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The variation of organic carbon concentrations in the surface water in Cua Luc Bay, Ha Long Bay, Vietnam

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ABSTRACT

The total organic carbon (*TOC*) in the marine environment, which includes dissolved organic carbon (*DOC*) and particulate organic carbon (*POC*), is essential to the ocean's carbon cycling system. This research was carried out in 2023 to assess the variation in organic carbon concentration in the environment of Cua Luc Bay and Ha Long Bay at 22 survey stations. The results show that the average concentrations of *DOC* and *POC* are 1.59 ± 0.21 mgC/L and 0.74 ± 0.35 mgC/L, respectively. However, *DOC* and *POC* concentrations are still considered low compared with other rivers and estuaries in Vietnam and worldwide. The ratios of organic carbons like *DOC*/*POC* and *POC*/Chl-*a* in this study area were also calculated. The ratios' results are evidence of many fluctuations in the water environment in Ha Long Bay, Vietnam, in 2023.

Keywords: Organic carbon, *TOC*, *DOC*, *POC*, Cua Luc Bay, Ha Long Bay.

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INTRODUCTION

In the marine environment, organic carbon (*OC*) is vital in the carbon cycle and transporting materials from estuaries, bays, rivers, and lakes to the seas and oceans [1–3]. *OC* occurs in two different types [4]. Organic matter that may be separated from other components by passing through a filter larger than 0.45 um is known as dissolved organic carbon (*DOC*). Furthermore, particulate organic carbon (*POC*) refers to all non-carbonate carbon collected on the filter; it may comprise suspended particles in addition to live or dead microbes [5].

River systems wash an estimated 815 million tons of sediment into bays annually [6]. On the other hand, each year, 0.53 to 1.15 million tons of organic carbon (*OC*) in the form of *DOC* are deposited in rivers that drain into the ocean [7, 8]. The process of transporting organic matter through some river basins has been studied in Vietnam; in the Red River system, the load result was 31.5 × 10^{13} ± 4.0 × 10^{13} MgC.yr^{-1} [9]; in the Cam and Bach Dang River systems, the phytoplankton distribution and diversity have been impacted by the organic matter and heavy metal content [10]. Research conducted in the Baltic Sea reveals that *POC* and *DOC* concentrations in seawater environments depend on the time of day and season and are related to environmental parameters such as chlorophyll-*a*, $\delta^{13}C$, NO_3^-, NO_2^-, NH_4^+, PO_4^{3-}, salinity, pH, and temperature [11]. We can better assess or anticipate changes in environmental quality when we know the amount of organic carbon in the aquatic environment. Consequently, in the wet and dry seasons of 2023, the study team surveyed the current state of organic carbon content in the surface water environment at 22 points spread out over Cua Luc Bay and Ha Long Bay. The study's findings support preserving the environment in the newly extended Ha Long - Cat Ba world historic region, which UNESCO officially recognizes.

MATERIALS AND METHODS

Study area and sampling sites

Ha Long Bay has an area of 1,553 km^2 and nearly 2,000 large and small limestone islands. The Bay is an island region with a climate divided into two seasons: a hot and humid summer and a cold and dry winter, with an average annual rainfall of 2,000–2,200 mm. Research studies were conducted to collect surface water samples in the Cua Luc Bay area, including 4 points downstream of the Troi and Dien Vong Rivers (symbolized as N1, N2, N3, and N4) and 7 points inside Cua Luc Bay (symbols N5, N6, N7,..., N11). On the other hand, in the Ha Long Bay area, 11 points were distributed outside Cua Luc Bay in the Southwest direction as shown in Figure 1.

