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Spatial and temporal variabilities of suspended sediment and dissolved nutrients in the Ca River basin, North Central Vietnam

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ABSTRACT

The Ca River basin has an area of 27,200 km^2 distributed across the territories of two countries: Vietnam (65.2%) and Lao (34.8%). Spatial and temporal variations in suspended sediment (SS) and dissolved nutrients (PO_4^{3-}, NO_3^-, SiO_2) were determined in two hydrological stations located along the Ca River 4–6 times per month in the rainy season and 1–4 times per month in the dry season, between the months of August 2017 and July 2018. A loading–discharge (*L–Q*) curve was used to analyze the correlation among water physicochemical parameters with seasonal river discharge. The results indicate that SS was higher in upstream flows compared to downstream flows, which is primarily due to erosion. Seasonal SS and dissolved phosphate have an inverse correlation trend to that of dissolved silica. Results revealed that the concentration of phosphate and SS was higher in the rainy season than in the dry season. This finding proves that rain washes particulate matter from the surface runoff into the Ca River. Significant correlations between discharge and dissolved nutrient load were observed. This study provides useful information regarding variations of SS and water physicochemical parameters with seasonal water discharge in the Ca River.

Key words: agricultural catchment, Ca River, *C–Q* relationship, dissolved nutrients, suspended sediment, water quality

HIGHLIGHTS

- Quartz is the predominant mineral in the SS samples.
- SS concentrations were higher in upstream flows compared to downstream flows.
- A positive correlation between discharge and the dissolved nutrient load was shown.
- The strong influence of topography and agricultural land on nutrient levels in the Ca River.
- Dilution or chemostatic behavior occurs at a discharge rate of more than 500 m^3/s.

INTRODUCTION

Suspended sediment (SS) and dissolved nutrients (i.e. silicate, phosphate, and nitrate) play an important role in sustaining riverine, coastal, and oceanic ecosystems (Meire *et al.* 2016). Suspended sediment concentration (SSC), which is defined as the total value of both mineral and organic material carried in suspension by a river (Fryirs & Brierley 2013), is variable and depends on both natural and anthropogenic factors. SSC data in various rivers around the world range quite widely both during individual hydrological years and during multi-year periods (Walling & Fang 2003). Analyses of the SSC in several major rivers in Poland (Brański & Banasik 1996) indicate that the highest SSC has been reported for rivers flowing through mining areas, where the SSC on some days reaches up to 1,000–2,000 mg/L as a result of mine water contamination. Moreover, a high SSC is reached in highlands (200–300 mg/L) and upland rivers (values close to 100 mg/L). Significantly, lower SSCs are reported for lowland rivers (20–40 mg/L). In terms of dissolved nutrients, the silica content of natural waters is commonly in the 5–25 mg/L range (ASTM 2016). The dissolved silica (DSi) of the global average is 13.1 mg/L (Wallington *et al.* 2022) and among Asian rivers is 11.7 mg/L (Livingstone 1963). The presence of most silica in natural waters comes from the gradual degradation of silica-containing minerals. Compared to other major ions, DSi was relatively independent of lithology; however, DSi could be influenced by natural phenomena (e.g. geochemistry, precipitation) or human activities (e.g. irrigation) resulting in the increase or decrease of DSi concentration (Paudel *et al.* 2015; Venugopalan *et al.* 2020). Phosphate and nitrate are major nutrients needed by living microorganisms for their physiological processes. However, the excessive input of these nutrients may accelerate the eutrophication process. Agricultural lands are responsible for increased sediment and nutrient loads into waterways (Ekholm *et al.* 2000), which has been associated with the degradation of water quality in freshwater and estuarine ecosystems (Sharpley 2013).

Concentrations of SS and dissolved nutrients in water bodies are affected by the topography of a landscape, the intensity of a rainfall event, and the rate of movement of water over the surface or through the soil profile (McDowell *et al.* 2001). During rain events, the nutrients accumulated in surface soil are flushed out by runoff to rivers and then transported into estuaries. Paudel *et al.* (2019) revealed that water quality parameters (SS, dissolved nutrients) changed with seasonal and river discharge. SS increases are associated with higher precipitation (Zhang *et al.* 2018). Nitrogen and phosphate respond quite differently to rainfall. Nitrogen is much more mobile, and therefore movement is primarily via subsurface pathways, while phosphate transport generally occurs as surface runoff and tends to be dependent on the phosphate status of the soil (Dougherty *et al.* 2008). However, subsurface transport of phosphate is also possible through preferential flow and in sandy soils (Nash & Halliwell 1999). Silica in estuaries is primarily carried by sediments transported by freshwater inflow to estuaries (Humborg *et al.* 2000). Silica minerals in estuary sediments can control DSi concentration (Rickert *et al.* 2001). The above studies have investigated nutrient transport in undisturbed streams and rivers, but information on tropical rivers' nutrient load in an agricultural catchment area is limited.

