

# Identifying feasible nonpoint source pollutant sampling intervals for watersheds with paddy field and urban land uses

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## ABSTRACT

Monitoring provides data and information necessary for water quality assessment, but often it is prohibitive, especially when frequent sampling is required. In this study, we explored feasible sampling intervals for improved efficiency of nonpoint source (NPS) pollution assessment. We compared NPS pollutant loads calculated with concentration samples collected at 1, 2, 3, 4, and 6-hour intervals for the first 24 hours of 13 storm events and investigated the effect of different sampling intervals on load estimation for three watersheds that have different land uses. When compared to load estimates made from concentrations sampled at the reference (1-hour) interval, differences in load estimates were less than 10% in the cases of the 2-hour and 3-hour intervals in the urbanized and agricultural watersheds, respectively, except in the case of suspended solids (SS). When it comes to the total load estimation, up to 3-hour interval sampling provided load estimates with acceptable accuracy, except for SS. Thus, the 3-hour sampling interval was considered feasible for long-term pollutant load assessment, while the 2-hour sampling interval was suggested for SS. Such findings are expected to facilitate NPS pollution assessment by providing information required to improve monitoring efficiency.

**Key words** | load estimation, nonpoint source pollution, sampling frequency, sampling interval, storm event, water quality monitoring

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## HIGHLIGHTS

- The efficiency and accuracy of different water sampling intervals were assessed for improved feasibility of nonpoint source pollutant monitoring.
- The sampling intervals of equal to or less than 3 hours could provide accurate and efficient pollutant load estimates in agricultural areas.
- Urbanized areas required relatively frequent water sampling to satisfy the required accuracy.

## INTRODUCTION

Nonpoint source (NPS) pollution is closely associated with hydrological processes including the generation and

accumulation of pollutants during a dry period and their transport and loading to downstream waterbodies during a rainfall event. Thus, there are various environmental factors such as land use, management practices and weather events that influence NPS pollution processes (Beman *et al.* 2005). A frequent sampling can capture the details of highly

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variable pollutant generation and transport processes, and thus it is recommended as a method to quantify NPS pollution (Halliday *et al.* 2012; Frazar *et al.* 2019). Such a monitoring strategy is also required to establish control measures and identify the characteristics of NPS pollutants (Kirchner *et al.* 2004; Kal *et al.* 2017). In relatively small watersheds, the best method for determining the contribution of these sources is likely to be a high-frequency sampling strategy using an autosampler (Harmel *et al.* 2003; Harmel *et al.* 2006b). Factors that affect uncertainty in data produced by automated samplers (sampling threshold, sampling interval, discrete or composite sample type) have been evaluated and discussed (e.g., Shih *et al.* 1994; Miller *et al.* 2000, 2007; Stone *et al.* 2000; Harmel *et al.*, 2002, 2003, 2006b; King & Harmel 2003, 2004; Harmel & King 2005; Harmel *et al.* 2010).

A frequent sampling strategy is recommended for its accuracy, but it requires additional costs, which sometime makes monitoring impractical. Efficient water quality monitoring requires a balance between cost and accuracy. Thus, it is critical to find a threshold sampling interval that provides insignificant differences between actual loads and load estimates made from the limited amount of water quality sampling data (Han & Kim 2005; Harmel *et al.* 2006a). The US Environmental Protection Agency (USEPA 1993) recommends obtaining at least 10 samples per rainfall event for water quality characterization.

Thompson *et al.* (2014) considered suspended solids (SS) loads estimated from concentration measurements made at a 15-minute interval as a true value. They investigated the effect of sampling interval on load calculation and found that the 7-hour sampling interval is efficient. Defew *et al.* (2013) found that total phosphorus load was relatively accurately estimated from 2-hour interval sampling compared to load estimates made from other longer sampling intervals such as daily and weekly. King & Harmel (2003) evaluated the loading calculation accuracy of various combinations of sampling intervals and flow velocities and found that short sampling intervals of less than 15 minutes may provide relatively accurate nutrient loading estimates. Toor *et al.* (2008) estimated nutrient and sediment loads with concentration data from four low-frequency sampling strategies (single stage, random, peak, and rise fall) and reported

that load estimates were often poor. Low-frequency sampling programs can still be appropriate in some larger watersheds when paired with statistical techniques to estimate constituent loads (Haggard *et al.* 2003). Bowes *et al.* (2009) and Jordan *et al.* (2012) found that more than 80% of the annual phosphorus load is generated by two to three large rainfall events, highlighting the importance of monitoring nutrient concentrations at short sampling intervals for high flow rates. The previous studies tried to identify efficient water quality sampling frequency, but they focused on a few specific pollutants and/or agricultural watersheds without paddy fields under a monsoonal climate.