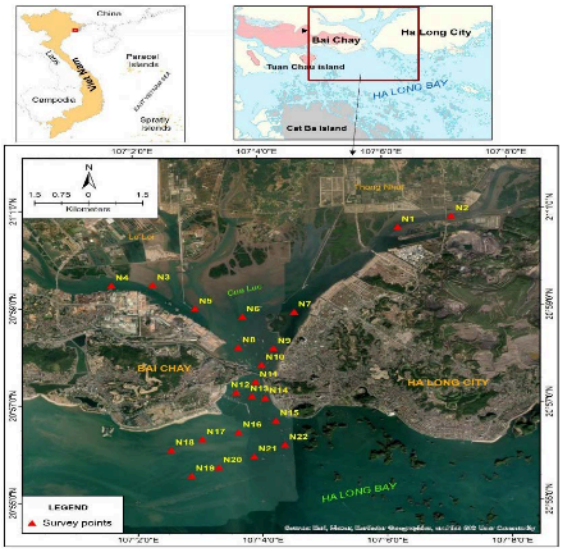

Figure 1. The research area's map and survey stations

The researcher method

Time and frequency of field sampling surveys: during the dry season (March 2023) and the rainy season (July 2023). To ensure the sample was evaluated without being affected by the tide's ups and downs, the sampling period was selected on a day with a variation in the low tide water level.

Surface water samples for the field were collected using a Niskin device at a depth of 1 m above the water according to the "Procedure for Investigation and Survey of Marine Resources and Environment—Environmental Chemistry Part". Samples were collected in 500 mL transparent PE plastic bottles and placed in an insulated box to maintain temperature, while field samples were transported to the laboratory for analysis. The bottles were placed in an acidic environment with a pH of 2 (H_3PO_4 85%) at 4°C [12].

Sample analysis:

This study uses an organic carbon analyzer (Multi N/C 2100S Analytik Jena). All organic carbon in samples oxidized to CO_2 form in the presence of the catalyst, which was quantified using an absorption detector non-dispersive infrared sub-infrared (NDIR) [13–15] by measurement as *TC* - *TIC*. According to "The Association of Official Analytical Chemists" (AOAC) standards [16], the recovery value of the method reached a value of 91–107% within the sample unit range from 1–100 pm.

The sample was brought to room temperature at the lab, where the total organic carbon (*TOC*) concentration was determined. Firstly, it is automatically pumped into the furnace at a temperature of 720°C along with the catalysts in the reaction column to convert carbon to CO_2, which leads to a detector that measures NDIR to define total carbon (*TC*). The sample is the pumped into the *TIC* system with a 10% H_3PO_4 acid catalyst, converting the inorganic carbon to CO_2 gas and defining inorganic carbon (*TIC*) like the *TC* system. The *TOC* concentration will be calculated using the formula (1):

$$TOC = TC - TIC \quad (1)$$

Like the process of determining *TOC*, an amount of the sample is passed through a 0.7 um MGF Sartorius filter. The solution obtained after filtration is used to define the *DOC* concentration. The *DOC* was calculated by the formula (2) via total dissolved carbon (TC_t) and dissolved inorganic carbon concentration (TIC_t).

$$DOC = TC_t - TIC_t \quad (2)$$

Particulate organic carbon (*POC*) concentration is determined through the concentration of total organic carbon and dissolved organic carbon [17] according to formula (3).

$$POC = TOC - DOC \quad (3)$$

Chlorophyll-*a* (Chl-*a*) was quantified using a UV-VIS machine after water samples were filtered via filter paper and extracted in 90% acetone solvent, per APHA 2017 procedure 10200 [18]. Following centrifugation, the samples underwent UV-VIS Hach DR3900 measurements at 750, 664, 647, and 630 nm wavelengths. Afterward, the concentration of Chl-*a* was determined using Jeffrey and Humphrey's three-equation technique (1975).

RESULTS AND DISCUSSION

The results of organic carbon analysis at Cua Luc and Ha Long Bay over two periods in 2023 are shown in Table 1.

