



Article What Is the Suitable Sampling Frequency for Water Quality Monitoring in Full-Scale Constructed Wetlands Treating Tail Water?

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Abstract: Three years of hourly COD and NH_4^+ -N measurements for two full-scale integrated constructed wetlands (CWs) treating secondary effluents from sewage treatment plants (STPs) were used to quantify the proper sampling frequency (SF). The modified coefficient of variation (CV_m) and average variation rate (VR_a) were calculated to monitor the dynamics and annual average performance, respectively. It was found that (1) under CV_m 5%, VR_a 5%, and VR_m 5%, the sampling intervals (SI) of COD can be set as 1.19 h, 526.5 h, and 110.1 h, respectively, and the *SI* of NH₄⁺-N should be 4.51 h, 66.3 h, and 26.8 h, respectively; (2) under CV_m 10%, VR_a 10%, and VR_m 10%, the monitoring intervals of COD can be set as 11.92 h, 1401.7 h, and 233.5 h, respectively, and the monitoring intervals of NH₄⁺-N should be 30.73 h, 139.3 h, and 50.5 h, respectively. Therefore, to meet the need of monitoring the dynamic changes in data, hourly and 4 h *SI*s were recommended for COD and NH₄⁺-N evaluation, respectively, when it is necessary to consider the operation and maintenance costs at the same time, 11 h and 30 h *SI*s were proper for COD and NH₄⁺-N evaluation, respectively. The methods proposed in this study could provide reference to improve the management and evaluation level of full-scale CWs.

Keywords: integrated constructed wetland; secondary effluent; sampling frequency; dynamics monitoring; performance evaluation

1. Introduction

As an economic and environmentally friendly type of technology for wastewater treatment, constructed wetlands (CWs) have developed rapidly worldwide in recent decades, especially in China, with increasing requirements for surface water environmental quality. CWs have been widely used in many fields for the improvement of water quality [1], such as the deep purification of secondary effluent from sewage treatment plants (STPs), the centralized treatment of rural decentralized wastewater, and the pretreatment of polluted river water before flowing into lakes [2–6]. The evaluation of treatment efficiency is an important component of CW development, and it requires the dynamic monitoring of water quality for the influent and effluent. Due to the effect of numerous factors, such as investment, operating cost, and scale, different monitoring strategies were used, including the high sampling frequency (SF) of automatic monitoring by the establishment of stations, the low SF of manual sampling and laboratory measurement, and irregular sampling and measurement. Furthermore, the sampling interval (SI i.e., the reciprocal of SF) ranged from 15 min to one month [6,7].

Currently, although some studies have shown the importance of high-frequency and continuous monitoring as well as the problems of sporadic sampling for CWs [7–9], only a few studies have evaluated the effect of the SF on the estimation accuracy of water quality or removal efficiency (RE) and the proper SF for full-scale CWs. In related fields,



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). numerous studies have been carried out on the proper spatial or temporal SF as well as its influencing factors in relation to the monitoring of water quality of rivers [10,11]. These results could provide a valuable reference for the determination of a proper SF for full-scale CWs. However, in contrast to most natural rivers, in which water quality variation is dominantly influenced by rains and human-induced change [10], CWs are relatively closed systems, in which the rains have relatively lower effects on water quality due to the decreased catchment function of CWs relative to that of rivers regarding water volume control. In addition, different objectives drive the monitoring strategies of rivers and CWs, with the main purposes of load calculation and RE evaluation for rivers and CWs, respectively. As a result, the sampling strategies developed for rivers cannot be directly applied to CWs.