Urbanized watersheds usually have a relatively short time of concentration, compared to agricultural ones, due to pavements and sewer systems. The Korean Ministry of Environment (MOE 2012) recommends sampling water quality at a 1-hour interval for the first 24 hours of a storm event in watersheds with various land uses including urban landuse, so that the monitoring can capture the initial surface runoff (or first flush) that disproportionately delivers most of the pollutants (Jeung *et al.* 2019). However, such high frequency sampling can be too expensive to be implemented in routine monitoring practice. We investigated if sampling intervals longer than the MOE (2012) recommendation can provide the acceptable level of accuracy when estimating NPS pollutant loads to develop a 'feasible' sampling interval that can help save funds if implemented. It is feasible, because it suggests proper sampling intervals without loss of accuracy in constituent load estimates and also can minimize cost both in sampling time and sample analysis. This study monitored runoff discharge and the concentrations of various NPS pollutants at the outlets of three study watersheds with different urban settings, upland and paddy fields. It included 13 storm events observed between 2015 and 2017 and a set of constituents including biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), suspended solids (SS), total nitrogen (T-N), and total phosphorus (T-P). We compared pollutant loads calculated from the pollutant concentrations sampled at different time intervals for the first 24 hours of storm events and evaluated the differences between the load estimates to identify feasible sampling frequencies for NPS pollutant monitoring.

## MATERIALS AND METHODS

### Study areas

The three watersheds are nested and located within the larger Pungyeongjeongcheon (PYJ) watershed in Southern Korea (Figure 1). The watershed drains 68.9 km<sup>2</sup>, and the stream is 14 km long. NPS pollutant monitoring was conducted at the outlets of the subwatersheds, Woljeong (WJ) (35°13'47.98"N, 126°48'31.85"E), Jangsu (JS) (35°10'43.60"N, 126°48'43.28"E), and PYJ (whole watershed outlet) (35°9'56.16"N, 126°49'10.97"E). The three study watersheds are covered by mixed land uses including paddy fields, upland farming areas, urban, and forest, but their areal coverage is distinct to each watershed (Table 1). The WJ watershed is mostly covered by agricultural areas (62.2%, mostly rice paddy fields) with small urban land uses (6.2%), while the JS watershed is relatively highly

urbanized (36.0%) including industrial areas, residential areas, offices and restaurants, and agricultural areas cover about 28.8% of the watershed. Overall, the PYJ watershed consists of agricultural land uses (46.9%) and urban area (25.7%) (Table 1).

Weather data collected at one of the Korea Meteorological Administration's stations, Gwangju, showed that the study areas receive rainfall of 1,391 mm annually on average, and the average annual maximum and minimum temperatures are 29.3 °C and 1.9 °C, respectively. More than half of the rainfall (50–60%) concentrates in summer (June through September), which makes the study areas belong to the monsoon climate region. The study areas are 11 m above mean sea level (MSL), and the highest elevation of 548 m from MSL is observed in the WJ watershed. The soils are characterized by silty clay loam and silt loam. The population densities of the study watersheds are 201, 7,500, and 3,483 persons/km<sup>2</sup> for

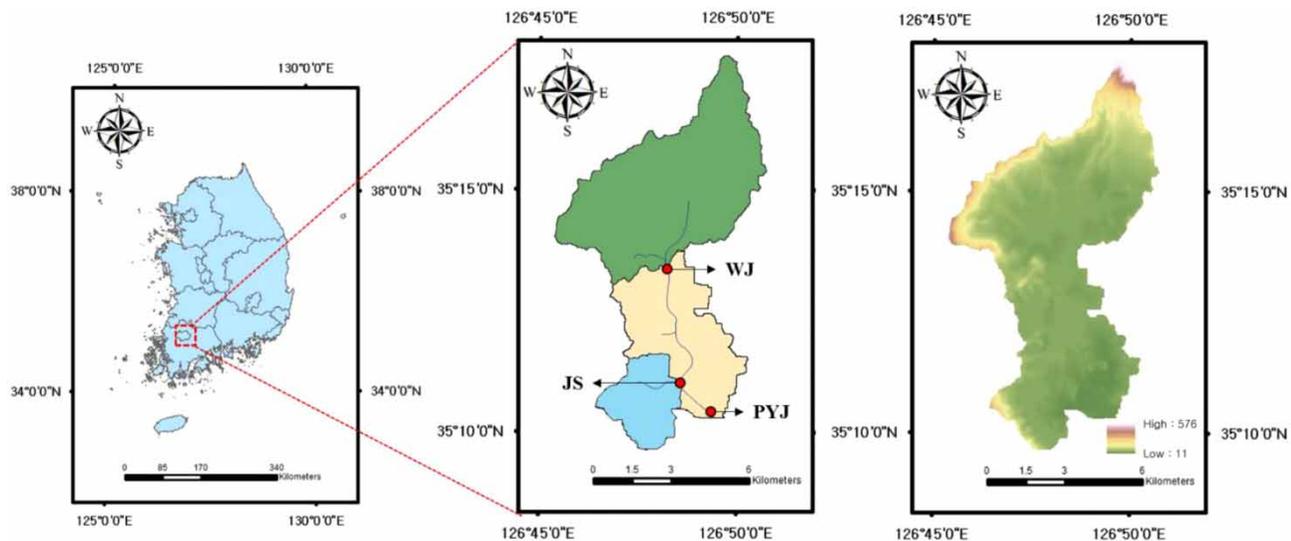


Figure 1 | Locations of the study watersheds and NPS pollutant monitoring stations.

Table 1 | Area and land uses of the study watersheds in Km<sup>2</sup> (with percentages in parentheses)

Watershed	Paddy	Upland	Urban	Forest	Others	Total
WJ	12.6* (36.1)**	9.1 (26.1)	2.17 (6.2)	8.4 (24.0)	2.7 (7.7)	34.9 (100.0)
JS	1.0 (12.5)	1.3 (16.3)	2.9 (36.0)	1.6 (20.0)	1.2 (15.3)	8.0 (100.0)
PYJ	16.9 (24.5)	15.4 (22.4)	17.7 (25.7)	11.0 (16.0)	7.9 (11.4)	68.9 (100.0)

\*Area (km<sup>2</sup>); \*\*area percentage (%).

