# SEASONAL VARIATION OF SURFACE WATER QUALITY IN THE MAINSTREAM AND TRIBUTARIES OF THE CA RIVER BASIN

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**ARTICLE INFORMATION**

***Journal:*** *Vinh University Journal of Sciences*
***ISSN:*** *1859-2228*

***Volume: 52***
***Issue: 2A***
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***Received:*** *15 November 2022*
***Accepted:*** *17 March 2023*
***Published:*** *13 June 2023*

***Citation:***
*Ho Thi Phuong, Ha Thi Kim Thanh (2023). Seasonal variation of surface water quality in the mainstream and tributaries of the Ca River Basin.* ***Vinh Uni. J. Sci.*** *Vol. 52 (2A), pp. 5-17*
*doi: 10.56824/vujs.2022a040*



**ABSTRACT**

The purpose of research is to assess the seasonal changes of water quality in mainstream and in specific tributaries in the Ca River Basin. Water samples were collected in the dry season (May 2021) and in the beginning of the rainy season (September 2021) from 4 sites located on Ca River's mainstream and 5 sites located on Ca River's tributaries to analyze water quality parameters. Results indicated that physical parameters (pH, EC, salinity, DO) and and heavy metals (As, Cu) are within the standard values according to the National Technical Regulation on Surface Water Quality QCVN 08-MT:2015/BTNMT for domestic water supply purposes (Columne A1). The concentration of nutrients measured in the tributaries is higher than those in the mainstream due to the contribution of nutrients and organic materials from agricultural runoff. In addition, the water flow in the tributaries is lower than in the mainstream, as a result, the concentration of nutrients tends to be higher in the tributaries. The samples revealed that the concentration of nutrients ($NO_3^-$, TN, $PO_4^{3-}$, TP) and chemical oxygen demand (COD) appeared higher in the beginning of the rainy season than in the dry season. The increase of nutrient concentrations can be explained by the leaching of nutrients into the river. In general, the water quality of Ca River's tributaries during the rainy season have a high nutrient concentration and also the risk of eutrophication.

**Keywords:** Water quality; nutrients; eutrophication; Ca River.

## 1. Introduction

Vietnam has 697 inter-provincial rivers, streams, and canals, as well as 38 lakes, that are part of 16 major river basins, and 3,045 intra-provincial rivers and streams. One of seven transboundary rivers is the Ca River. Transboundary rivers and streams transfer approximately 520 billion $m^3$ of water to our country, accounting for approximately 63% of the total average annual water volume of the river system, of which the Ca River accounts for about 3 billion $m^3$ [1].

The Ca River is a large basin and plays an especially significant role in the socio-economic development of local provinces containing the basin in particular provinces of the North Central Region. Moreover, this river basin is recognized as important to the country in general. The Ca River Basin drains a total area of 27,200 $km^2$, spanning the territory of two countries Vietnam (65.2%) and Lao PDR (34.8%). In Vietnam, the Ca River Basin is located on the administrative boundaries of three provinces: Nghe An, Ha Tinh, and Thanh Hoa, however the majority of the basin area is located in Nghe An Province. The Ca River Basin runs from the northwest to the southeast direction, gradually flowing towards the sea. The entire upstream region in Laos has an average elevation of over 1,000 m. In Vietnam, more than 80% of the land area is mountainous. Land satisfying the criteria for agricultural development accounts for only 19% of the entire land area in Vietnam and 14% of the entire basin.

Recently, the Ca River Basin has been impacted by climate change. Previous studies by Hoang Minh Tuyen and Pham Quy Giang [2], [3] have predicted that climate change will increase the negative effect on water resources in the Ca River Basin, such as flooding, droughts, sea level rise, and saltwater intrusion. In addition, the degradation and pollution of water sources are also one of the adverse factors of climate change, seriously threatening the living environment and the ability to exploit and use surface water in the Ca River Basin [4].

The degradation of water quality is mainly the result of human activities, including industrial production, agriculture, and urbanization. In Vietnam, most river basins have quite high total suspended solids concentration (TSS) and turbidity values, exceeding QCVN 08-MT: 2015/BTNMT - National technical regulation on surface water quality, column A2 [1]. In the Ca River Basin, there are 34 periodic surface water environment monitoring points. According to monitoring data from the General Department of Environment for the period 2018-2020, Ca River's water quality has signs of organic and nutrient pollution, which is concentrated primarily at downstream points, the majority of which are affected by domestic wastewater in Vinh City or the surrounding area with frequent fishing boats, the nitrite and $BOD_5$ parameters exceed the QCVN 08-MT:2015/BTNMT A2 threshold [1]. Water quality degradion is a threat to aquatic life, aquatic ecosystem health and human health [5]. Recently, the impact of agricultural activities on water quality in Ca River Basin has not been well studied.

