshot sampling from a fluctuating concentration pattern is that the measured concentrations depend strongly on the exact moment of sampling. To illustrate this effect, we selected from the continuous data the minimum and maximum concentrations within the time interval represented by the snapshot measurements. From these concentrations we calculated the minimum and maximum loads that could have been deduced from a grab sampling monitoring program.

## Results

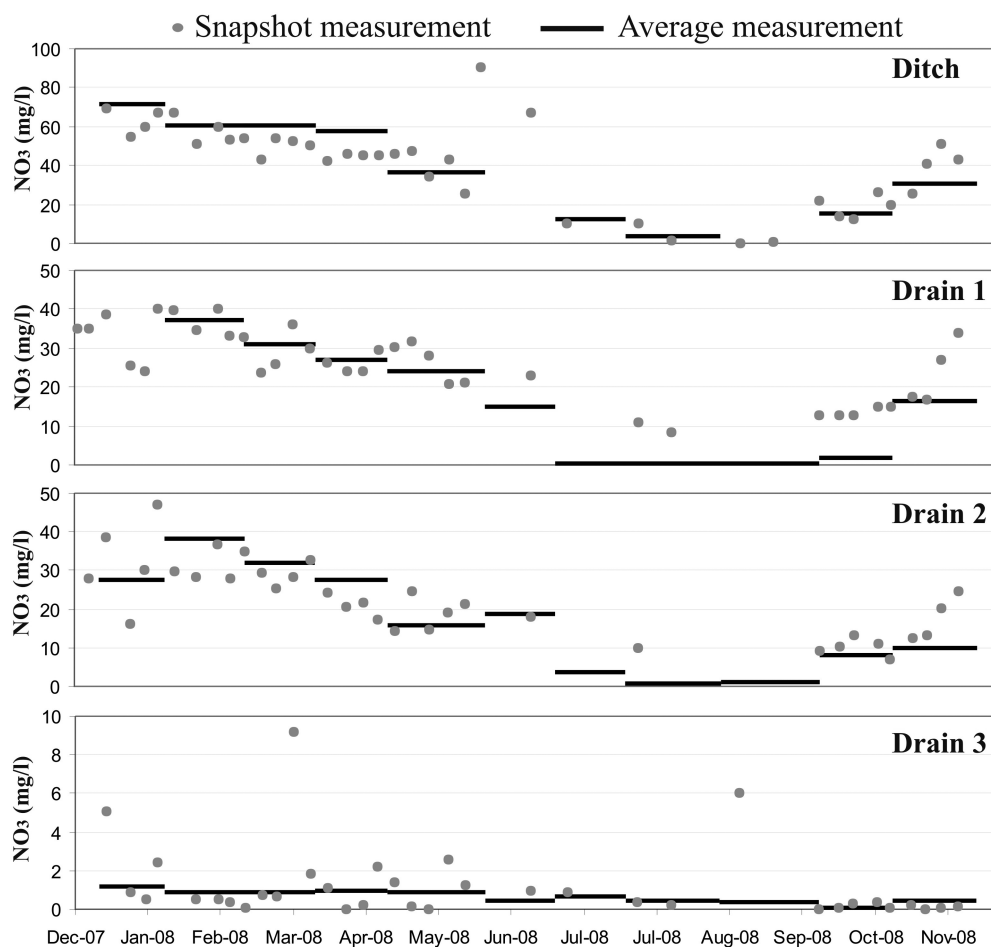
**Field Measurement Results.** From September 2007 to June 2008 we optimized the SC-samplers based on field experience and measurement results. We improved the flow velocity control and the sample volume capacity of the SC-samplers. The modifications that were applied to the SC-samplers during the optimization period are summarized on pages S5–S6 of the Supporting Information. In the remainder of this paper, we will focus on the optimized SC-sampler measurements of December 2007 to April 2009.

A summary of the results of all SC-sampler measurements in groundwater, surface water, and tile drain water is given in the Supporting Information (pages S7–S8). We also included the results of P-concentration measurement that were performed from July 2008 onward. The SC-samplers produced a valuable overview of  $\text{NO}_3$  and P concentrations and their temporal and spatial variability throughout the catchment.

For the catchment outlet, the measured SC-sampler  $\text{NO}_3$  concentrations can be compared to the weekly grab sampling snapshots and to the continuous measurements. In addition, the SC-sampler measurements of tile drain effluent and ditch water at the experimental field can be compared to weekly grab samples. The results for the catchment outlet are presented in Figure 2 and the results for the experimental field are presented in Figure 3. For the catchment outlet, Table 1 compares the average SC-sampler  $\text{NO}_3$  concentrations to the average  $\text{NO}_3$  concentrations derived from the continuous data and the grab sampling measurements.