WJ, SJ, and PYJ, respectively. The urbanized areas in the study watersheds are equipped with combined sewer systems.

### NPS pollutant concentration monitoring and load calculations

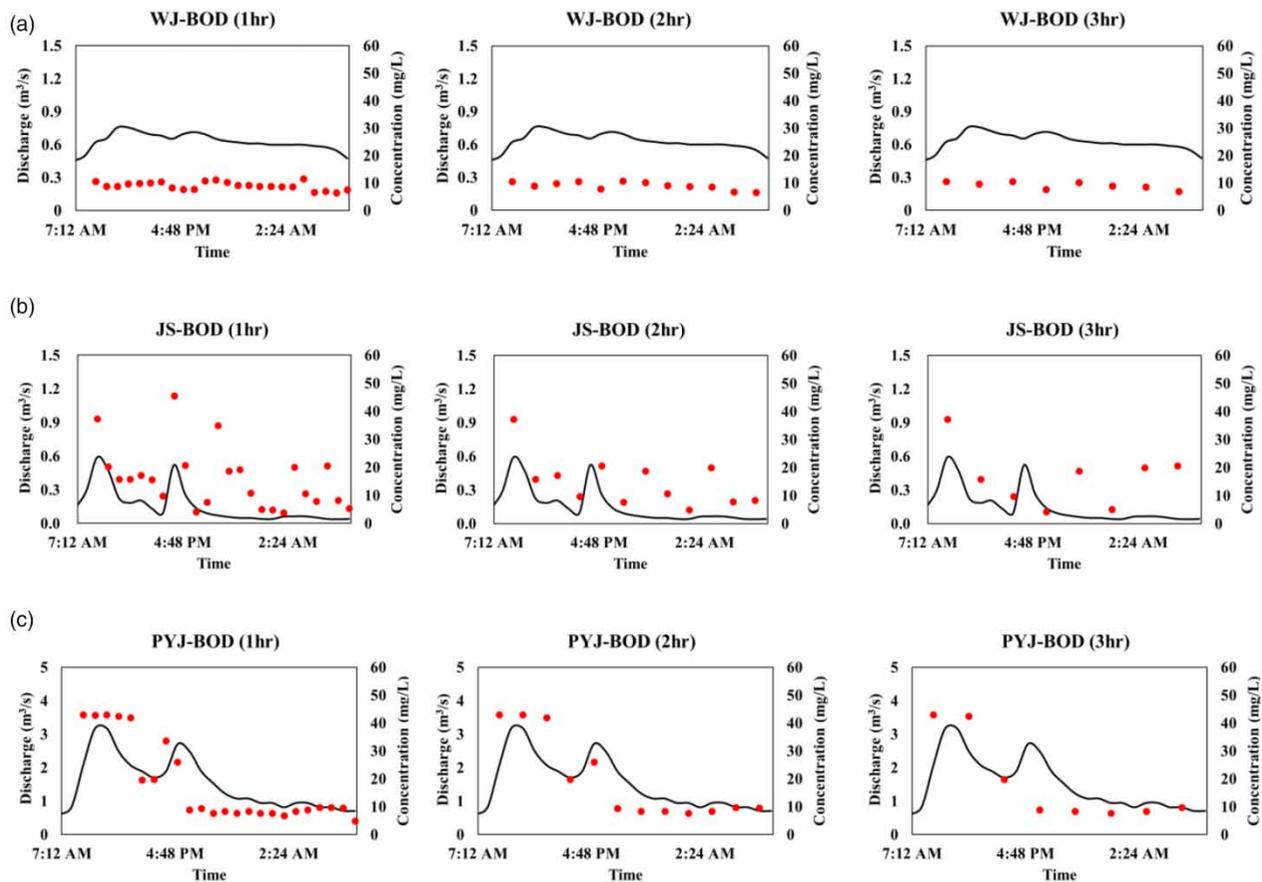
The stream water level was measured every 10 minutes using an automated water level gauge installed at the outlet of the WJ and JS watersheds, and the water levels were converted to flow discharges using rating curves developed for each outlet. Flow discharge records made at the outlet of PYJ were obtained from the Ministry of Land, Infrastructure and Transport. Water quality monitoring was carried out using an ISCO 1570 sampler, according to the method suggested by MOE (2012). The collected water samples were analysed in accordance with the standard

water pollution test method (APHA 2001). Then, the NPS loads were calculated by multiplying the observed concentrations by the corresponding flow discharges.

### Load estimations using different sampling intervals

The sampling intervals were manipulated to compare NPS pollutant load estimates made from different sampling frequencies (Figure 2). For instance, the 1-hour and 3-hour interval sampling strategies gave 24 and 8 pollutant concentration measurements in the first 24 hours of a storm event, respectively. In this study, the sampling intervals were increased from 1 hour to 2, 3, 4, and 6 hours.

In addition, a feasible sampling frequency was identified when the differences in load estimates made using the concentrations of water samples taken at the finest (or



**Figure 2** | Variations of flow discharges (solid line) and BOD concentrations (dots) made from employing the different sampling intervals of 1, 2, and 3 hours, on May 9, 2017. (a) WJ, (b) JS, and (c) PYJ.

reference) sampling interval (i.e., 1 hour) and the other intervals became less than 10%.