The Ca River basin has an area of 27,200 km^2 distributed across the territory of two countries: Vietnam (65.2%) and Lao PDR (34.8%). Agricultural land comprises more than 75.8% of the watershed in this study. In recent years, the Ca River basin is severely affected by the significant impact of global climate change. Studies by Hoang (2010) and Pham *et al.* (2014) predict that floods, droughts, and saline intrusion become irregular and increasingly serious in the Ca River. In addition, water quality degradation greatly threatens the living environment and the use of surface water from the Ca River basin (MONRE 2018). This study aims to investigate the characteristics and temporal variation of SS and dissolved nutrients in the Ca River basin. Understanding the correlation of nutrient transport change with flow regimes and their responses during hydrological episodes may become essential in determining the current site status and making short-term predictions concerning water availability and potential related risks in the Ca River basin.

MATERIALS AND METHODS

Study area

The Ca River basin is located in a monsoon climate, and rainfall is distributed over the year, which has two distinct seasons: a rainy season (from May to October) and dry a season (from November to April). The average annual precipitation in the basin is from 1,100 to 2,500 mm. On average, the Ca River is located at an altitude of 294 m and with an 18.3% slope. The river and stream densities in this catchment area are 0.6 km/km^2. The topography of the Ca River basin is relatively complex, diverse, and strongly fragmented. The Ca River, which is the third largest river in North-Central Vietnam, plays a particularly important role in the socio-economic development of the provinces in the basin.

Sampling and analysis of water samples

Water samples were collected at the Dua and Yen Thuong hydrological stations from August 2017 to July 2018 (Figure 1). Dua hydrological station (105°02′20″E and 18°59′20″N) and Yen Thuong hydrological station (105°26′56″E and 18°04′10″N) are located along the Ca River basin. The Dua station has an elevation of 16 m and the Yen Thuong station has an elevation of 4 m. The respective basin areas at Dua and Yen Thuong are 20,800 and 23,000 km^2 (Chikamori *et al.* 2012).

Water samples were collected 4–6 times per month during the rainy season and 1–4 times per month during the dry season. A total of 48 water samples were collected at a depth of 10 cm, stored in a cool box, and then delivered immediately to the laboratory of Vinh University. Each sample was stored in two polyethylene bottles. One bottle of the sample was filtered by a 0.45-μm filter and concentrations of phosphate (PO_4^{3-}), nitrate (NO_3^-), and silica (SiO_2) were determined by using a colorimeter (DR900, HACH). Another sample was used to determine the levels of SS. Instantaneous discharge was obtained from the Dua and Yen Thuong hydrological stations.

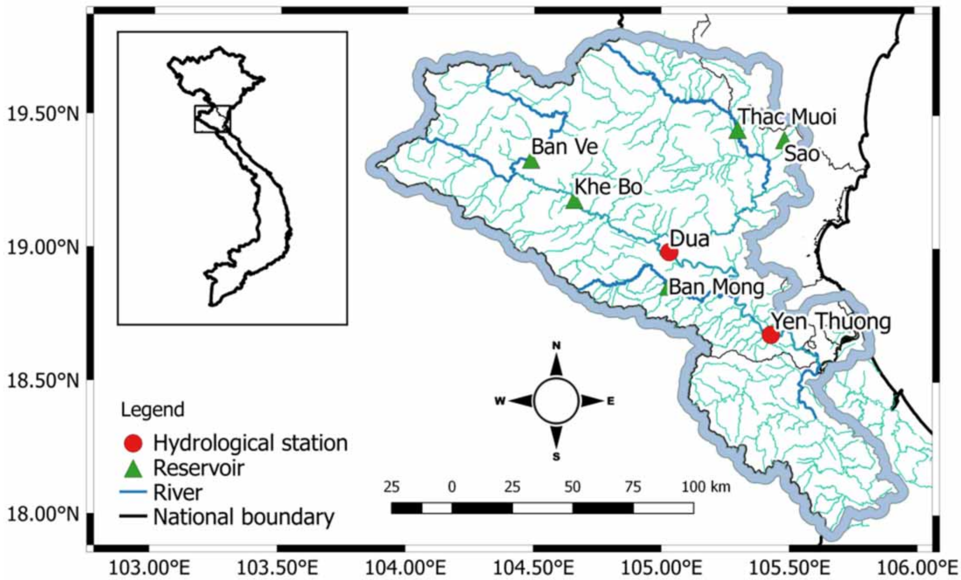

Figure 1 | The Ca River basin.

Meanwhile, the qualitative mineralogy and surface morphology of sediment samples were delivered to the laboratory of Okayama University, Japan for further analysis. The qualitative mineralogy of the sediment samples was determined by the standard interpretation procedures of X-ray diffraction (XRD) (Rigaku RINT2100). The surface morphology and microstructure of the suspended sediments were visualized using scanning electron microscopy (SEM) (Hitachi/S-3500N). The SEM images of sediment particles were obtained at 9,000, 3,500, 1,000, 800, 470, and 320 times magnification. The size distribution of microplastics was determined with a Coulter counter (Multisizer 3) equipped with a 2- to 62-μm aperture.