Despite the inherent differences between the measurement methods, the overall average SC-sampler  $\text{NO}_3$  concentration deviates only 2% from the grab sampling average  $\text{NO}_3$  concentration (Table 1). Furthermore, all three sampling methods reproduced the same seasonal concentration pattern, with decreasing concentrations in spring and increasing concentrations in autumn (Figures 2 and 3). Only in the November–December 2008 installation period, the SC-sampler concentrations were generally lower than the grab sample results and the continuous measurements. This difference was caused by partial disintegration of the absorption reservoir, which resulted in suboptimal contact between the adsorbent and the sample water. The disintegration occasionally occurred in case of larger sample volumes, due to the contraction of the salt tracer reservoir. An improved fixation of the absorption reservoir solves this problem. Minor structural differences between the three methods for measuring  $\text{NO}_3$  concentrations can be observed in Figure 2 and Table 1. For the entire period, the Hydrion





**FIGURE 3.** Graphs with the two types of  $\text{NO}_3$  concentration measurements that were applied for the ditch and the three tube drains at the experimental field: grab sample snapshot measurements and SC-sampler average concentration measurements.

**TABLE 1.** Average  $\text{NO}_3$  Concentrations at the Catchment Outlet Derived from SC-Sampler Measurements, Continuous Hydron Measurements, and Discrete Grab Sample Measurements

period	number of days	SC-sampler $\text{NO}_3$ (mg/L)	Hydron $\text{NO}_3$ (mg/L)	grab samples	
				number of samples	average $\text{NO}_3$ (mg/L)
14 Dec 2007 – 10 Dec 2008	321	33.8	37.5	43	34.5
14 Dec–10 Jan	27	70.9	72.4	4	54.8
10 Jan–12 Feb	33	61.7	59.2	5	47.5
12 Feb–12 Mar	29	43.0	54.8	5	43.8
12 Mar–11 Apr	30	39.8	43.3	4	37.2
11 Apr–21 May	40	45.7	48.0	6	38.3
21 May–19 Jun	29	30.6	36.9	2	43.7
19 Jun–18 Jul	29	13.7	24.7	2	17.2
18 Jul–26 Aug	39	1.7		3	10.4
26 Aug–6 Oct	41		8.1	4	6.3
6 Oct–5 Nov	30	17.3	20.3	5	19.2
5 Nov–10 Dec	35	21.8	41.6	5	42.8

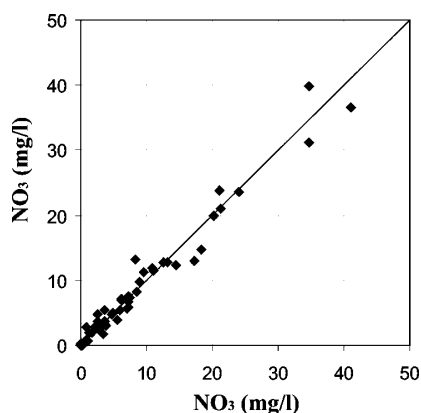
continuous  $\text{NO}_3$  concentrations were structurally somewhat higher than the SC-sampler and the grab sampling concentrations.

**Duplicate Analysis.** Figure 4 shows scatter plots of the 64 duplicate analyses for  $\text{NO}_3$ . Table 2 presents for each installation period the number of duplicates, the average  $\text{NO}_3$  concentration, the average absolute difference between the duplicates (see eq 1), the standard deviation between the duplicates (see eq 2), and the relative standard deviation between the duplicates.

The duplicate SC-sampler average  $\text{NO}_3$  concentration measurements showed rather good precisions (Figure 4 and Table 2). The relative standard deviation of the 64 duplicate pairs is 16.1%. Table 2 also gives the duplicate analyses results

for the individual installation periods. Understandably, the low  $\text{NO}_3$  concentrations that were measured during summer resulted in relatively high relative standard deviations. In the winter months, the relative standard deviations for the  $\text{NO}_3$  concentration measurements were much lower. In particular the 3-month installation period in January–April 2009 shows high precision, considering the relatively low relative standard deviation of 9.2%.

**Load Estimates.** The results of the  $\text{NO}_3$  load estimates, based on the different types of concentration measurements, are given in Figure 5. The February 12 to May 21 load estimate based on the SC-sampler average concentrations deviate less than 10% from those based on the continuous measurements



**FIGURE 4. Scatterplot of the SC-sampler duplicate measurements.**

and the grab sampling. The deviations among the load estimates is partly caused by the difference in average  $\text{NO}_3$  concentrations that were derived from the three types of measurement (Table 1). However, the differences also partly originate from the use of average concentration and discharge values for the load calculation (see eq 6).