Considering the potential total uncertainty associated with sediment and nutrient load estimation processes, the threshold of 10% is reasonable (Harmel *et al.* 2006a). A null hypothesis was made on the differences between the NPS load estimates for different sampling intervals, which presumes that there is no difference in load calculations with varying sampling intervals at the significance level of 0.05. A normality test implemented in this study showed that the measurements do not follow the normality assumption; thus, the non-parametric Wilcoxon signed-rank test was employed to test the null hypothesis.

## RESULTS AND DISCUSSION

Observed date, rainfall amount, duration and intensity, and antecedent dry days of each storm event are summarized in Table 2. The observed rainfall amount ranged from 5 to 54 mm. The monitoring data showed that average COD, TOC, T-N and T-P concentrations and their ranges, observed from 13 storm events occurring in 2015 through 2017 are similar across the three study watersheds (Table 3). On the other hand, JS and PYJ had relatively higher BOD concentrations than did WJ, and JS produced much higher SS

**Table 3** | Observed averages and ranges (values in parentheses) of concentrations of water quality constituents measured in the three studied watersheds

	WJ (agricultural, mg/L)	JS (urban, mg/L)	PYJ (mg/L)
BOD	4.90 (1.60 ~ 26.1)	8.8 (1.90 ~ 57.8)	8.0 (1.5 ~ 43.0)
COD	9.1 (3.60 ~ 31.9)	10.2 (3.7 ~ 50.6)	10.5 (4.6 ~ 58.0)
TOC	6.7 (3.40 ~ 28.5)	7.8 (2.1 ~ 57.5)	7.7 (2.5 ~ 30.8)
SS	46.7 (3.1 ~ 737.1)	353 (8.7 ~ 4,025)	90.6 (3.1 ~ 767)
T-N	2.45 (1.02 ~ 13.7)	2.38 (0.773 ~ 5.83)	2.47 (0.703 ~ 10.9)
T-P	0.195 (0.015 ~ 0.515)	0.238 (0.008 ~ 1.79)	0.238 (0.023 ~ 1.21)

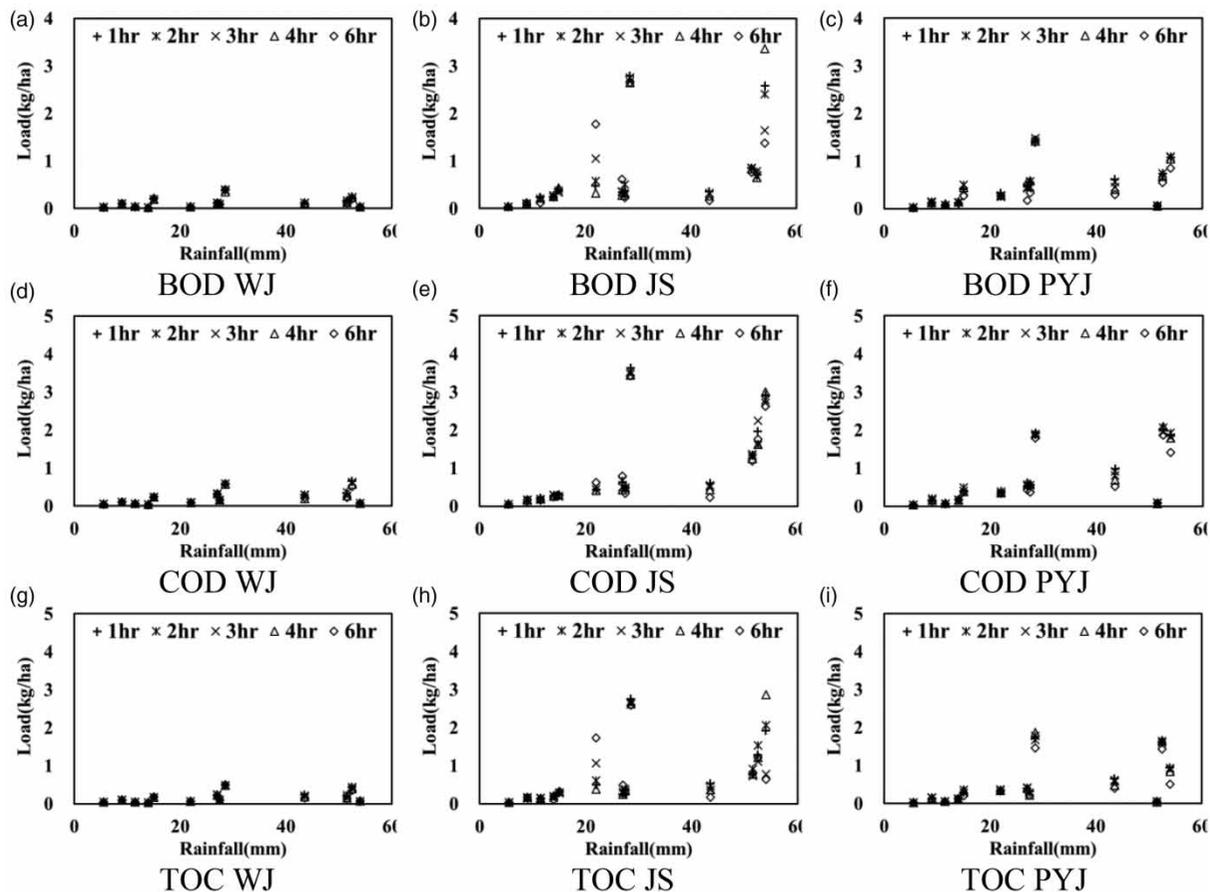
concentrations compared to WJ and PYJ. There must be many factors that contributed to the watershed-wise differences in the NPS pollutant concentrations, and the land use differences would be one of them. WJ has a relatively large percentage of area in agriculture compared to JS and PYJ. This is a good analogy to studies that found higher organic matter concentrations in water discharged from urban watersheds than agricultural ones (Lee *et al.* 2010; Liyanage & Yamada 2017; Wen *et al.* 2017). In addition, the SS for JS (a relatively more urbanized watershed) showed higher concentrations than those of WJ where rice paddy fields are dominant. Paddy fields are known to help reduce soil erosion and sediment transport because of their water ponding conditions (Lee *et al.* 2011; Chen *et al.* 2013; Slaets *et al.* 2016).