The correlation coefficient was calculated using Microsoft® Excel 2019. Critical levels of the correlation coefficient serve as the foundation for the statistical test for significance. Spearman's correlation coefficients were calculated between SS and nutrient concentration with discharge, and between SS and nutrient loading with discharge.

Loading–discharge (*L*–*Q*) curve

The concentrations of PO_4^{3-}, NO_3^-, SiO_2, and SS from the monitoring stations was used to demonstrate the relation of nutrient concentration (C) and nutrient load (L) with discharge, known as C–Q and L–Q rating curves (Tsushima *et al.* 2009).

The relationship among instantaneous nutrient load L (g/s), volumetric concentration C (mg/L), and instantaneous discharge Q (m^3/s) is expressed as:

$$C = aQ^b \tag{1}$$

Multiplying the above equation by discharge, we can determine the nutrient discharge as:

$$L = CQ = aQ^{b+1} \tag{2}$$

where a and b are rating curve model parameters.

The weather of North-Central Vietnam is characterized by two seasons: the dry season and the rainy season. The characteristics of the early stage of the rainy season and the end stage of the rainy season differ. Therefore, in this study, all data were divided into three periods: Period 1 from August to October of 2017 (the end stage of the rainy season), Period 2 from November 2017 to April 2018 (the stage of the dry season), and Period 3 from May to July of 2018 (the early stage of the rainy season).

RESULTS AND DISCUSSION

The characteristics of SS

The SEM images of surface morphology and microstructure of the suspended sediments indicate the diversity of sediment particle sizes. The largest particle size observed is approximately 120 μm and the smallest particle had a size of less than 5 μm (Figure 2). The large sedimentary particles are mainly composed of mineral fragments that are packed and aggregated in a larger size. In addition, the SEM images also showed the serried pores in the sediment particles, which can provide a lot of space for the absorption of nutrients (Wang *et al.* 2020).

The SS size distribution of the sediment particles ranged from 2 to 29.2 μm and from 2 to 24.4 μm at Dua and Yen Thuong stations, respectively. At the Dua station, particles with a size less than 3 μm account for a large proportion of the total number of the particles at 56.6%. In the rest of the samples, particles with a diameter from 3 μm to less than 5 μm, from 5 μm to less than 10 μm, from 10 μm to less than 20 μm, and from 20 to 29.2 μm account for 30.5, 11.3, 1.5, and 0.1%, respectively. There was a similar SS particle size distribution obtained at