Similar to rivers, the use of an arbitrary SF for CW monitoring likely introduces redundancy or underrepresentation [12,13], which demonstrates the importance of research on the proper sampling strategies for CWs. During the stable operation period, a relatively low SF was applied to monitor CWs, and the *SI* typically ranged from one week to one month [14,15]. The occurrence of storm events can cause large fluctuations in water quality in both the influent and the effluent, and thus, a higher SF was applied after the storm [15]. The variability of effluent water quality in CWs was also influenced by the variability of the purification function of CWs, which is related to microbial activities, plant growth rate, and residue decomposition [7]. To the best of our knowledge, no studies have quantified the proper SF for CW treating secondary effluent from STPs, which has rapidly developed in recent years in China. Meanwhile, both the influent and the effluent water quality of the secondary CW are directly influenced by artificial operations, and thus, a different SF should probably be applied for different types of CW.

Therefore, the objective of this study was to quantify the proper SF for influent and effluent water quality and provide references for the management and evaluation of full-scale CWs, although it is not possible to define a proper SF for different CW and variables [16]. This study used two full-scale CWs for the deep purification of the secondary effluent from STPs that respectively treat industrial and municipal wastewater as examples. The water quality parameters were focused on chemical oxygen demand (COD) and NH₄⁺-N, which are two commonly used monitoring parameters for water quality in most CWs and surface water monitoring stations. To identify the suitable respective SF values for the dynamic monitoring and average performance evaluation in a period with the influent and effluent COD and NH₄⁺-N, there were three sub-objectives: (1) develop the parameters for identifying the suitable SF; (2) quantify the relationship between SF and monitoring accuracy; and (3) identify the suitable SF at the acceptable accuracies of 5%, 10%, and 15%.

2. Materials and Methods

2.1. Study Area

Both of the full-scale integrated CWs were situated in Hongze District, Jiangsu Province, East China (118°55′27″ E, 33°20′13″ N) (Figure 1), where the climate is sub-tropical with an annual average temperature of 14.9 °C and presents a clear distinction between the four seasons. The annual average precipitation is 913.3 mm [17,18].

The first CW system (named CW1 in the following text) possessed a designed wastewater treatment capacity of 40,000 m³·day⁻¹, which is composed of an aeration pond (AP), a facultative pond (FP), a free water surface flow CW (FWS), an ecological pond (EP), and an ecological canal (ECs) with hydraulic retention times (HRTs) of 6.7, 4.1, 3.4, 2.5, and 0.22 days, respectively. The influent of CW1 was mainly the secondary effluent from a municipal STP. The other system (named CW2 in the following text) had a designed wastewater treatment capacity of 60,000 m³·day⁻¹, which is composed of an AP, an FWS, a facultative pond (FP), a subsurface-flow CW (SSF), an EP, and ECs. The whole HRT of CW2 was 17.4 days. The influent of CW2 was mainly the secondary effluent from an industrial STP. More than 15 species of aquatic macrophytes were planted in CW1 and CW2, with *Phragmites australis* and *Typha orientalis* Presl as the dominant ones.



Figure 1. Geographic location and layout of (**a**) CW1 and (**b**) CW2 (AP, aerated pond; FP, facultative pond; FWS, free water surface flow constructed wetland; EP, ecological pond; SSF, subsurface flow constructed wetland).

2.2. Online Water Quality Monitoring

The influent and effluent water quality parameters were measured using online water quality monitoring systems, termed Inf-CW1 and Inf-CW2 for the influents of CW1 and CW2, and Eff-CW1 and Eff-CW2 for the effluents of CW1 and CW2, respectively. The wastewater was pumped into auto-measurement systems for measurement of COD and NH_4^+ -N, set up indoors with stable temperature, humidity, and lighting conditions. COD and NH_4^+ -N were detected using the potassium dichromate method and Nessler reagent spectrophotometry method, respectively. The hourly sample interval was set for the influent and the effluent of CW1 and CW2. Due to the absence of data in December 2018, the data from December 2015 to November 2016, December 2016 to November 2017, and December 2017 to November 2018 were regarded as the data in 2016, 2017, and 2018, respectively.