In the first stage, *DOC* and *POC* concentrations in Cua Luc Bay varied respectively from 0.41 mgC/L to 1.55 mgC/L and 0.28 mgC/L to 0.94 mgC/L; in the second stage, DOC concentrations ranged from 0.23 mgC/L to 2.05 mgC/L while POC concentrations fell to 0.55 mgC/L to 0.71 mgC/L. The average POC was 0.82 ± 0.42 mgC/L, while the average *DOC* concentration for the entire region was 1.57 ± 0.26 mgC/L. On the one hand, in Ha Long Bay, the first-step values for *DOC* and *POC* ranged from 0.84 mgC/L to 1.55 mgC/L and 0.46 mgC/L to 0.66 mgC/L. The second-step values for *DOC* ranged from 0.24 mgC/L to 1.96 mgC/L and *POC* from 0.44 mgC/L to 0.66 mgC/L. The average *DOC* concentration throughout the region was 1.62 ± 0.17 mgC/L and the average *POC* was 0.66 ± 0.16 mgC/L. Overall, organic carbon levels ranged from 0.99 to 3.76 mgC/L in Cua Luc, with an average of 2.39 ± 0.53 mgC/L. In Ha Long, however, the range was 1.49 mgC/L to 3.37 mgC/L, with an average of 2.28 ± 0.23 mgC/L.

In two surveys, the *POC* and *DOC* concentrations in Cua Luc were higher than

those at stations outside of Ha Long, especially when the *POC* was 0.71–0.94 mgC/L as opposed to 0.66 mgC/L. This concentration makes sense since Cua Luc Bay is situated downstream of river branches (Man, Troi, and Dien Vong Rivers), which have the potential to carry *POC* here before flowing out to Ha Long Bay through data at stations N1, N2, N3, N4, and from station N9 to N14. It may be possible that part of the carbon source will come from residential wastewater from Ha Long and Bai Chay Cities.

The average *DOC*/*POC* ratio worldwide is 1.5. This ratio can assess an area's hydrological and environmental features [19]. Over the whole study area, the average *DOC*/*POC* ratio was 2.39 ± 2.10 in March and 7.38 ± 12.41 in July. It was specifically 1.60 ± 1.42 and 5.43 ± 3.93 at the Cua Luc region, but at stations in the Ha Long region, it was 3.18 ± 2.43 on average and peaked at 9.32 ± 17.30 in phase 2. The calculated *POC* concentration also fit with the geography of the study area and was similar to what other researchers have found in Vietnam in Yen Bai (1.7 ± 2.0), Hoa Binh (5 ± 2.3), Vu Quang (2.9 ± 2.6), and Hanoi (2.7 ± 3.4) [9]. Besides that, there are other places, such as the USA's Mississippi River, which has a *DOC*/*POC* ratio of 4.4 [20]; and the Tana River, which has a range of 0.02 to 16.4 [21]. Consequently, the Man, Troi, and Dien Vong Rivers affect the amount of organic carbon that builds up and is transported to the water environment in the research region.

Table 1. The current state of *TOC*, *DOC*, and *POC* in the study research

Area	Locations	Stage 1			Stage 2		
		TOC (mgC/L)	DOC (mgC/L)	POC (mgC/L)	TOC (mgC/L)	DOC (mgC/L)	POC (mgC/L)
Cua Luc	N1	2.62	1.08	1.54	2.50	2.01	0.49
	N2	0.99	0.41	0.58	1.84	1.69	0.15
	N3	2.20	1.45	0.75	2.37	2.12	0.25
	N4	2.18	1.55	0.63	3.28	1.77	1.51
	N5	1.12	0.76	0.36	2.31	2.11	0.20
	N6	1.37	0.60	0.77	2.85	1.85	1.00
	N7	2.54	1.14	1.40	2.52	2.21	0.31
	N8	1.79	1.51	0.28	2.29	2.07	0.22
	N9	2.26	1.30	0.96	3.66	2.56	1.10
	N10	2.80	1.04	1.76	3.03	2.09	0.94
	N11	2.32	1.04	1.28	3.76	2.11	1.65
Ha Long	N12	2.34	1.25	1.09	3.02	1.90	1.12
	N13	1.55	1.38	0.17	2.25	1.67	0.58
	N14	2.50	0.84	1.66	2.00	1.87	0.13
	N15	1.50	1.32	0.18	2.75	2.16	0.59
	N16	1.94	1.46	0.48	2.39	2.10	0.29
	N17	1.64	1.21	0.43	3.37	1.88	1.49
	N18	2.66	1.55	1.11	2.45	2.41	0.04
	N19	1.65	1.29	0.36	2.85	1.96	0.89
	N20	2.16	1.37	0.79	2.49	1.52	0.97
	N21	1.97	1.42	0.55	2.65	2.02	0.63
	N22	1.49	1.10	0.39	2.52	2.04	0.48