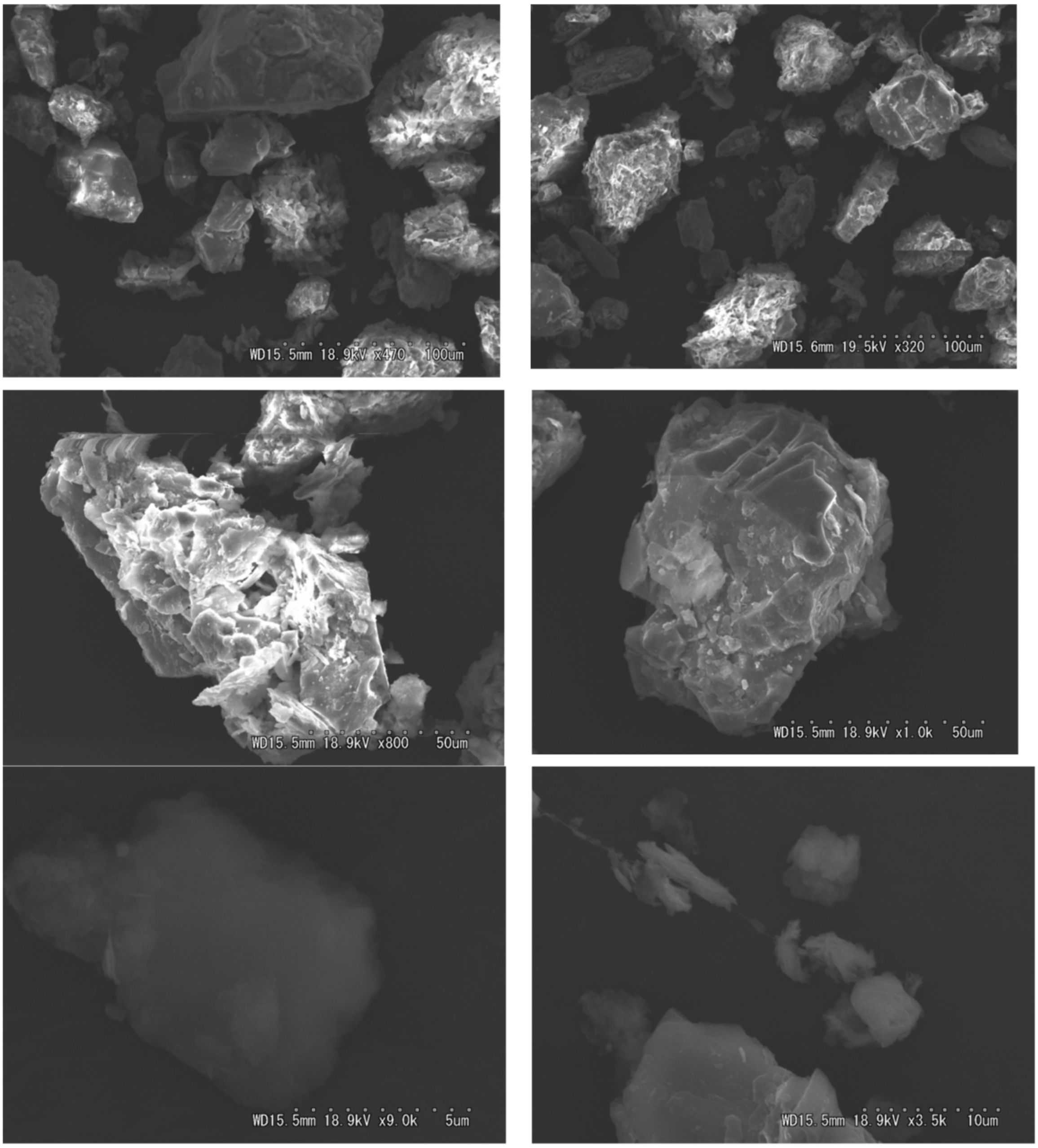

Figure 2 | The SEM image of SS.

the Yen Thuong station, where the proportion of particles with sizes less than 3 μm, from 3 μm to less than 5 μm, from 5 μm to less than 10 μm, from 10 μm to less 20 μm, and from 20 to 29.2 μm account for 56.1, 30.2, 11.8, 1.8, and 0.1%, respectively. SS act as contaminants and pathogens are carried on the surface of the particles. A higher proportion of small particle size of SS (less than 3 μm) was observed at both stations, and this is noteworthy because small particles can carry higher amounts of contaminants (nutrients, heavy metals, organic contaminants).

The results of the mineral content in the sediment deposited obtained by the XRD shows that quartz (SiO_2) is the predominant SS in the samples. Quartz (SiO_2) is a common material and a ubiquitous mineral, the second most abundant mineral in the earth's crust after feldspar. It is present in many types of rocks. Consequently, quartz has a major influence on geochemical processes, including the formation of mineralized deposits of economic value. More importantly, the dissolution and crystallization of quartz may play a part in controlling the concentration of silica in water and hydrothermal systems, providing controls on natural waters (Crundwell 2017).

Temporal and spatial variations of SS and dissolved nutrient

The concentration of SS fluctuated between the seasons and the locations, ranging from 3 to 369 mg/L at the Yen Thuong station and from 3 to 867 mg/L at the Dua station (Figure 3(a)). In the dry season, the concentration of SS was quite low, constant at an average of 11 mg/L, and similar at both stations with an exception of April 7, 2018 at the Dua station). However, in the rainy season (Period 1 from August to October 2017, and Period 3 from May to July 2018), the SSC was highly variable. Generally, SSC was higher at the downstream station (Yen Thuong) than at the upstream station (Dua) during the rainy season. However, the SSC shows an opposite trend during periods of heavy rain (e.g. September 17, 2017, October 8–15, 2017, and May 20, 2018). In other words, there are higher values of SSC at the upstream station compared to the downstream station. The intensity of a rainfall event induces a higher flow rate, and due to the higher slope causes erosion at the upstream station. This indicates that the topography of a landscape and hydrodynamic features affect the dynamics of SS in the watershed to the estuary (Zhang *et al.* 2017; Paudel *et al.* 2019).