According to statistics in 2014, the total land area in Nghe An Province is 1,648,997 hectares, of which agricultural land is about 1,249,176 hectares, accounting for 75.8% of the province's land area. Agricultural activities significantly to the nutrient pollution of water, paricularly by nitrogen (N) and phosphorus (P), which leach from chemical fertilizers, organic fertilizers, as well as animal manure. These nutrients usually exists in water in the form of nitrate ($NO_3^-$), ammonium ($NH_4^+$), or phosphate ($PO_4^{3-}$) [6]. Fertilizer residues in soils that are not absorbed by plants will be washed away by rainwater runoff into the basin, thereby affecting the environment and aquatic ecosystems [7].

This study aims to assess the seasonal changes of water quality in the Ca River's mainstream and tributaries. The study' results contributes to providing a database of surface water quality in the Ca River Basin, one of the major transboundary rivers. In addition, the study also contributes to the detection and warning of changes in water quality for appropriate management and treatment solutions, helping to prevent adverse impact on human health and the ecosystem.

## 2. Materials and methods

### *2.1. Study area*

The Ca River Basin is located in the North Central Vietnam, at geographical coordinates $17^0$50' to $20^0$50' North latitude, $103^0$14' to $106^0$10' East longitude. The total area of the basin is 27,200 km$^2$, of which 17,730 km$^2$ is in Vietnamese territory, accounting for 65.2% of the total basin area. The length of river is 531 km, of which 361 km is in Vietnam [8]. The tributaries flowing into the mainstream are short and steep, originating from high mountains in the provinces of Xieng Khouang (Laos), Nghe An, and Ha Tinh (Vietnam). The major tributaries of the Ca River are Nam Mo, Huoi Nguyen, Hieu, Giang and La. These rivers contribute a significant amount of flow to the mainstream.