2.3. Data Evaluation Method

It is known that the coefficient of variation is the ratio of the standard deviation of a set of data to the mean value, which can reflect the dispersion of these data. The calculation formula is as follows.

$$CV = \frac{\sqrt{\frac{\sum(x-\bar{x})^2}{n-1}}}{\bar{x}} \times 100$$
(1)

To evaluate the short-term temporal variability of COD and NH_4^+-N , one of the important factors influencing the SF, the modified coefficient of variation (CV_m) was developed. Because the sample number (*n*) is two in each calculation, the equation can be simplified as follows:

$$CV_{m} = \frac{\sqrt{2} \times |x_{t1} - x_{t2}|}{(x_{t1} + x_{t2}) + c} \times 100$$
(2)

where x_{t1} and x_{t2} are the measured COD or NH₄⁺-N at times *t*1 and *t*2, respectively. The difference between *t*1 and *t*2 is the *SI*. To decrease the drastic fluctuation of the CV under conditions with very low COD or NH₄⁺-N, a constant c was added. The constant c was calculated using 5% of the potential maximum COD or NH₄⁺-N values. In this study, the constant c values were set to 5 mg/L and 2 mg/L for COD and NH₄⁺-N, respectively.

To obtain the average or overall performance in a certain period, the variation rate (VR) was calculated to quantify the variation of the average COD or NH_4^+ -N using a certain *SI* in a certain period from the average COD or NH_4^+ -N using the hourly *SI* data. In this study, two types of VR were developed to evaluate the effect of *SI* on the estimation accuracy, i.e.,

the average variation rate at a certain SI (VR_a) and the maximum variation rate at a certain SI (VR_m), which were obtained from the calculated VR:

$$VR = \frac{|\overline{x}_{SI-t} - \overline{x}|}{\overline{x}} \times 100$$
(3)

where \overline{x} is the average COD or NH₄⁺-N of all the measured values in this study, i.e., the hourly *SI* data. The \overline{x}_{SI-t} was the average COD or NH₄⁺-N of a certain *SI* with the measured COD or NH₄⁺-N at time *t* as the first value, i.e., one duplicate of a certain *SI*. For example, for the calculation of the average COD in 2018 at an *SI* of 10 h, there would be ten duplicates, i.e., the first measurements were at 0:00, 1:00, 2:00, 3:00, 4:00, 5:00, 6:00, 7:00, 8:00, and 9:00 on 1 January 2018, respectively. The VR_a and VR_m were the average values of the ten duplicates and the maximum VR in the ten duplicates, respectively.

3. Results and Discussion

3.1. The Average Value and Coefficient of Variation of COD and NH₄+-N

The statistics suggested that between 2016 and 2018, the average influent COD was 34.7 mg L⁻¹ and 40.4 mg L⁻¹, while the average effluent COD was 31.3 mg L⁻¹ and 33.1 mg L⁻¹ for CW1 and CW2, with REs of 10.0% and 18.1%, respectively (Table 1), which suggested that both CW1 and CW2 performed a slight removal of COD, probably related to the relatively low amount of readily biodegradable COD in the effluent wastewater from the STPs [19,20]. For CW1 and CW2, the NH₄⁺-N RE was 61.8% and 71.5%, respectively, suggesting that both of the CWs showed a high removal of NH₄⁺-N. The high NH₄⁺-N RE is probably related to the relatively high dissolved oxygen concentration and long HRTs [17].

Table 1. The average value and the coefficient of variation of COD and NH_4^+ -N in the influent and effluent water.

| Site | COL |) | NH4 ⁺ -N | | |
|---------|---------------------|--------|----------------------------|--------|--|
| | Mean (mg L^{-1}) | CV (%) | Mean (mg L ⁻¹) | CV (%) | |
| Inf-CW1 | 34.7 | 82.3 | 2.41 | 182.9 | |
| Eff-CW1 | 31.3 | 100.6 | 0.92 | 302.2 | |
| Inf-CW2 | 40.4 | 100.0 | 6.21 | 183.9 | |
| Eff-CW2 | 33.1 | 46.1 | 1.83 | 316.0 | |