**Table 2** | Observed date, rainfall amount, duration, rainfall intensity, and antecedent dry days

Event	Date	Rainfall (mm)	Rainfall duration (hr)	Rainfall intensity (mm/hr)	Antecedent dry days (days)	Rainfall for the first 24 hr (mm)
1	04/03/2015	11.5	2.6	4.36	0	11.5
2	05/11/2015	27.5	14.0	1.96	7	27.5
3	07/11/2015	43.5	43.9	0.99	1	37.5
4	08/11/2015	22.0	22.9	0.96	2	22.0
5	09/23/2015	14.0	10.0	1.40	17	14.0
6	10/01/2015	54.0	22.2	2.43	7	54.0
7	04/26/2016	51.5	37.1	1.39	4	43.5
8	08/26/2016	27.0	25.0	1.08	2	22.0
9	09/28/2016	5.5	25.0	0.22	9	5.0
10	10/16/2016	52.5	26.0	2.02	7	52.0
11	04/11/2017	9.0	8.0	1.13	4	9.0
12	05/09/2017	15.0	28.8	0.52	3	14.0
13	07/08/2017	28.5	21.9	1.30	1	28.5

BOD, COD and TOC loads estimated for the watersheds were investigated by the different sampling intervals (Figure 3). The urban watershed (JS) showed relatively higher loads than the rural watershed (WJ). Toor et al. (2008) reported that annual nutrient and sediment concentration and load measurements varied considerably in cultivated and mixed land use watersheds but not in a pasture watershed. Such difference is attributed to the annual variability in constituent source and transport mechanisms that vary according to the vegetative cover conditions, fertilizer inputs and application timing, and precipitation timing and intensity, all of which affect the relation between daily flow and NPS pollutant concentrations. A similar trend was found in this study (Figure 3). The temporal variations of load estimates made in the rural watershed (WJ) that has relatively many paddy fields were relatively smaller than those of the other watersheds (Figure 3).

In the case of the rural watershed (WJ), the BOD, COD and TOC load estimates were made using the different sampling intervals. No statistically significant differences were detected between the sampling intervals (Figure 3(a), 3(d) and 3(g)). Such findings indicate that the pollutant concentrations and loadings are relatively stable (or constant) over time, and the first flush effects (FFE) were small in the rural watershed. This may be attributed to the fact that rice paddy fields cover the large part (36.1%) of the WJ watershed. On the other hand, significantly large differences were found between BOD and TOC load estimates in the case of the more urbanized watershed, JS, especially with relatively large storm events (e.g., rainfall of 22 and 54 mm). The differences would be attributed to the inflow of point sources such as the combined sewer overflow (CSO). In general, TOC follows the loading patterns similar to those of COD in urban storm runoff (Choi et al. 2013);