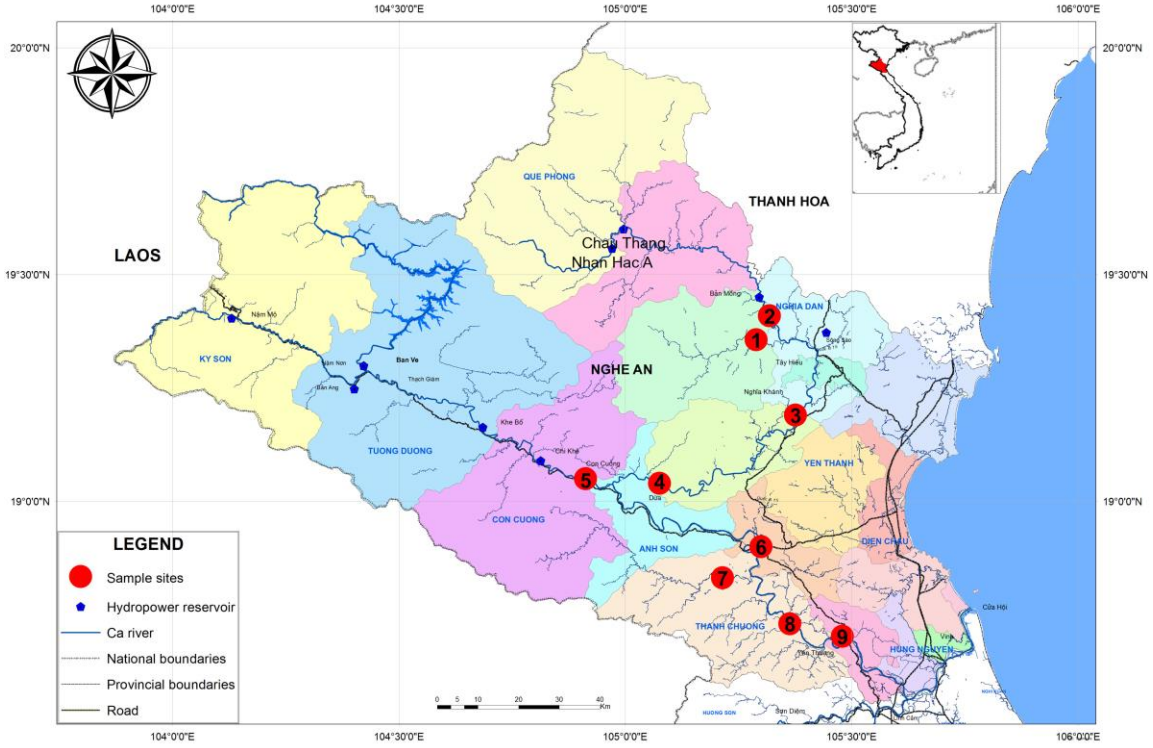



**Figure 1:** *Sample sites in the Ca River Basin*

### *2.2. Sampling and analytical methods*

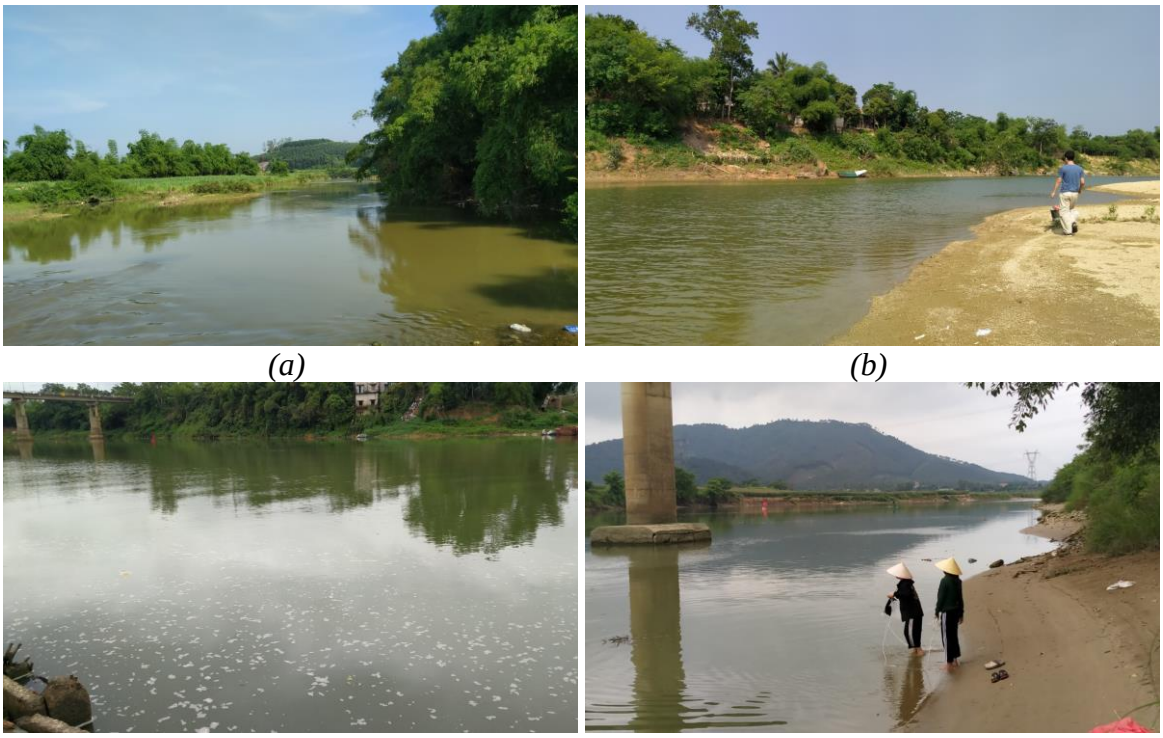
Nine sample sites were selected along the Ca River to assess the impact of topography and agricultural activities on water quality (5 sites on tributaries and 4 sites on the mainstream) (Table 1). In tributaries, water samples are taken at the river's terminus before confluence with the mainstream. The selected tributaries represent the Dinh, Hieu, and Giang River basins. Sampling sites were selected at tributaries and mainstream of the Ca River Basin (the middle basin and lower basin), which is the area affected by human activities. In addition, sampling sites are taken at hydrological stations in the Ca River Basin in order to collect discharge data which were measured and

provided by the Hydrometeorological Center for North Central Region of Vietnam. Water samples were collected during the dry season (16/5/2021) and the rainy season (25/9/2021) at nine sites. Each sample of 500 ml was collected at the water depth of approximately 10 cm at the riverside. Figure 2 shows some pictures during the water sample collection process of the research team in the field.

Water sample collection and preservation were conducted according to the National Standard TCVN 6663-6:2018. The parameters of dissolved oxygen DO ($mgO_2/l$), pH, conductivity EC (Millisiemens/meter-mS/m), salinity (‰), and temperature ($^oC$) was quickly measured in the field by the Multiparameter Portable Meter HandyLab 680 (Germany). Samples for heavy metal analysis (As, Cu) were fixed with acid $HNO_3$ (pH<2) in the field. Water samples were filtered with Whatman Grade GF/F filters (0.7 µm pore size, 47 mm diameter) and stored separately in plastic bottles (PE) to analyze inorganic nutrients ($NO_3^-$, $NH_4^+$, $PO_4^{3-}$). Unfiltered water samples were used to analyze total nitrogen (TN), total phosphorus (TP), and chemical oxygen demand (COD). The samples were stored at 4 $^oC$ and immediately transferred to the laboratory at Institute of Natural Products Chemistry, Ha Noi. The heavy metal (As, Cu) and COD determination was based on Methods SMEWW 3125B:2017 and SMEWW 5220D:2017, respectively. Total nitrogen, ammonium and nitrate were analyzed according to the National Standards TCVN 6638: 2000, TCVN 6179-1:1996 and TCVN 6180:1996, respectively. The TP and $PO_4^{3-}$ were determined according to to the National Standards TCVN 6202:2008. The concentration of $NH_4^+$, $NO_3^-$, TN, $PO_4^{3-}$, TP, and COD (mg/L) were determined by a spectrophotometer (JASCO V-630).