In the past three years, both COD and NH_4^+ -N fluctuated in relatively large ranges in both the influent and the effluent of the two CWs (Figure 2), with an average CV value of 82.3% and 246.3% for COD and NH_4^+ -N (Table 1), respectively. The fluctuation range was much larger than most of the published results of full-scale CWs from the literature [21–23]. The large fluctuation of COD and NH_4^+ -N, on one hand, further proved the importance of SF in water quality monitoring for full-scale CWs; different *SIs* should be applied in both seasons and sampling sites for the monitoring of COD and NH_4^+ -N in CWs. On the other hand, the measured water quality by automatic monitoring systems in both the influents and the effluents of full-scale CWs; the seasonal average COD and NH_4^+ -N, as well as their variation in the effluent, is probably determined by numerous factors, such as the temperature dependence of the purification function of the CW [23,24], the influent water quality, and the rainfall events, while the water quality of the influent from STPs was most was likely influenced by numerous factors, such as rainfall events, human activities related to wastewater discharge, and process choice selected by the STP.





Figure 2. The temporal dynamics of the measured COD (**A**) and NH_4^+ -N (**B**) from 10 November 2015 to 28 November 2018 (n = 26,038). A logarithmic scale was used for the y-axis to improve the discrimination between samplings with values concentrated over relatively narrow regions (relatively low regions). The symbol "+" represents a data.

3.2. The Suitable Sampling Frequency in Modified Coefficient of Variation

As expected, the CV_m of NH_4^+ -N and COD between two samplings significantly increased with the SI for all four sampling sites, which could be well modeled using either exponential or power functions, with R² values of 0.998, 0.989, 0.991, 0.994, 0.990, 0.989, 0.985, and 0.991, respectively (Figure 3). For COD, when the SI increased from 2 h to 168 h, the average CV_m gradually increased from 6.7% to 23.6%, from 5.6% to 16.9%, from 7.9% to 27.1%, and from 5.5% to 17.4% for Inf-CW1, Inf-CW2, Eff-CW1, and Eff-CW2, respectively. Therefore, in CV_m , the COD for the four sites was relatively stable. However, the standard deviation (SD) values ranged from 11.6% to 23.1%, from 8.6% to 16.3%, from 10.6% to 25.1% and from 10.6% to 21.2%, with averages of 20.2%, 14.6%, 22.3%, and 18.3% for Inf-CW1, Inf-CW2, Eff-CW1, and Eff-CW2, respectively. For NH₄⁺-N, similar results were observed, i.e., the average CV_m ranged from 5.0% to 27.2%, from 3.7% to 13.8%, from 3.5% to 21.0%, and from 6.2% to 18.4% for Inf-CW1, Inf-CW2, Eff-CW1, and Eff-CW2, respectively. However, the average SD of NH_4^+ -N ranged from 20.2% to 28.8% for the four sampling sites. For the widely used daily and weekly SF, the variation rates in CV_m were 13.0% and 19.8% for COD and 14.0% and 20.7% for NH_4^+ -N, respectively. In addition, the relatively large SD values showed large temporal fluctuation in both COD and NH₄⁺-N, which suggested that there were large uncertainties in studying the temporal dynamics of COD or NH₄⁺-N without high SF data. The current widely used SF is not sufficient for studying the dynamics of water quality for secondary CW.

At 5%, 10%, and 15% CV_m , the SIs were statistically analyzed (Table 2). For the overall data of the three years, the SIs ranged from 0.2 to 1.7 h, 3.4 to 17.8 h, and 16.0 to 92.3 h for COD at 5%, 10%, and 15% CV_m , respectively; additionally, for NH_4^+ -N, the SIs ranged from 1.7 to 5.3 h, from 6.6 to 35.1 h, and from 16.3 to 291.6 h at 5%, 10%, and 15% CV_m, respectively. At 10%, the average SIs were 9.8, 16.6, 12.9, and 9.9 h for COD in spring, summer, autumn, and winter, respectively; for NH_4^+ -N, the values were 18.2, 44.8, 64.2, and 10.1 h in spring, summer, autumn, and winter, respectively. Therefore, between seasons, both COD and NH₄⁺-N were generally stable and thus allowed relatively larger SIs in summer and autumn; in contrast, COD and NH_4^+ -N varied more drastically and thus allowed relatively smaller SIs in winter. Between sampling sites, the effluent COD and NH_4^+ -N had larger SIs than that in the influent for both CW1 and CW2 in the same CV_m standard, with the exceptions of NH_4^+ -N in CW2 at 5% and 10% CV_m . The results suggested that, at 5%, 10%, and 15% acceptable variation in CV_m , the average SIs were 1.19, 11.92, and 80.53 h for COD and 4.51, 30.73, and 192.24 h for NH₄⁺-N, respectively. Generally, there requires a higher SF in winter than that in summer or autumn and a higher SF in the influent than that in the effluent.