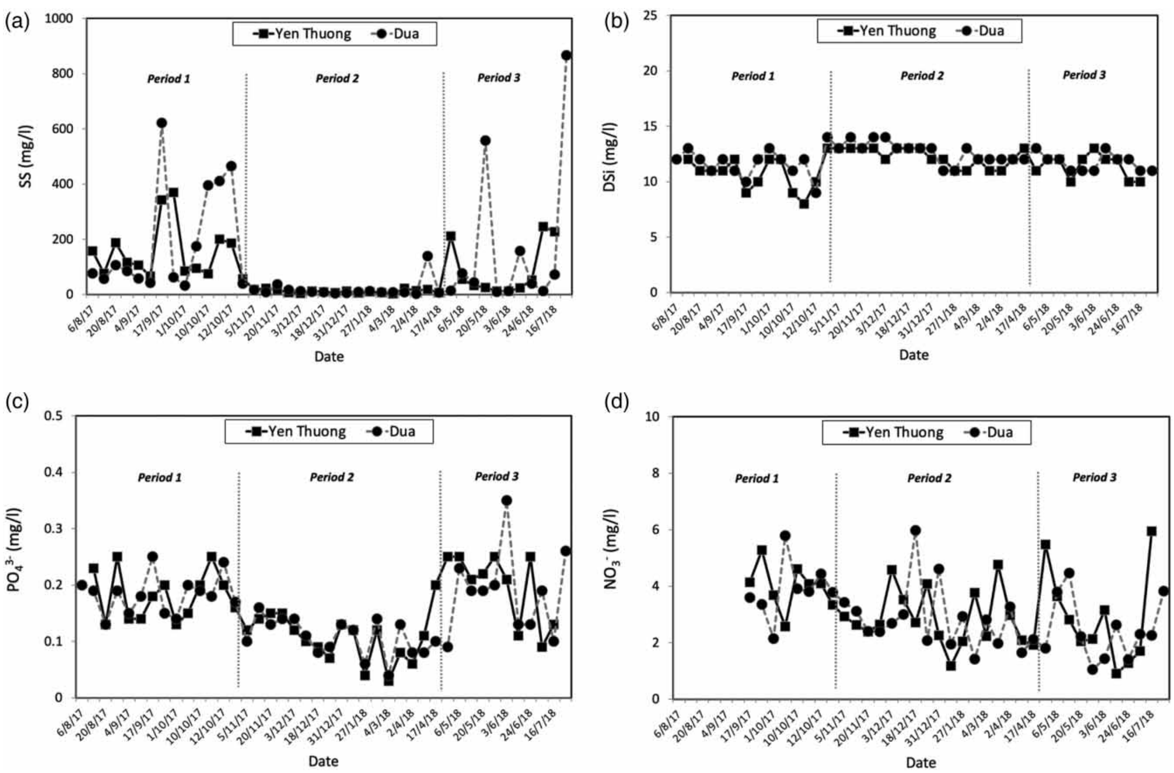

Figure 3 | Temporal variations of SS (a), dissolved silica (b), phosphate (c) and nitrate concentration (d) of Yen Thuong and Dua stations.

The results of DSi indicate a similar trend of temporal variation at both stations. DSi concentration range from 8 to 14 mg/L for a year, with an average of 11.3 mg/L for Period 1, 12.4 mg/L for Period 2, and 11.6 mg/L for Period 3 (Figure 3(b)). The results show that DSi was diluted in the rainy season causing a lower concentration than in the dry season.

In contrast to DSi, phosphate concentrations in the rainy season were higher than in the dry season. An average PO_4^{3-} concentration was 0.18, 0.11, and 0.19 mg/L for Period 1, Period 2, and Period 3, respectively (Figure 3(c)). Such nutrients come from different sources, including surface runoff, infiltration runoff, and erosion. In the dry season, PO_4^{3-} from the infiltration source is significant. At the early stage of the rainy season (May 1–June 3), PO_4^{3-} increases quickly, indicating a significant contribution of PO_4^{3-} from the surface runoff and erosion. The surface runoff washed away PO_4^{3-} deposits stored from urban, agricultural, and forestry land during the dry season into the catchment basin. In addition, erosion accompanied by the transport of high SS causes an increase in PO_4^{3-} (Zhang *et al.* 2017; Paudel *et al.* 2019).

Finally, nitrate concentrations (NO_3^-) have a similar trend at both stations, fluctuating between 1.05 and 5.97 mg/L (Figure 3(d)). There was no remarkable seasonal variation of nitrate concentrations in the Ca River. The previous studies revealed that in agricultural catchments, nitrate concentration is high during the rainy period, and low during the dry period (Reynolds *et al.* 1992; Chen *et al.* 2010). Nitrate produced in the soil by biogeochemical processes such as summer mineralization is flushed into the streams and rivers during rainy periods (Creed & Band 1998). Another hypothesis cited nitrate is stored temporarily in the groundwater. During the rainy season, high nitrate concentrations are the result of high nitrate-rich shallow hillslope groundwater (Altman & Parizek 1995; Hill 1996). The conceptual model for determining stream water NO_3^- seasonality showed NO_3^- concentrations increased not only during the high groundwater season but also during the low groundwater season (Ohte *et al.* 2003). NO_3^- is mobile and therefore can enter the catchment via subsurface pathways.

The concentrations of NO_3^- and PO_4^{3-} in the Ca River basin were higher compared to other main river catchments in Southern (Saigon and Dongnai Rivers, Lower Mekong River) and Northern Vietnam (Nhue River) (Table 1) (Nguyen *et al.* 2016, 2019; Trinh *et al.* 2016). Nutrient concentration in natural water depends on some catchment characteristics such as land use, fertilizer application rate, soil type, and hydrological pathways between the land and the stream (Heathwaite & Johnes 1996). Rivers in the Central Region of Vietnam often have narrow riverbeds, steep slopes, and small catchment areas. In the rainy season, the flow is often concentrated quickly with high discharge rates (MONRE 2018). Due to the region's topography, high concentrations of nutrients in surface soil are flushed out by erosion and runoff to rivers and then transported into estuaries.