**Table 1:** *Water sample collection sites in the Ca River Basin*

| Symbol | Sample sites | Number on the map | Coordinates | |
|---|---|---|---|---|
| | | | X | Y |
| *Tributaries* | | | | |
| T1 | Dinh bridge | (1) | 19°20'59.29"N | 105°18'35.47"E |
| T2 | Hieu bridge | (2) | 19°23'19.00"N | 105°19'20.56"E |
| T3 | Nghia Khanh hydrological station | (3) | 19°12'21.76"N | 105°23'35.75"E |
| T4 | Cay Chanh (Hieu River) | (4) | 19°3'42.63"N | 105°0'56.37"E |
| T5 | Giang River bridge | (7) | 18°50'10.09"N | 105°15'0.32"E |
| *Mainstreams* | | | | |
| M1 | Cay Chanh (Ca River, located before joining the Hieu River) | (5) | 19°2'56.66"N | 104°55'40.56"E |
| M2 | Do Luong bridge | (6) | 18°54'45.32"N | 105°17'58.17"E |
| M3 | Yen Thuong hydrological station | (8) | 18°40'35.90"N | 105°25'46.17"E |
| M4 | Nam Dan hydrological station | (9) | 18°42'3.94"N | 105°29'23.31"E |



*(a)* *(b)*

*(c)* *(d)*

**Figure 2:** *Some pictures of samples taken in the field (a) Dinh River (T1), (b) Giang River (T5), (c) Ca River at Do Luong (M2), and (d) Ca River at Nam Dan (M4)*

### *2.3. Data analysis methods*

The data were statistically analyzed by season (dry and rainy season) and by river basin location (mainstream and tributary) and then compared between different bodies of water in the same sampling period as well as between sampling periods. In addition, measured parameters were also compared with QCVN 08-MT:2015/BTNMT - the National technical regulation on surface water quality, column A1 to assess water quality [9].

## 3. Results and discussion

### *3.1. Physical parameters*

The water discharge values indicated a difference in spatial patterns along the Ca River catchment area. The average water flow in the rainy season (1,332 $m^3/s$) was 12 times higher than in the dry season (112 $m^3/s$), and at mainstream sites the average water flow was higher than in tributary sites. The temperature of water samples collected in May at 9 points fluctuated between 30.0 and 33.6 $^oC$, with an average of 32.0 $^oC$. Meanwhile, the temperature of water samples collected in September at 9 points fluctuated between 24.6 and 27.5 $^oC$, with an average of 26.3 $^oC$.

The pH value ranged from 6.4 to 7.9, with an average of 7.5. The pH value did not significantly fluctuate between the rainy season and the dry season and remained within the standard values in the QCVN 08-MT:2015/BTNMT (6.0-8.5). Fluctuations in

EC values and salinity showed a similar trend. EC and salinity in the dry season were higher than in the rainy season, but there was no significant difference across the two sampling periods and the sampling locations.

Results showed that dissolved oxygen (DO) concentration fluctuates between monitoring points and seasonally. DO ranged from 6.1 to 8.2 mg/L, with an average of 7.1 mg/L. The average DO concentration in the dry season was 6.9 mg/L, lower than in the rainy season, which measured at 7.3 mg/L. DO in the rainy season was higher than in the dry season at most of the sampling locations and was within the standard values according to the QCVN 08-MT:2015/BTNMT (≥ 6), (Figure 3).The monitoring results showed that there was a correlation between the water flow and the content of physical parameters. Low water flow in the dry season in tributaries explains the results of high EC and salinity when compared to the results seen during the rainy season at the sample sites along the mainstream. The decomposition of organic matter consumes dissolved oxygen content, combined with low water flow in the dry season, there is a reduction of DO in water.