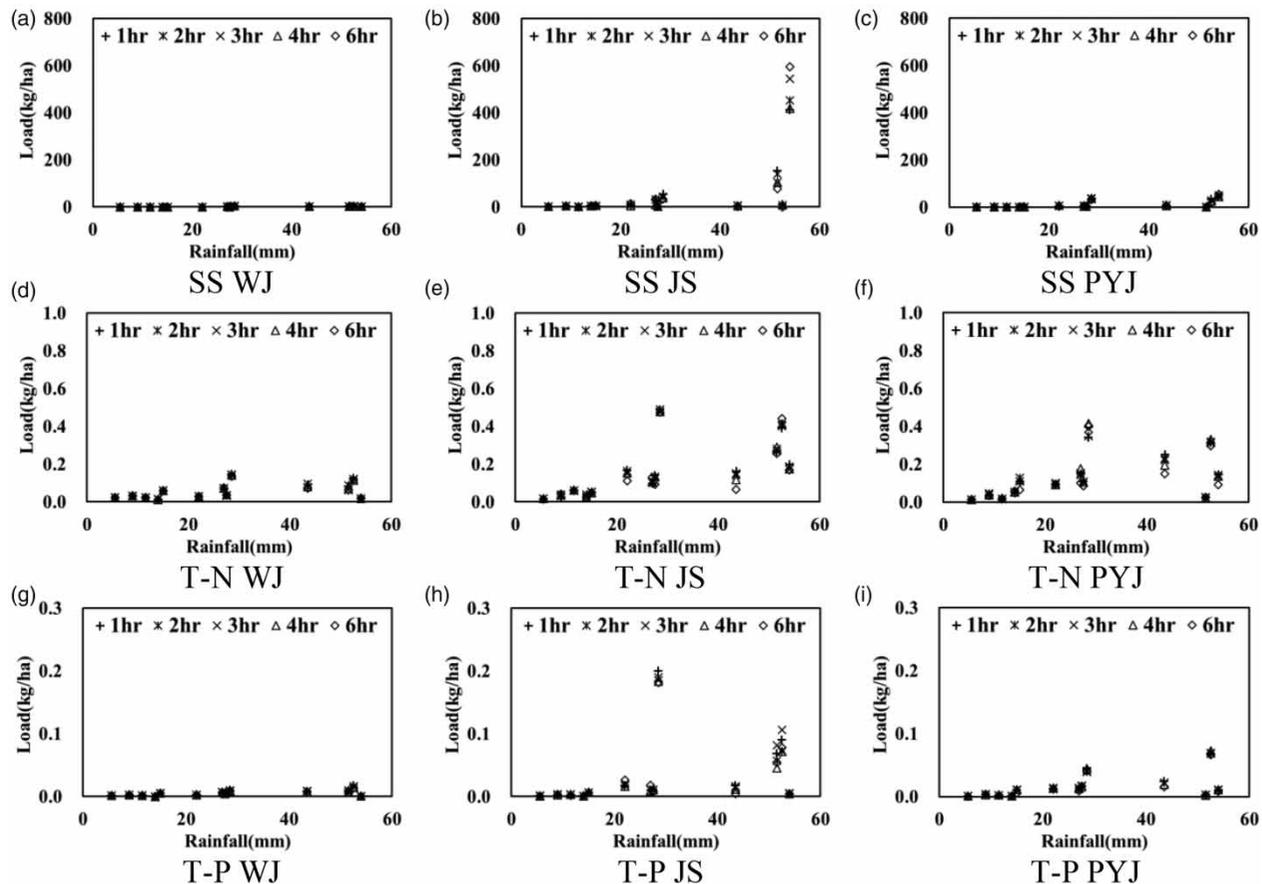
**Figure 3** | NPS pollutant (BOD, COD and TOC) load estimates made from using the different sampling intervals as a function of rainfall amounts. (a) BOD WJ. (b) BOD JS. (c) BOD PYJ. (d) COD WJ. (e) COD JS. (f) COD PYJ. (g) TOC WJ. (h) TOC JS. (i) TOC PYJ.

however, the TOC pattern closely resembles that of BOD in JS. Li *et al.* (2017) reported that the FFE was weak in a paddy watershed due to the detention function of paddy fields. Kim *et al.* (2002) demonstrated that pollutant concentrations in runoff varied quickly in urbanized areas compared to those of agricultural and forested areas, which agrees with our findings.

Differences between the SS load estimates were great in the cases having large rainfall of 51.5 mm and 54.0 mm in JS (Figure 4). Kim *et al.* (2002) demonstrated that the SS concentrations of runoff varied rapidly in urban watersheds. Kwak *et al.* (2012) found that SS concentrations quickly increased from 5.0 mg. L<sup>-1</sup> to 865.7 mg. L<sup>-1</sup> within a storm event in Korea. Soil detachment and transport are highly complicated with spatiotemporally varied rainfall and overland flow processes, and large storm events tend to have higher spatiotemporal heterogeneity in their rainfall,

sediment erosion and transport processes. In addition, sediment and dirt are accumulated on the roads and quickly transported along a sewer system in an urbanized area. Wastewater treatment facilities can also produce solid-laden water (Carter *et al.* 2003; Taylor & Owens 2009) that discharges to the surface waters. According to a study implemented in the highly urbanized Kyeongan river watershed in Korea, a large amount of SS tended to be generated at the beginning of a storm event (Kim *et al.* 2002). Such characteristics of an urban watershed are reasonably suspected to contribute to the differences found in the case of SS in JS compared to the other two watersheds, as seen in the wide range in minimum and maximum concentrations (Table 2).

Nitrogen compounds, such as nitrogen effluent from CSO, are considered to affect nitrogenous BOD (NBOD) concentrations by depleting oxygen content in water. Jang



**Figure 4** | NPS pollutant (SS, T-N and T-P) load estimates made from using the different sampling intervals. (a) SS WJ. (b) SS JS. (c) SS PYJ. (d) T-N WJ. (e) T-N JS. (f) T-N PYJ. (g) T-P WJ. (h) T-P JS. (i) T-P PYJ.

*et al.* (2010) found that nitrogen compounds, including  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , promoting nitrification were abundant in urban watersheds, which supports the results of this study. The difference in the load estimates did not show a clear relationship with rainfall (Figure 4). Park *et al.* (2014) compared the T-N concentrations made in storm periods in the Han River basin of Korea and found there was no significant change in the T-N concentrations in the first parts of rainfall events, which agrees with the results of our study. The constant T-N concentrations might be due to the high mobility of nitrogen and its derivative compounds such as nitrate and nitrite.