Table 1 | Comparison of nutrient concentrations among main river catchments in Vietnam

River basin	Concentration (mg/L)	Sources
Nhue River	NO_3^- (0.0–0.1)	Trinh *et al.* (2016)
Ca River	NO_3^- (1.05–5.97); PO_4^{3-} (0.18)	This study
Saigon and Dongnai rivers	NO_3^- (<2.5)	Nguyen *et al.* (2016, 2019)
	NO_3^- (0.002–0.395)	
	PO_4^{3-} (0.1); PO_4^{3-} (0.05 – 0.2)	

Relationship of SS and nutrient concentration with discharge

The relationship between SS, nutrient concentration, and water discharge was obtained using the C–Q equation ($C = aQ^b$). Particles and solutes C–Q relationships in various catchments have been explored in past decades and can represent the integration of hydrological and biogeochemical responses of catchments to understand the riverine solute source, transport, and reaction (Rose *et al.* 2018). The slope of regression b was used to identify nutrient concentration behaviors as 'chemostatic' or 'non-chemostatic'. When b is between -0.1 and <0, nutrient concentration showed only minimal effects of dilution by meteoric water and was defined as chemostatic (Godsey *et al.* 2009). In contrast, non-chemostatic elements were defined by exhibiting dilution behavior ($b < -0.1$) when concentrations decreased with an increasing Q or exhibiting enrichment behavior ($b > 0$) when concentrations increased with an increasing Q.

In this study, the *C*–*Q* relationship was investigated for three periods. The results indicate that the concentrations of SS, SiO_2, PO_4^{3-}, and NO_3^- are chemostatic, or exhibit enrichment behavior, with the increase of discharge across all periods (except for dilution patterns of SiO_2 in Period 1) (Table 2). The stronger relationship of SS, SiO_2, PO_4^3, and NO_3^- with the discharge was observed in Period 1 ($R^2 > 0.2$) followed by Periods 2 and 3 ($R^2 < 0.11$, except for SS). This indicates the significant influence of infiltration runoff during the dry season and erosion during the early stage of the rainy season, resulting in unstable concentrations of particles and solutes in the river. In contrast, at the end stage of the rainy season, saturation may occur and the concentration of particles and solutes are impacted by surface runoff, which carries a high load of sediments on soil surfaces, resulting in

Table 2 | Slopes of regression lines fit to C–Q data

	SS	SiO_2	PO_4^{3-}	NO_3^-
Period 1 (August–October 2017) – the end stage of the rainy season				
Slope	0.8431[b]	– 0.1210[c]	0.1425[b]	0.1899[b]
R^2	0.5437	0.5202	0.2565	0.2297
Period 2 (November 2017–April 2018) – the stage of the dry season				
Slope	0.3287[b]	0.0495[a]	0.3458[b]	0.0363[a]
R^2	0.0302	0.1027	0.1066	0.0008
Period 3 (May 2018–July 2018) – the early stage of the rainy season				
Slope	0.8971[b]	– 0.027[a]	– 0.083[a]	0.141[b]
R^2	0.6284	0.0673	0.0294	0.067

[a]Chemostatic, [b]enrichment, [c]dilution.