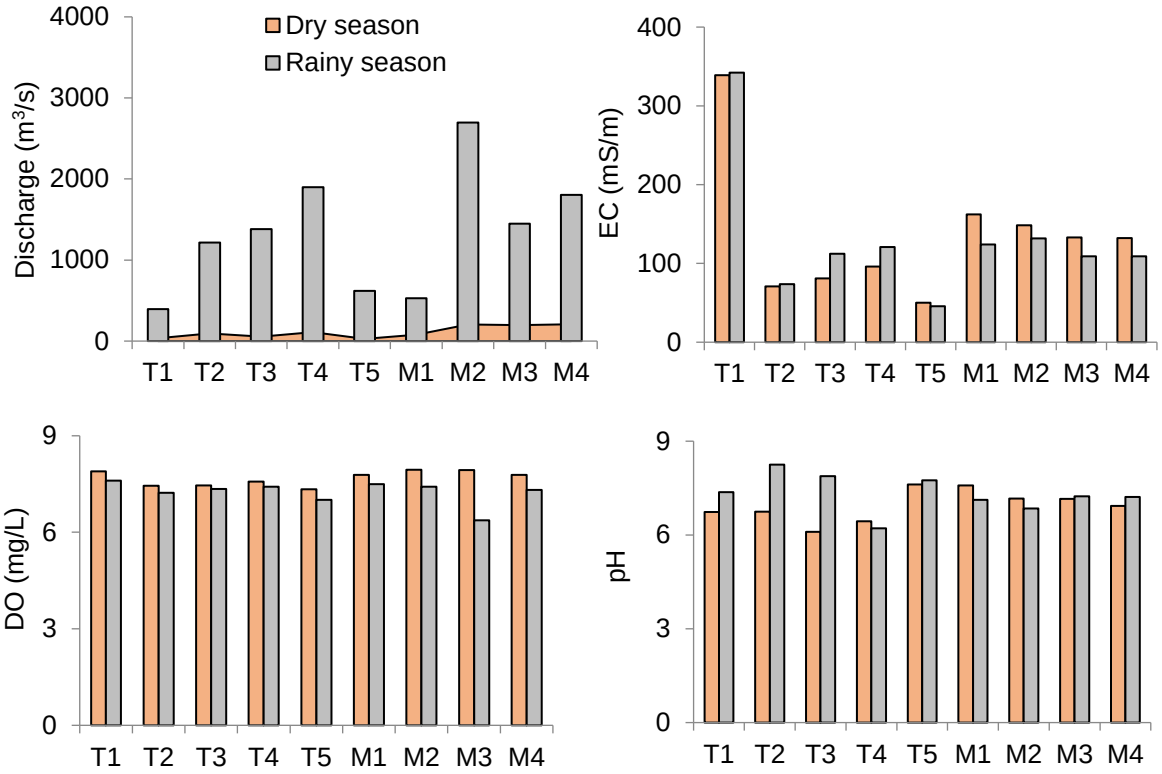



**Figure 3**: *Physical and chemical parameters measured at monitoring points on the mainstream and tributary of the Ca River in two seasons*

### *3.2. Nutrients*

The concentration of $NH_4^+$ ranged between 0.05 and 0.58 mg/L, with an average of 0.12 mg/L. Average concentration of $NH_4^+$ in the tributaries were higher than in the mainstream and in the dry season. Monitoring results in the dry season, at site T5, show that $NH_4^+$ was recorded the highest (0.58 mg/L), exceeding limits in the QCVN 08:2015/BTNMT for domestic water supply purposes (0.3 mg/L).

Nitrate concentrations in the mainstream and tributaries of the Ca River ranged between 0.13 and 1.53 mg/L, with an average value of 1.05 mg/L. Higher concentrations of $NO_3^-$ were reported in the rainy season in the tributary sites. TN concentrations ranged from 0.65 - 3.21 mg/L. TN and $NO_3^-$ showed a similar trend. Lower concentrations of $NO_3^-$ and TN were documented in the dry season possibly due to a decrease in rainfall and runoff. In the dry season, $NO_3^-$ accumulates in soils due to mineralization of organic nitrogen. In the beginning of the rainy season (September), high rainfall intensity enhances the flushing of $NO_3^-$ accumulated in the organic layer of shallow soil surfaces during the dry season, increasing associated nutrient flow into the rivers [10]. In addition, there is the deposition of eroded sediment onto the riverbed and oxidation of inorganic nitrogen compounds ($NH_4^+$ to $NO_3^-$), resulting in $NO_3^-$ accumulation, accounting for a large proportion of TN in all measured-water samples. Nitrogen oxidization may have been activated by the supply of fresh water containing high DO concentrations from rainwater.

To minimize the possibilities of eutrophication, TN should not exceed a limit value of 3 mg/L [11]. A high possibility of eutrophication can occur when TN is greater than 1.7 mg/L [12]. The survey results showed that TN concentration exceeded 1.7 mg/L at all the sampling sites in the rainy season (September). In the dry season most of the sampling sites were < 1.7 mg/L except for site T5. The results of the water flow from May to September indicated that the flow in the rainy season (September) increases dramatically due to large amounts of rainfall at the beginning of the season. The rainwater will wash nutrients and organic matter on the surface of agricultural soils, resulting in higher TN levels. Therefore, the concentrations of nutrients measured at the beginning of the rainy season were higher than that of the dry season.