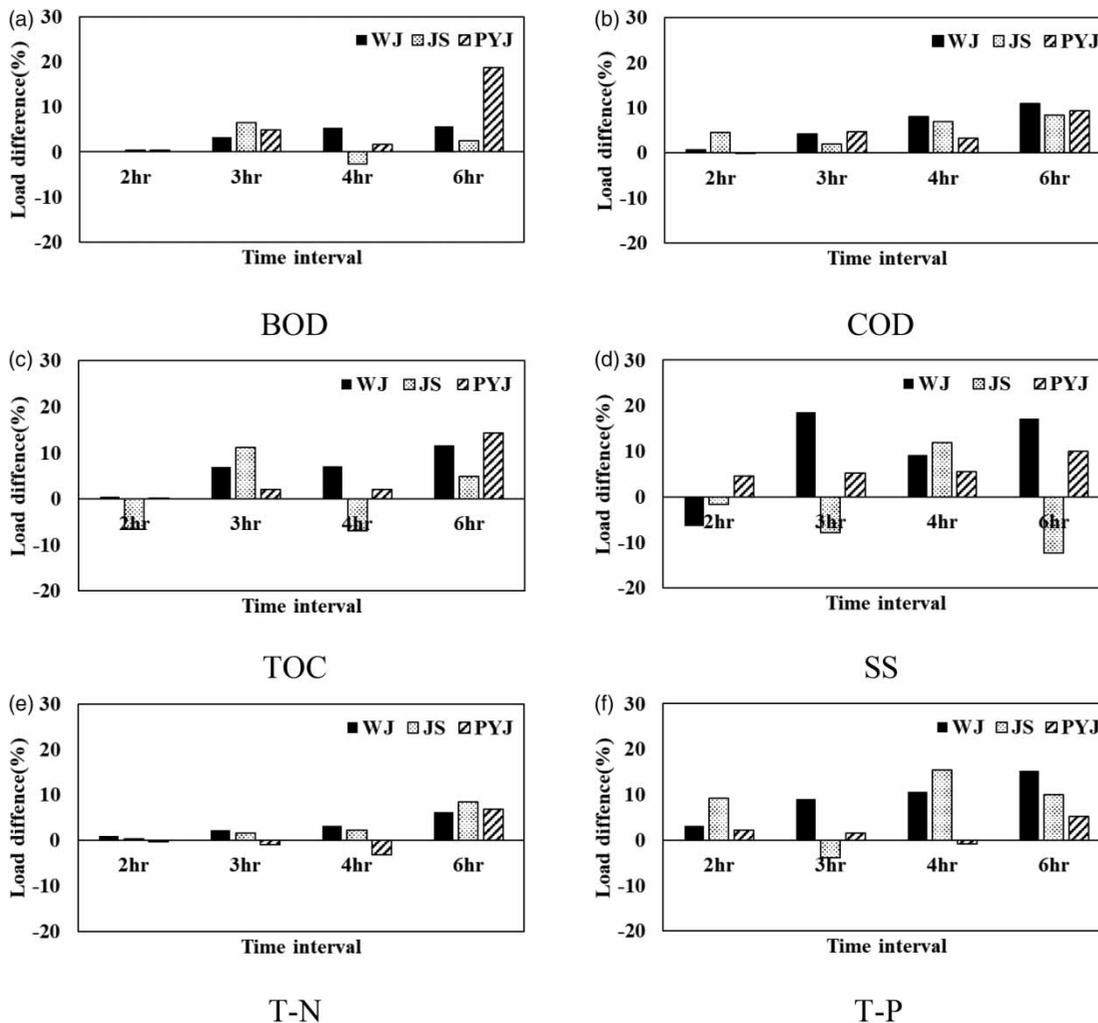
The load estimates made by using pollutant concentration samples taken in the different intervals were compared with those of the reference 1-hour interval sampling (Table 3). The differences between the NPS load estimates tend to increase with increases in the sampling intervals; however, it was not always the case (Table 4). The Wilcoxon test results showed there was no significant difference between load estimates made with the 1-hour sampling interval and the other intervals for all the NPS pollutants in JS at the significance level of 0.05. In the case of the whole watershed (PYJ), BOD, COD, TOC and T-P

estimates were significantly different from those made from the 6-hour sampling interval. In the rural watershed (WJ) where paddy fields are dominant, TOC from the 3-hour sampling, and T-P from the 3-hour and 6-hour sampling showed significant differences (Table 3). In terms of the percentage difference threshold of 10%, the BOD, COD, TOC, T-N and T-P estimates made from the sampling intervals of 4 hours could be regarded as acceptable in WJ. On the other hand, the acceptable sampling intervals decreased to 3 hours and 2 hours in the cases of PYJ and JS, respectively. The same explanation of urban areas' high organic matter contributions can be applied to such differences between the watersheds. When it comes to SS, only the 2-hour sampling interval produced acceptable estimates in the WJ and PYJ watersheds but unacceptable in JS.