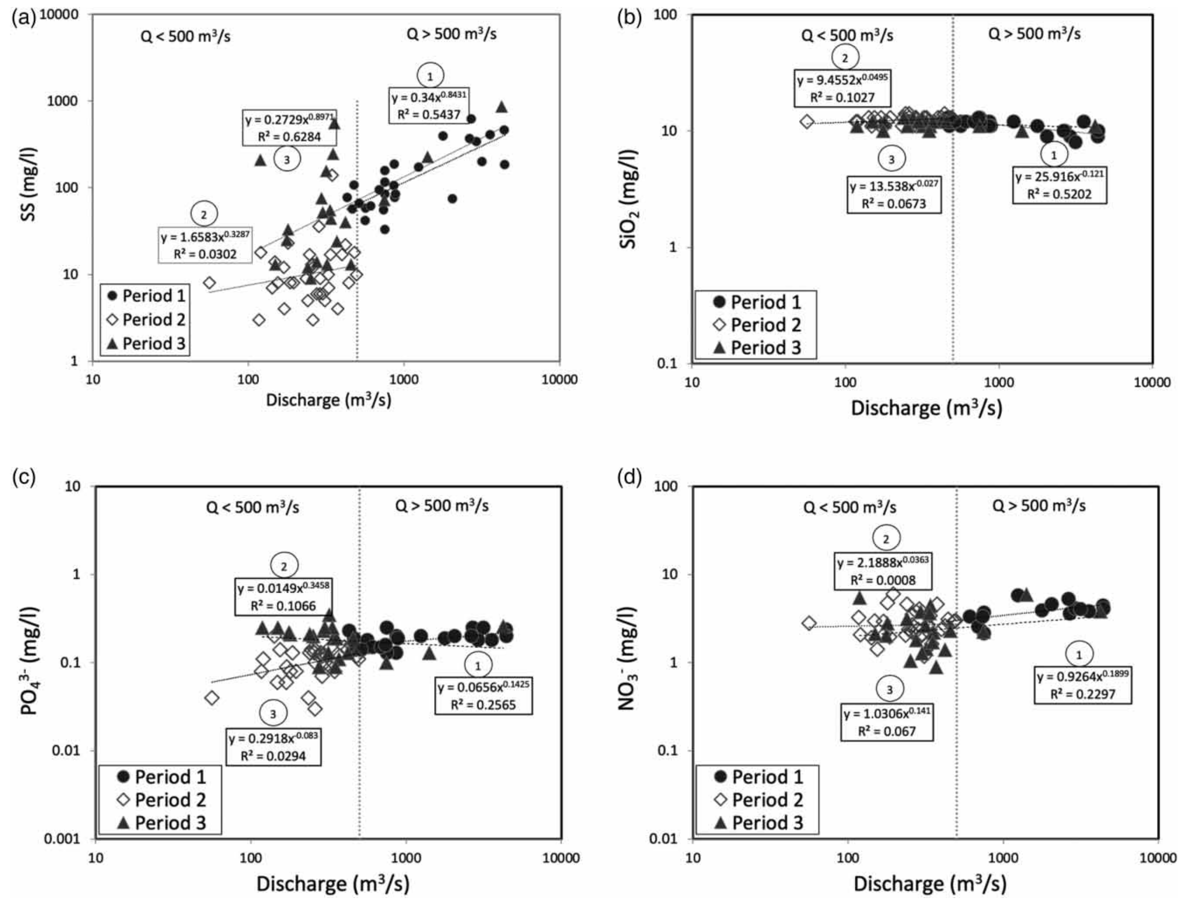

Figure 4 | Relationship between discharge with SS (a), dissolved silica (b), phosphate (c) and nitrate concentration (d) of both stations.

dilution behavior in receiving water bodies. In general, dilution or enrichment behavior occurred at a discharge rate of more than 500 m^3/s, meanwhile, the chemostatic or enrichment behavior, with a quite high variation, occurred at a discharge rate of fewer than 500 m^3/s in the Ca River (Figure 4).

It has been reported that the contents of biological solutes are often linked to anthropogenic sources, influencing solute-flushing behaviors in forested and agricultural catchments, especially in extreme climate events (Rose *et al.* 2018). However, as a result of weathering, SiO_2 can accumulate in the weathered zone. During intensive rainfall, it can be washed out from this zone into surface water. According to Johnson *et al.* (1969) dilution can result during rainfall events as water stored in a catchment is diluted by less concentrated meteoric water. Enrichment can result if a more concentrated source (e.g. surface runoff, infiltration runoff, erosion) mixes with river water during high-flow discharges due to rainfall. In contrast, chemostasis cannot be explained by the simple mixing of multiple sources and therefore has been attributed to processes such as chemical reactions with the solid phase along the pathway of water flow (Godsey *et al.* 2009). Nutrient concentration responses to seasonal Q variations revealed a large dispersion in C–Q plots. This supports the observations from previous studies (Duncan *et al.* 2017; Li *et al.* 2019) showing that C–Q relationships may vary across different time scales because the variety of processes shaping C–Q curves has different temporalities.

Relationship of SS and nutrient load with discharge

The seasonal relationship of dissolved nutrient load with the discharge was plotted as a log–log relationship, as seen in Figure 5. Fluxes of particles or solutes in outflow water exhibit a strong positive relationship to seasonal discharge. Since fluxes are equal to concentration times discharge, this is consistent with the relatively small decrease in concentrations of particles or solutes coupled with large increases in the amount of water leaving the system (Clow & Drever 1996). The SS and dissolved nutrient load increases with the increase of discharge, however behavior of the relationship differs by the type of minerals and the season. The SS load increases with the increase of discharge; however, there were seasonal shifts seen in SSC–Q relationships. From previous results, it has been found that the shift occurs in the dry season possibly due to dam construction that trapped the