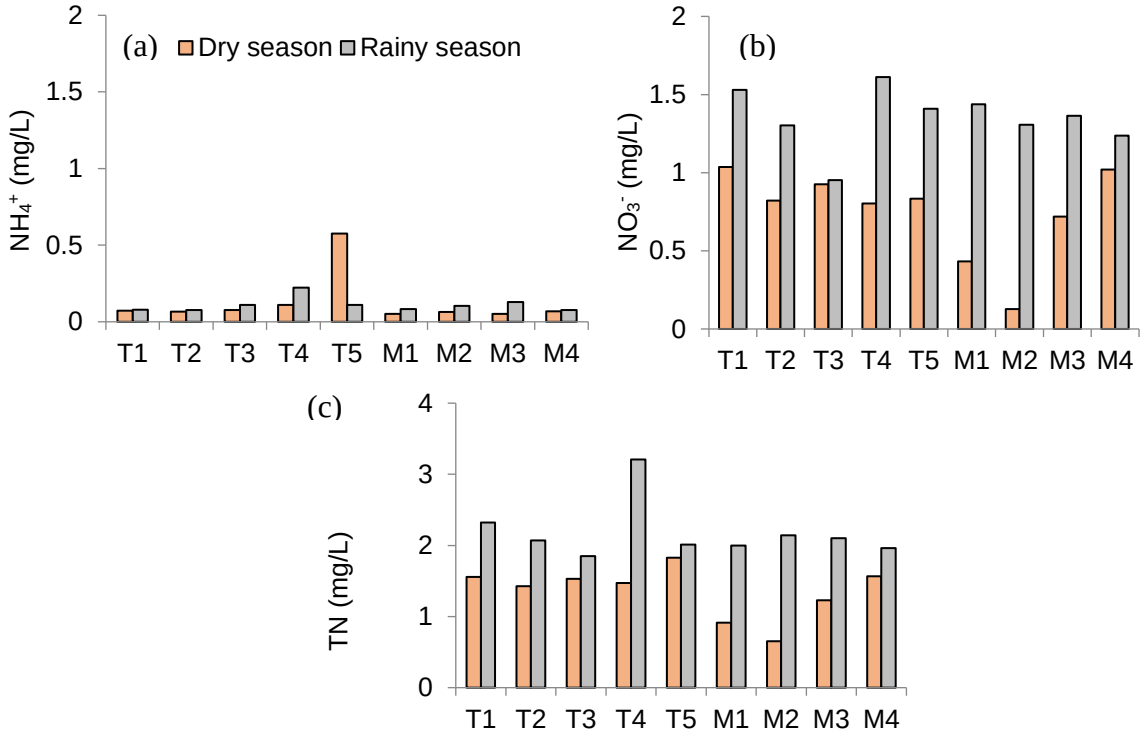



**Figure 4**: *Concentration of (a) $NH_4^+$, (b) $NO_3^-$, (c) TN in mainstream and tributary sites*

Phosphate concentration varied between 0.06 and 0.23 mg/L, with an average value of 0.1 mg/L. The higher concentrations were observed in the tributaries and in the rainy season. According to QCVN 08-MT:2015/BTNMT, the maximum concentration of $PO_4^{3-}$ in surface water for domestic water supplies should be 0.1 mg/L. During the rainy season, $PO_4^{3-}$ concentration at all tributary sites exceeded the limits in the QCVN 08-MT: 2015/BTNMT, with the highest at site T4 (0.2 mg/L).

The concentration of TP ranged between 0.05 and 0.6 mg/L, with an average of 0.23 mg/L. In general, TP concentration was higher in the tributary than in mainstream, and showed little seasonal variation. The TP measured in the Ca River catchment was more than 0.1 mg/L, representing the presence of eutrophication [11].