Temporal variability is one of the dominant factors influencing the SF [16]. The parameter CV_m is probably not suitable for evaluating the overall performance of a CW in a certain period [9,25]. However, if the main purpose of monitoring is focused on the detailed process as well as the driving factors of the CW purification function, CV_m is probably a robust parameter that can quantify the temporal variation rate of water quality. Considering the inevitable error in the process of chemical analysis (or measurement instrument) and sampling, the 10–15% CV_m is probably more acceptable than the 5% standard for most cases in determining the proper SF, at which the suitable *SI* for the secondary CW ranged from the half-days to the weekly. However, the relatively large SD values suggested that, at such *SIs*, some detailed process information will be inevitably lost for secondary CWs, which is consistent with the results of previous studies [9].

| Site | Season – | COD | | | NH4 ⁺ -N | | |
|---------|----------|-----|------|-------|---------------------|-------|-------|
| | | 5% | 10% | 15% | 5% | 10% | 15% |
| Inf-CW1 | Spring | 0.3 | 4.0 | 17.8 | 1.3 | 3.3 | 8.2 |
| | Summer | 1.4 | 13.6 | 51.9 | 3.0 | 8.0 | 21.5 |
| | Autumn | 1.1 | 12.7 | 53.7 | 4.3 | 12.8 | 38.2 |
| | Winter | 0.9 | 8.3 | 29.8 | 3.6 | 6.9 | 13.5 |
| | Overall | 0.8 | 8.4 | 33.9 | 2.7 | 6.6 | 16.3 |
| Eff-CW1 | Spring | 1.1 | 8.9 | 72.6 | 4.2 | 50.6 | 611.4 |
| | Summer | 1.0 | 11.2 | 121.3 | 2.9 | 17.1 | 100.4 |
| | Autumn | 1.4 | 24.4 | 413.5 | 22.1 | 204.0 | 748.0 |
| | Winter | 1.3 | 12.4 | 47.3 | 2.9 | 15.9 | 86.0 |
| | Overall | 1.7 | 12.2 | 89.0 | 4.2 | 35.1 | 291.6 |
| | Spring | 1.4 | 4.7 | 15.9 | 4.6 | 12.7 | 35.4 |
| Inf-CW2 | Summer | 1.1 | 12.7 | 53.7 | 10.5 | 88.4 | 744.8 |
| | Autumn | 0.4 | 4.9 | 21.2 | 4.0 | 9.2 | 21.0 |
| | Winter | 1.8 | 4.1 | 9.5 | 3.6 | 15.0 | 34.2 |
| | Overall | 0.2 | 3.4 | 16.0 | 5.3 | 14.7 | 40.7 |
| Eff-CW2 | Spring | 2.2 | 21.6 | 81.7 | 1.5 | 6.2 | 26.5 |
| | Summer | 3.4 | 28.8 | 247.4 | 5.5 | 65.5 | 775.6 |
| | Autumn | 0.3 | 9.6 | 66.6 | 1.6 | 30.6 | 170.6 |
| | Winter | 0.9 | 14.6 | 75.5 | 0.7 | 2.5 | 8.1 |
| | Overall | 1.1 | 17.8 | 92.3 | 1.7 | 9.4 | 52.8 |

Table 2. The average SI (h) for the acceptable CV_m values of 5%, 10%, and 15%.