Figure 6 gives the results of the load estimates based on the subsampled hypothetical grab sample and SC-sampler data sets. See the "Methods: Load Estimates" section for the explanation and aims of the subsampling procedure. By subsampling from the "true" continuous  $\text{NO}_3$  time series, we eliminated the structural differences between the measurement methods. Consequently, the difference between the "true" loads and the load estimates based on the subsampled average "SC-sampler" concentrations is exclusively caused by the averaging bias (eq 6). For the total period from February 12 until May 21 2008, this averaging bias amounts +6.0%.

The results of the load estimates based on equally distributed "snapshot" subsamples are also shown in Figure 6. In addition, the minimum and maximum possible load estimates that could be deduced from snapshot sampling are given. Compared to the load estimates based on the subsampled SC-sampler-like concentrations, the load estimates based on the hypothetical snapshot samples generally show larger differences from the "true" loads. The large uncertainty in load estimates based on low-frequency snapshot sampling is also illustrated by the large differences between the potential minimum and maximum loads. With less samples, the actual and potential deviations in load estimates increase even further.

## Discussion

During this study, we tested and optimized the SC-sampler—a new passive sampling technique that measures average concentrations. Placing the SC-samplers at multiple sites enabled us to obtain a catchment-scale overview of spatial

and temporal variability in  $\text{NO}_3$  concentrations in surface water and tile drain effluent. Duplicate analysis produced relative standard deviations of 16.1%. The SC-samplers  $\text{NO}_3$  concentration levels and seasonal patterns were similar to those observed with weekly conventional grab sampling and continuous water quality measurements.

These results are rather promising, especially when considering the common uncertainties of field measurements of water quality (7–9). These uncertainties do not just arise from the laboratory procedures, but also follow from the sample collection and the sample preservation and storage. Harmel et al. (7) quantified the cumulative error in field measurements of  $\text{NO}_3$  loads in streamwater during events from 8% up to 104%.

Regional surface water quality monitoring networks are sampled 12 times per year in most European countries (25). Our results show that monthly average concentration measurements produce more reliable load estimates than monthly, biweekly, or even weekly snapshot sampling. The laboratory and labor costs per SC-sampler are similar to the costs of one grab sample. This illustrates that the introduction of SC-samplers potentially increases the cost-efficiency of a monitoring program.

We optimized the SC-samplers based on our practical field experiences. An improved control of the flow velocities through the samplers helped to obtain the sampling volumes within the optimal range of 50–250 mL. Because flow conditions cannot be known beforehand, we still recommend installing two or more samplers with different conductivities at the same location. At the end of the installation period, the sampler with the best sampling volume can be selected for the laboratory analysis.

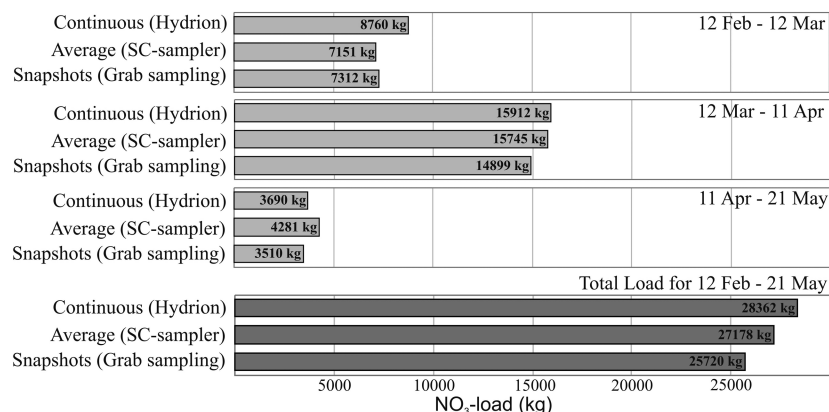
More field-based testing could increase the flexibility of SC-sampler application in various water quality monitoring programs. Laboratory testing has already yielded promising results for other contaminants, but additional field-based experience with measuring heavy metals, pesticides, and VOCs is desirable. Furthermore, little is known of SC-sampler performance in brackish or salty aquatic environments. The large amounts of ions in salt water would probably require a larger capacity of the adsorbent reservoir. A larger adsorbent reservoir may also be needed for longer installation periods and larger sample volumes, which might be preferred in specific monitoring studies. Our 3-month installation period showed consistent results, but longer installation periods have not been tested so far.

We showed that the averaging bias should be taken into account when using average concentration measurements for estimating solute loads. In general, a positive covariance between stream discharge and solute concentrations leads to an underestimation and a negative covariance leads to an overestimation of loads based on average concentrations (see also Supporting Information, Figure S5).