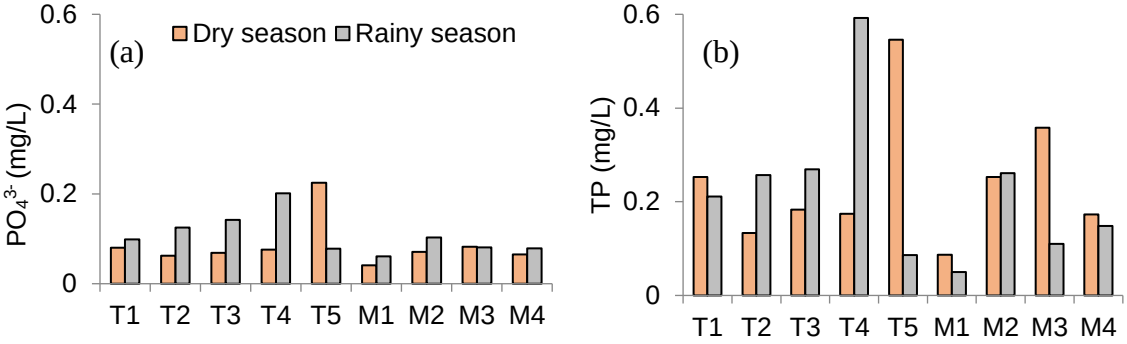



**Figure 5**: *Concentration of (a) $PO_4^{3-}$, (b) TP in mainstream and tributary sites*

Measured value of nutrients in rainy season recorded higher than in dry season. At the beginning of the rainy season, rainwater washes away substances nutrients in soils into the river basin, increasing the nutrient content on the tributaries. Tributary site of T4 was the highest of nutrient concentrations in rainy season among the monitoring sites, due to its location as the end point of the tributary river, receiving nutrients and organic matter from monitoring sites T1-3. At the same time, the water flow in the tributaries is lower than in the mainstream, so the concentration in the tributaries tends to be higher.

In dry season, T5 site revealed the highest concentration of $NH_4^+$, TN, $PO_4^{3-}$, and TP. Basin area of the T5 sites is 1,089 $km^2$ while the tributary is narrow and water discharge is low (27.7 $m^3/s$). We supposed that nutrient concentrations would not be diluted, resulting in the highest value being recorded in T5 site during the dry season.

Nutrient concentrations were found to be higher in the Ca River basin than in other main river catchments in Southern (Lower Mekong River) [13] and Northern Vietnam (Nhue River) [14]. According to Dodds et al. (1998), Dodds and Wetch (2000) [15, 16], the measured values of DO, TN, TP in the rainy season at tributary sampling sites of Ca River are high risk of eutrophication (Table 2).

**Table 2**: *Classification of trophic levels of river [15, 16]*

| **DO mg/L** | **TN mg/L** | **TP mg/L** | **Chl-a µg/L** | **Trophic status classification** |
|---|---|---|---|---|
| >5 | <0.7 | <0.025 | <10 | Oligotrophic |

| **DO mg/L** | **TN mg/L** | **TP mg/L** | **Chl-a µg/L** | **Trophic status classification** |
|---|---|---|---|---|
| 1 - 5 | 0.7 - 1.5 | 0.025 - 0.075 | 10 - 30 | Mesotrophic |
| 0 - 1 | >1.5 | >0.075 | >30 | Eutrophic |

The concentration of nutrients in natural water is affected by a variety of watershed characteristics, including agricultural use, fertilizer application rate, soil type, and hydrological hydrological flow paths between the land and the stream [17]. Rivers in Vietnam's Central Region have narrow riverbeds, steep slopes, and small catchment areas. During the rainy season, the flow is frequently concentrated quickly, resulting in high discharge rates [4]. Large concentrations of nutrients in surface soil are flushed out by erosion and runoff to rivers and then transported into estuaries.

### *3.3. Chemical oxygen demand (COD)*

The organic matter content in water is assessed by the COD parameter. The results showed that COD fluctuated significantly from 8.7 to 32.2 mg/L, with an average of 18.4 mg/L. The average COD in the rainy season (23.6 mg/L) is higher than in the dry season (13.2 mg/L). In the rainy season, the COD concentration measured in the mainstrem is higher than in the tributary. This trend is the opposite during the dry season.

Most of the sample sites (except for the site M3 in dry season) have a COD exceeding 10 mg/L, which is 1.0 to 3.2 times higher than the standard set for surface water quality according to the QCVN 08-MT:2015/BTNMT. The Ca River Basin is affected by agricultural activities and at the beginning of the rainy season (September), rainwater will wash nutrients and organic matter on the surface of the agricultural soil layer into the river, increasing COD concentrations in the entire river basin. Similarly the seasonal variation of COD was observed to be increasing during the rainy season and decreasing during the dry seasons [18, 19]. This may be that during the dry season, the reduced water quantity result to decreased COD value.

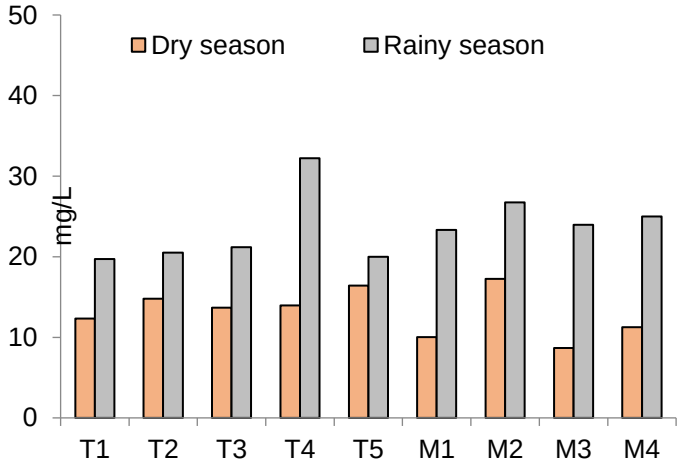



**Figure 6**: *Concentration of COD in mainstream and tributary sites*

### *3.4. Heavy metals*

The analysis results of heavy metals (As, Cu) at the sampling sites on the river basin through 2 seasons show that all values are within the allowable limits of the QCVN 08-MT:2015/BTNMT. Water quality of the Ca River was not contaminated with heavy metals (Table 3).