The water quality variation in the influent from the STP is influenced by the factors related to the STP operation performance, the artificial adjustment, and the wastewater discharged to the STP, which differs from polluted rivers and lakes [16,26]; thus, the variation characteristics of the influent water quality are different between the CW treating the secondary effluent from the STP and the CW treating other polluted water. Compared with the influent from polluted rivers or lakes, our results suggested that the influent from the STP varied more rapidly [10,16,23]. In this study, the influents of CW1 and CW2 were from the secondary STPs treating industrial and municipal wastewater, respectively. The difference in the source of the wastewater could also result in the difference in the water quality variation between CW1 and CW2. Our results suggested that the influent water quality variation rate of CW1 was more rapid than that of CW2.

The water quality variation rate of the effluent was mainly determined by the influent characteristic and the purification function of the CW. A linear relationship generally exists between the influent and effluent water quality of CWs [6,27], which can be weakened by the buffering function of CWs, especially for full-scale CWs [28]. The short-term fluctuation of the CW purification function is determined by the microbial activity, plant growth rate, and residue decomposition, which are related to environmental factors such as temperature. The diurnal and irregular fluctuation of temperature influences the effluent water quality fluctuation [29,30], which can also be weakened by the buffering function of the CW. Our result, i.e., the generally larger variation rate of the effluent water quality than that of the influent, can be explained by the buffering function of the CW [28], which is different from the CW treating the polluted river water [7].



Figure 3. The relationships between the sampling interval (*SI*) and the variation between the two sampling times in the modified coefficient of variation (CVm) for monitoring the temporal dynamics of COD (**A**) and NH₄⁺-N (**B**) (n = 26,038). R² values represent the coefficient of determination of the exponential or power model between the *SI* and CVm for monitoring the temporal dynamics of COD and NH₄⁺-N.

3.3. *The Proper Sampling Interval in Average Variation Rate and the Maximum Variation Rate* 3.3.1. Average Variation Rate (VR_a)

As expected, significant relationships were observed between the VR_a values and the *SIs* for both COD and NH_4^+ -N, which could be well modeled using power functions,

with R^2 values ranging from 0.82 to 0.93 and 0.79 to 0.90, respectively (Figure 4). When the *SIs* fluctuated between 2 h and 334 h, 1.37%, 1.29%, 2.30%, and 1.31% average VR_a values in COD and 6.18%, 11.2%, 4.12%, and 13.39% in NH₄⁺-N were observed for Inf-CW1, Inf-CW2, Eff-CW1, and Eff-CW2, respectively. According to the power models, the VR_a value at a certain *SI* could be quantified. For example, at *SIs* of 1, 7, and 14 days, an average VR_a of 0.49%, 1.61%, and 2.46% in COD and an average VR_a of 2.18%, 9.01%, and 15.00% in NH₄⁺-N was observed at the four sites, respectively. The results suggested that, for COD, increasing the *SI* from 2 h to 2 weeks only slightly decreased the monitoring accuracy in VR_a, while for NH₄⁺-N, the monitoring accuracy substantially decreased. For NH₄⁺-N, the estimation accuracy had only a slight decrease when the *SI* increased from 1 h to 1 day. Therefore, in VR_a, the daily *SI* was suitable for monitoring the average performance of COD and NH₄⁺-N.



Figure 4. The relationships between the sampling intervals (*SIs*) and the average variation rates (VR_a) for the evaluation of the three-year average performance of COD (**A**) and NH₄⁺-N (**B**) between 10 November 2015 and 28 November 2018. R² values represent the coefficient of determination of the power model between the *SIs* and VR_a for the evaluation of the three-year average performance of COD and NH₄⁺-N.