The total NPS pollutant load estimates made from the 13 events were compared by sampling intervals (Figure 5). Overall, the 3-hour interval sampling provided acceptable accuracy of load estimates (the differences are less than the threshold of 10%), compared to the reference interval of 1 hour, except for SS. The differences between the total load estimates increased with increases in the sampling intervals. In the case of SS, only the 2-hour

**Table 4** | Statistics of the differences between the load estimates made using the reference (1-hr) and other sampling intervals

		Average load difference in percentages (and standard deviations by sampling interval, in parantheses)			
	Watershed	1 hr vs. 2 hr	1 hr vs. 3 hr	1 hr vs. 4 hr	1 hr vs. 6 hr
BOD	WJ(Rural)	3.17 (1.97)	5.92 (6.14)	8.48 (5.37)	10.21 (10.89)
	JS(Urban)	12.06 (12.28)	23.99 (33.27)	17.45 (14.61)	49.39 (71.53)
	PYJ(Mixed)	8.40 (7.33)	9.05 (7.45)	15.42 (13.37)	23.43 (19.29)
COD	WJ(Rural)	2.56 (2.08)	4.44 (5.28)	8.68 (10.24)	11.38 (11.53)
	JS(Urban)	9.14 (10.98)	13.84 (15.04)	14.38 (15.85)	24.75 (21.22)
	PYJ(Mixed)	5.66 (5.66)	5.89 (5.18)	10.66 (9.68)	16.90 (11.71)
TOC	WJ(Rural)	3.15 (3.75)	6.96 (7.43)	9.01 (9.47)	12.47 (13.08)
	JS(Urban)	10.48 (11.11)	28.28 (34.10)	17.28 (19.25)	51.80 (66.91)
	PYJ(Mixed)	6.56 (6.24)	5.51 (4.03)	11.66 (9.96)	17.85 (14.16)
SS	WJ(Rural)	6.86 (5.39)	16.98 (12.70)	12.97 (7.82)	17.77 (14.16)
	JS(Urban)	18.80 (14.45)	34.46 (19.81)	31.61 (24.34)	55.60 (35.80)
	PYJ(Mixed)	5.51 (4.92)	13.16 (10.36)	21.08 (23.89)	22.86 (15.54)
T-N	WJ(Rural)	3.40 (3.81)	5.33 (6.11)	6.24 (3.61)	7.82 (7.44)
	JS(Urban)	5.75 (8.09)	12.28 (14.77)	12.49 (12.49)	23.57 (19.87)
	PYJ(Mixed)	4.73 (4.79)	5.94 (3.77)	10.73 (7.26)	20.60 (12.83)
T-P	WJ(Rural)	4.69 (4.17)	8.11 (7.89)	9.59 (7.11)	11.85 (9.67)
	JS(Urban)	7.48 (8.53)	16.75 (14.00)	13.42 (9.63)	31.61 (29.32)
	PYJ(Mixed)	5.58 (4.70)	5.92 (4.83)	9.05 (6.72)	15.57 (16.79)



**Figure 5** | Comparison of total NPS pollutant load estimates made from using the reference 1-hour and other sampling intervals. (a) BOD. (b) COD. (c) TOC. (d) SS. (e) T-N. (f) T-P.

sampling interval was precise enough to provide estimates close (with differences less than 10%) to those of the 1-hour interval. The acceptable sampling interval increased to 3 hours for T-P, 4 hours for BOD, COD, TOC and 6 hours for T-N, respectively. *Toor et al. (2008)* reported that load estimates with low-frequency sampling strategies were often poor for individual years but improved substantially for the combined 3-year period. They suggested that regression methodology can produce reasonably accurate long-term loads where multiple years of water quality data are available. Thus, a 3-hour sampling interval was considered feasible for the study watersheds for long-term monitoring, except SS.

## CONCLUSIONS

This study showed that the sampling intervals of equal to or less than 3 hours could provide NPS pollutant load estimates with an acceptable accuracy of 10% difference in a watershed (i.e., PYJ) with mixed land uses including agriculture and urban. The urbanized watershed, JS, required more frequent sampling as pollutant loads tend to concentrate in the beginning of a storm event (or first flush effect). On the other hand, the agricultural watershed (WJ) with many rice paddy fields was likely to show relatively constant pollutant loadings over the storm duration due to the water ponding effect; thus, sparse sampling

frequencies could provide acceptable accuracy when estimating pollutant loads. This study demonstrated that there is a trade-off between the accuracy and sampling intervals of NPS pollutant monitoring, and the 3-hour sampling interval could improve monitoring efficiency while providing acceptable long-term NPS load estimates, except for SS. Such findings are expected to help find more feasible sampling frequencies and reduce the cost of water quality monitoring. The study results suggest that the sampling strategies balanced between accuracy and efficiency can facilitate NPS pollutant monitoring and in turn help in the quality assessment of water resources.

Water quality monitoring requires substantial financial and personnel resources. Often the monitoring costs are prohibitively expensive, and thus in most areas around the world, water quality is not observed. This study evaluated the performance of the different sampling frequencies to estimate the loads of water pollutants discharged from watersheds under the implementation of the Korean total maximum daily load program (TMDL), which requires 1-hour sampling interval for the first 24 hours of storm runoff. The results demonstrated that sparse sampling intervals such as 3 hours can accurately estimate loads within the acceptable errors, compared to the standard 1-hour interval, in agricultural watersheds. The urbanized watershed required more frequent sampling as pollutant loads tend to concentrate in the beginning of a storm event (i.e., first flush effect). On the other hand, the agricultural watershed with rice paddy fields was likely to show relatively constant pollutant loadings over time due to the water ponding effect. Such findings could help relax the intensive water quality sampling interval requirement of 1 hour in Korea, yet be sufficient for the TMDL assessment. The approach and methods demonstrated in this study are expected to help investigate feasible sampling strategies when monitoring resources are limited regardless of climate and watershed conditions.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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