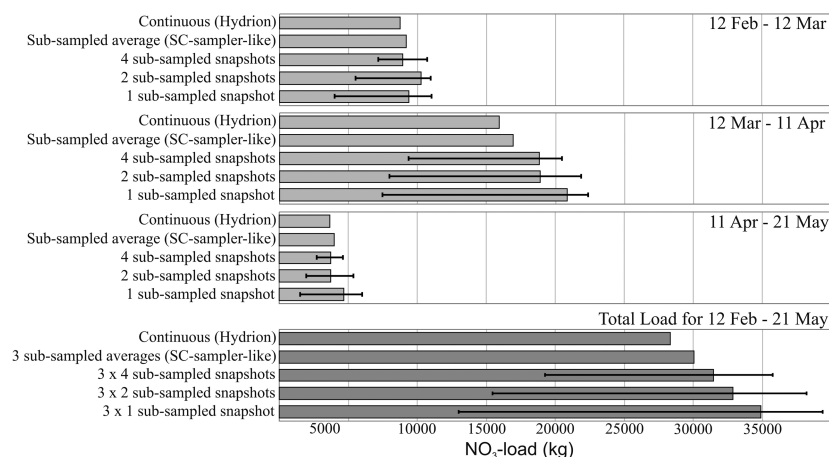
Correction for the averaging bias is possible when the covariance is known or can be estimated. The covariance

**TABLE 2. Results of the Duplicate  $\text{NO}_3$  Measurements with SC-Samplers (June 2008 – April 2009); Number of Duplicate Pairs, Average  $\text{NO}_3$  Concentration of Duplicates, Average Absolute Difference between Duplicates, Standard Deviation between Duplicates, and Relative Standard Deviation between the Duplicates**

period	number of dupl. pairs	average concn. (mg/L)	avg. abs. difference (mg/L)	standard deviation (mg/L)	relative st. dev.
Jun 2008 – Apr 2009	64	30.8	4.1	4.9	16.1%
19 Jun – 18 Jul	9	31.3	3.6	5.1	16.3%
18 Jul – 26 Aug	7	1.3	0.8	1.0	79.3%
26 Aug – 6 Oct	3	1.8	0.8	0.7	38.2%
6 Oct – 5 Nov	6	23.9	4.8	5.5	22.9%
5 Nov – 10 Dec	16	42.0	6.1	6.5	15.5%
10 Dec – 21 Jan	10	50.7	6.6	6.2	12.2%
21 Jan – 9 Apr	13	26.6	0.9	2.5	9.2%



**FIGURE 5.** Load estimates (in kg NO<sub>3</sub> over the indicated period) based on continuous (Hydriion), average (SC-samplers), and snapshot (grab sample) NO<sub>3</sub> measurements.



**FIGURE 6.** Load estimates in kg NO<sub>3</sub> based on “true” continuous NO<sub>3</sub> concentrations (Hydriion measurements), subsampled hypothetical SC-sampler-like average concentrations, and subsampled snapshot (grab sampling-like) data. The bars give the range of possible load estimates based on grab sampling, depending on the exact moment of sampling (see text for explanation).

can be estimated from short periods with high frequency measurements or from high frequency data from similar catchments. From our continuous water quality and discharge records, we found that NO<sub>3</sub> concentrations generally decreased with increasing discharges. This gives a negative covariance, which results in an overestimation of the loads when using average concentrations. Our continuous P concentration records (26) structurally showed a positive covariance with discharge, which would result in underestimation of loads when using average concentrations.

Another option to overcome the averaging bias is to measure flow-averaged concentrations instead of time-averaged concentrations. This would be achieved when the sample flow through the SC-sampler is proportional to the discharge. Laboratory tests showed that the sample flow velocity through the SC-sampler responds linearly to the water pressure gradient over the sampler. When the water pressure gradient also responds linearly to the discharge, the SC-sampler measures a flow-proportional average concentration. This could be realized by installing the sampler on the upstream side of a calibrated weir. For tile drains, laboratory test with a new mounting system for flow proportional measurements gave promising results (De Jonge, personal communication). Still, measuring flow proportional average concentrations with SC-samplers needs further field testing and development.

In summary, this study showed that the SC-samplers for average solute concentration measurements produce consistent results and may be a cost-effective alternative for grab sampling in regional water quality monitoring programs.

Average concentration measurements produce more consistent load estimates than “snapshot” concentrations from conventional grab sampling.

## Acknowledgments

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## Supporting Information Available

Maps of the research catchment (Figure S1) and SC-sampler locations (Figure S2); description of the SC-sampler field installation methods and laboratory analysis procedures (pp S3–S4); SC-samplers modifications during the optimization period (pp S5–S6); summary of all SC-sampler measurements in groundwater, tile drain effluent, and surface water during December 2007 to April 2009 (pp S7–S8); figure demonstrating the effects of positive and negative covariance between solute concentration and discharge records on load estimations based on average concentrations (Figure S5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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