**Table 3:** *Results of heavy metal analysis at sampling sites on the mainstream and tributaries of the Ca River in two seasons*

| Sample sites | | As (mg/L) | Cu (mg/L) |
|---|---|---|---|
| **Dry season** | T1 | 0.01 | 0 |
| | T2 | 0 | 0 |
| | T3 | 0 | 0 |
| | T4 | 0 | 0 |
| | T5 | 0 | 0 |
| | M1 | 0 | 0 |
| | M2 | 0 | 0 |
| | M3 | 0 | 0 |
| | M4 | 0 | 0 |
| **Rainy season** | T1 | 0.01 | 0.03 |
| | T2 | 0 | 0 |
| | T3 | 0 | 0.02 |
| | T4 | 0.01 | 0.02 |
| | T5 | 0 | 0.01 |
| | M1 | 0 | 0.01 |
| | M2 | 0 | 0.02 |
| | M3 | 0 | 0.01 |
| | M4 | 0 | 0,02 |
| **QCVN 08-MT:2015, Columne A1** | | **0.01** | **0.1** |

## 4. Conclusion

Physical parameters (pH, EC, salinity, DO) and and heavy metals (As, Cu) are within the standard values according to the National Technical Regulation on Surface Water Quality QCVN 08-MT:2015/BTNMT for domestic water supply purposes (Columne A1). Average water flow in the rainy season (1,332 $m^3/s$) was 12 times higher than in the dry season (112 $m^3/s$), and at mainstream sites the average water flow was higher than in tributary sites. Measured value of nutrients in rainy season recorded higher than in dry season. In rainy season, higher nutrient concentrations at

the tributary sites compared to those at the mainstream may be due to agricultural runoff. At the same time, water flow in the tributaries was lower than in the mainstream, thus increasing the concentrations.

Concentration of nutrients ($NO_3^-$, TN, $PO_4^{3-}$ and TP) and chemical oxygen demand **(**COD) were found to be higher in the Ca River basin than in other Vietnam's river catchments. Measured values of TN, TP in the rainy season at tributary sampling sites of Ca River pose risks of eutrophication.

**Acknowledgments:** The authors are grateful for financial support provided by the Science and Technology Project of the Ministry of Education and Training of Vietnam B2021-TDV-09.

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# TÓM TẮT

## ĐÁNH GIÁ SỰ THAY ĐỔI CHẤT LƯỢNG NƯỚC MẶT THEO MÙA TRÊN DÒNG CHÍNH VÀ MỘT SỐ SÔNG NHÁNH THUỘC LƯU VỰC SÔNG CẢ

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Ngày nhận bài 15/11/2023, ngày nhận đăng 17/3/2023

Nghiên cứu nhằm đánh giá sự thay đổi của chất lượng nước theo mùa trên sông chính và một số sông nhánh thuộc lưu vực sông Cả. Mẫu nước được thu vào mùa khô (tháng 5/2021) và đầu mùa mưa (tháng 9/2021) tại 4 vị trí trên sông chính và 5 vị trí trên sông nhánh để phân tích một số thông số chất lượng nước. Kết quả quan trắc các thông số lý học (pH, EC, độ muối, DO) và kim loại nặng (As, Cu) đều trong giới hạn quy định tại QCVN 08:2015/BTNMT về chất lượng nước mặt cho mục đích cấp nước sinh hoạt (cột A1). Nồng độ các chất dinh đưỡng đo đạc tại điểm sông nhánh cao hơn sông chính do tiếp nhận các chất dinh dưỡng và hữu cơ từ hoạt động nông nghiệp rửa trôi đổ về. Đồng thời lưu lượng nước ở sông nhánh thấp hơn sông chính, do đó nồng độ các chất dinh dưỡng có xu thế cao hơn. Hàm lượng chất hữu cơ (COD) và các chất dinh dưỡng ($NO_3^-$, TN, $PO_4^{3-}$ và TP) ghi nhận được khá cao; vào đầu mùa mưa cao hơn mùa khô do hiện tượng rửa trôi các chất dinh dưỡng chảy về lưu vực sông làm gia tăng hàm lượng dinh dưỡng. Nhìn chung, chất lượng nước vào mùa mưa tại các điểm quan trắc trên sông nhánh có mức độ dinh dưỡng cao, nguy cơ phú dưỡng.

**Từ khóa:** Chất lượng nước; hàm lượng dinh dưỡng; phú dưỡng; sông Cả.