At the 5%, and 10% variation rates in VR_a, the *SIs* were statistically analyzed (Table 3). For COD, an average of 526.5, and 1401.7 h of *SI* were obtained for the four sites at the VR_a of 5% and 10%, respectively. For NH₄⁺-N, at VR_a values of 5% and 10%, ranges from 10.8 to 200.9 h and from 28.4 to 421.8 h were obtained, respectively, with an average of 66.3 and 139.3 h of *SI*. The results suggested that, at a 5% acceptable error in VR_a, the average *SI* was 526.5 and 66.3 h for COD and NH₄⁺-N, respectively. Therefore, in VR_a, the weekly and daily *SI* were suitable for monitoring the annual average COD and NH₄⁺-N, respectively.

| C'L. | | COD | | NH4 ⁺ -N | |
|---------|------|--------|--------|---------------------|-------|
| Site | | 5% | 10% | 5% | 10% |
| Inf-CW1 | 2018 | 450.0 | 1124.3 | 21.6 | 51.1 |
| | 2017 | 342.7 | 811.4 | 94.7 | 179.8 |
| | 2016 | 427.4 | 1019.9 | 102.8 | 193.9 |
| Eff-CW1 | 2018 | 379.5 | 1083.7 | 44.4 | 88.5 |
| | 2017 | 817.6 | 2234.8 | 10.8 | 28.4 |
| | 2016 | 451.4 | 1020.3 | 53.9 | 129.4 |
| Inf-CW2 | 2018 | 459.9 | 1131.7 | 30.5 | 63.1 |
| | 2017 | 261.6 | 530.1 | 96.2 | 177.3 |
| | 2016 | 232.1 | 665.8 | 200.9 | 421.8 |
| Eff-CW2 | 2018 | 822.1 | 2175.4 | 34.7 | 84.7 |
| | 2017 | 1255.6 | 3753.9 | 62.9 | 160.7 |
| | 2016 | 417.9 | 1269.3 | 41.8 | 92.3 |

Table 3. The average SF (h) for the average variation rate (VRa) values of 5% and 10%.

3.3.2. The Maximum Average Variation Rate (VR_m)

In Figure 4, the SD values were relatively large, i.e., the average SD values were 1.14% and 6.31% for COD and NH_4^+ -N, respectively. Therefore, to be safe, we also analyzed the proper *SI* using the stricter parameter of the VR_m value (Figure 5). Significant relationships were observed between the *SI* and VR_m values for both COD and NH_4^+ -N at the four sites, with R² values of 0.95, 0.92, 0.89, 0.94, 0.92, 0.92, 0.83, and 0.84, respectively. Compared with VR_a, the VR_m value greatly increased at the same *SI*. With the *SI* fluctuating between 2 and 334 h, the average VR_m values for the four sites were 5.09% and 29.00% for COD and NH_4^+ -N, respectively. In the VR_m value, weekly and daily were the suitable *SIs* for the calculation of the annual average values for COD and NH_4^+ -N, respectively, which could obtain an average estimation accuracy of 5.13% and 4.91% for COD and NH_4^+ -N, respectively.

For COD, at the acceptable errors of 5% and 10% in VR_m, the *SI* ranges of 53.8–163.9 and 123.6–361.6 h were obtained, respectively, with an average *SI* of 110.1 and 233.5 h, respectively (Table 4). For NH₄⁺-N, *SI* ranges of 6.1–70.0 and 12.4–134.4 h were obtained for the acceptable errors of 5%, and 10% in VR_m, respectively, with an average of 26.8 and 50.5 h, respectively. Generally, NH₄⁺-N required a lower *SI* than did COD. At the acceptable error of 5% in VR_m, the average SF was 110.1 and 26.8 h, respectively. Therefore, four-day and one-day *SI*s were suitable for the evaluation of the annual performance of the COD and NH₄⁺-N, respectively.