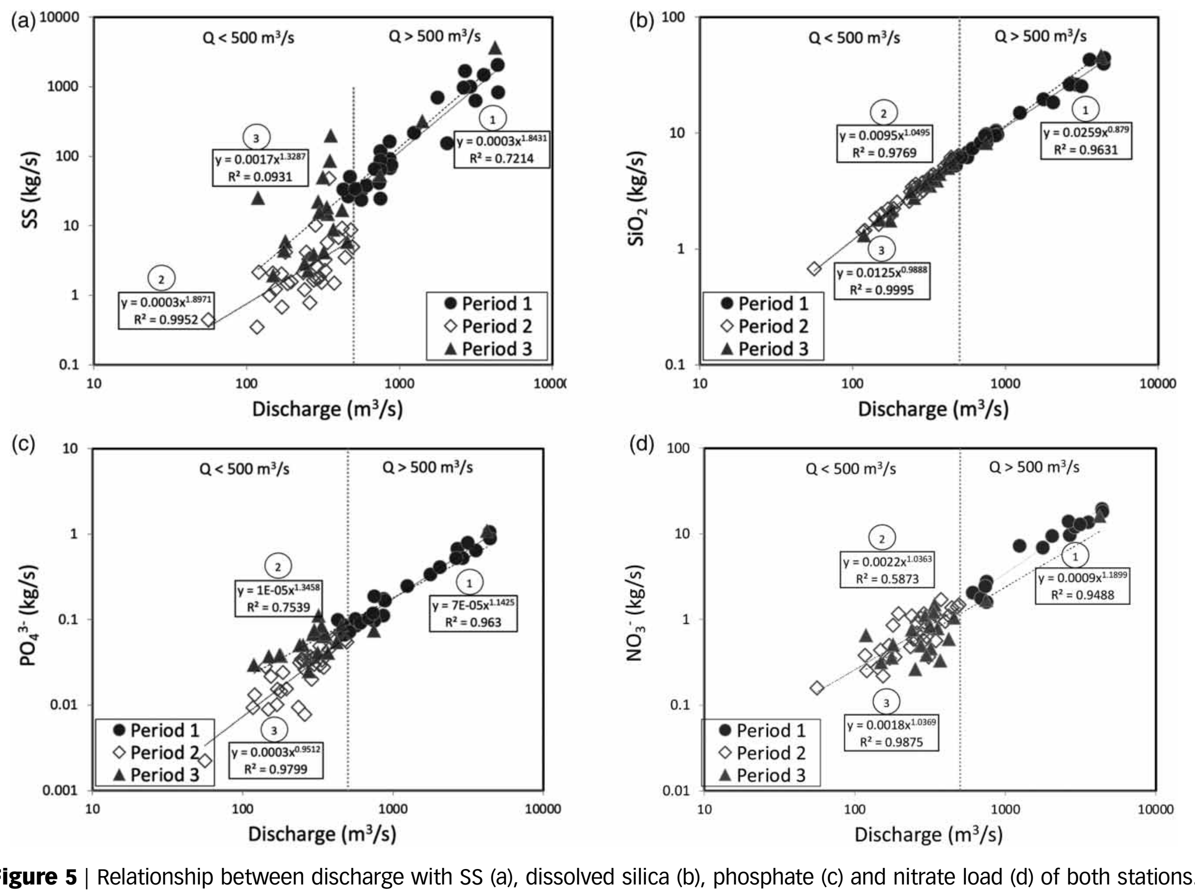

Figure 5 | Relationship between discharge with SS (a), dissolved silica (b), phosphate (c) and nitrate load (d) of both stations.

sediment (Phuong *et al.* 2019). The load of SiO_2 has a strong correlation with discharge in different seasons ($R^2 > 0.96$). The load of PO_4^{3-} and NO_3^- have strong relationships in Period 1 and Period 3 ($R^2 > 0.94$), and moderate relationships in Period 2 ($0.8 > R^2 > 0.5$). The load flow relationship for SiO_2 was higher than PO_4^{3-} and NO_3^-, indicating PO_4^{3-} and NO_3^- sensitivity to water discharge. The slope, b, indicates the rate of material transport as seen with an increasing order: $SiO_2 < PO_4^{3-}$, $NO_3^- <$ SS. The strong correlation between load and discharge could be relied on to calculate the seasonal or annual loading of a particle in a river.

CONCLUSION

SS particles sized less than 3 μm account for a large proportion of particles in the Ca River basin. Quartz (SiO_2) is the predominant mineral in the SS samples. SS was higher upstream compared to downstream, which is found to mainly be due to erosion. The trend in the correlation between seasonal SS and dissolved phosphate was opposite to that of DSi. Results reveal the concentrations of dissolved phosphate and SS were higher in the rainy season than those in the dry season. The strongest relationship of SS, SiO_2, PO_4^{3-}, and NO_3^- concentrations with discharge ($R^2 > 0.2$) was observed in Period 1, followed by Periods 2 and 3, respectively ($R^2 < 0.11$, except for SS). Significant correlations between discharge and dissolved nutrient loads were observed. In different seasons, the SiO_2 load has a strong correlation with discharge ($R^2 > 0.96$). The PO_4^{3-} and NO_3^- load have the strongest relationships in Periods 1 and 3 ($R^2 > 0.94$), but only moderate relationships in Period 2 ($0.8 > R^2 > 0.5$). Compared to the other main river catchments in Vietnam, the Ca River basin shows a higher concentration of phosphate and nitrate, which may be due to the strong influence of the topography and agricultural land surrounding the Ca River. This study provides pertinent and useful information for understanding the current state and status of the site, while also providing short-term predictions concerning water availability and risks in the Ca River basin.

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DATA AVAILABILITY STATEMENT

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

CONFLICT OF INTEREST

The authors declare there is no conflict.

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