Figure 5. The relationships between the SF and the maximum variation rate (VR_m) in COD (**A**) and NH_4^+ -N (**B**) using all the data from 2016 to 2018 with the hourly SF data.

| | | COD | | NH4 ⁺ -N | |
|---------|------|-------|-------|---------------------|-------|
| Site | | 5% | 10% | 5% | 10% |
| Inf-CW1 | 2018 | 107.0 | 215.2 | 11.6 | 20.8 |
| | 2017 | 88.4 | 179.2 | 40.8 | 72.4 |
| | 2016 | 108.9 | 221.3 | 44.3 | 76.0 |
| Eff-CW1 | 2018 | 79.7 | 181.3 | 20.7 | 39.3 |
| | 2017 | 161.6 | 357.0 | 6.1 | 12.4 |
| | 2016 | 125.0 | 248.8 | 19.3 | 40.2 |
| Inf-CW2 | 2018 | 109.7 | 228.8 | 12.0 | 23.0 |
| | 2017 | 91.6 | 171.4 | 42.7 | 77.2 |
| | 2016 | 53.8 | 123.6 | 70.0 | 134.4 |
| Eff-CW2 | 2018 | 156.1 | 338.1 | 14.8 | 30.6 |
| | 2017 | 163.9 | 361.6 | 21.5 | 45.5 |
| | 2016 | 75.3 | 175.3 | 18.2 | 34.5 |

Table 4. The average SF (h) for the maximum variation rate (VRm) values of 5% and 10%.

In contrast to CV_m , the parameter VR_m (or VR_a) at the annual scale generally experiences a relatively lower influence by the periodic variation in water quality, such as the variation related to the diurnal and seasonal variation in temperature. However, the SF should be high enough to obtain information on the short-term and strong fluctuation of water quality related to events such as storms and snow melting [9,10]. To decrease the direct effect of the toxic secondary effluent from STPs on human health, secondary CWs are generally built in areas isolated from residential communities; thus, water quality is seldom directly influenced by irregular human activity, such as the discharge of untreated polluted water. The catchment function of the secondary CW also decreases by building isolated rivers along with the secondary CW that prevent the outflow of the toxic secondary water, which can greatly decrease the effect of short-term and strong events, such as storms and snow melting [9,26,31]. These characteristics of the secondary CW can greatly decrease the SF requirement.

However, there are some factors that can increase the fluctuation of water quality and thus the SF demand. In CW, the relatively large biomass of aquatic macrophytes can induce the short-term strong fluctuation of water quality, especially at the early decomposition stage of the dead residue [18]. In addition, compared with polluted rivers or lakes, the water quality of the influent directly from the STP fluctuates more than that of the polluted rivers or lakes due to the buffering of rivers or lakes [10,16,23]. Therefore, the SF of the secondary CW must be high enough to obtain information about the short-term and probably strong fluctuations in water quality caused by these factors. As an alternative, instead of a constant SF, real-time adaptive sampling controlled by trigger variables may be more efficient because it balances the obtainment of the hot moments of nutrient dynamics and reduces data redundancy [26]. In future work, the suitability of the adaptive sampling strategy needs to be identified in secondary CWs.

4. Conclusions

The suitable sampling frequency was quantified at the acceptable errors of 5% and 10%. At 5% of CV_m , the average *SIs* were 1.1 h and 4 h for COD and NH_4^+ -N. At 10% of CV_m , the average *SIs* were 11.92 and 30.73 h for COD and NH_4^+ -N, respectively. At 5% of VR_a , the average *SIs* were 526.5 and 66.3 h for COD and NH_4^+ -N, respectively. At 5% VR_m , the average *SIs* were 110.1 and 26.8 h for COD and NH_4^+ -N, respectively. Therefore, to meet the needs of monitoring the dynamic change of data and annual effect evaluation at the same time, hourly and 4 h *SI* were recommended for COD and NH_4^+ -N evaluation, respectively, when strict requirements are required; when it is necessary to consider the operation and maintenance costs at the same time, 11 h and 30 h *SIs* were proper for COD and NH_4^+ -N

evaluation, respectively. This research developed the methods for quantifying the suitable sampling frequency in the dynamic monitoring and average performance evaluation and also identified the relationship between sampling frequency and monitoring error for the dynamic analysis and average performance evaluation in specific periods, which could be promoted to other full-scale CWs.

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