Chlorophyll-*a* concentration in the first stage saw a range of 0.40 µg/L to 0.99 µg/L, with an average of 0.80 ± 0.15 µg/L; the second stage saw a range of 0.42 µg/L to 0.96 µg/L, with an average of 0.70 ± 0.17 µg/L. According to research by Steven Bouillon from 2002, POC primarily originates from phytoplankton if the *POC*/Chl-*a* ratio reaches a value of roughly 30–

100 mgC/mg Chl-*a* [22]. On the other hand, higher rates (30–100 mgC/mg Chl-*a*) of POC may result from river system erosion and leaching [23]. Based on Cifuentes' (1988) experiments, phytoplankton is highly developed in an area if the *POC*/Chl-a ratio is less than 200 mgC/mg Chl-*a*, and vice versa if the POC/Chl-*a* value is greater than 200 mgC/mg Chl-*a*, showing a high organic matter concentration and breakdown [24]. *POC*/Chl-*a* ratios in the research region ranged from 305 mgC/mg Chl-*a* to 1,778 mgC/mg Chl-*a* and 289 mgC/mg Chl-*a* to 1,793 mgC/mg Chl-*a* in two stages. These results indicate a minor contribution of phytoplankton biomass to *POC* concentrations. Because of erosion and leaching, water gets more turbid and contains more total suspended particles. Additionally, they prevent phytoplankton growth, which raises *POC* concentrations and decreases Chl-*a*, raising the *POC*/Chl-*a* ratio.

According to Table 2, the *POC* concentration at Bach Dang estuary is 163.27 ± 68.30 µmol C/L, and four rivers in Hanoi (To Lich, Lu, Kim Nguu, Set) are 299.9 ± 74.97 µmol C/L higher than the research area at 61.65 ± 29.42 µmol C/L. Meanwhile, the *DOC* concentration is 132.81 ± 17.90 µmol C/L higher than at the Bach Dang estuary 95.80 ± 74.13 µmol C/L and lower than the river in Hanoi 129.11 ± 199.92 µmol C/L [25, 26]. The explanation for this problem is that the Bach Dang estuary is a downstream branch of the Red River system that flows through many cities before reaching the sea. As such, it is significantly impacted by numerous wastewater streams as well as the process of erosion. Similarly, *POC* concentrations also change widely, ranging from 15.83 µmol C/L to 1,084.9 µmol C/L at Korea's Geum and Seomjin estuaries [27], suggesting that the amount of leaching and erosion occurring there affects *POC* concentrations close to the river mouth. Following that, the *DOC* concentration is lower than that of the river in Hanoi since an amount of wastewater from Hanoi city is collected in the rivers, whose wastewater volume of 1,200,000 m^3/day/night has high significant BOD and COD concentrations [26]. Additionally, the concentration of DOC in surface water (0–5 m) at three places in the Southern Baltic Sea (Gdańsk Deep, Gotland Deep, and Bornholm Deep) ranges from 360–409 µmol C/L [28], which is greater than at Cua Luc - Ha Long Bay.

Table 2. Other findings from around the world

Locations	*DOC* (mgC/L)	POC (mgC/L)	References
Cua Luc, Ha Long Bay (Vietnam)	132.81 ± 17.90	61.65 ± 29.42	This study
Gdańsk Deep (Southern Baltic)	409.83 ± 118.28	60.81 ± 33.32	[28]
Gotland Deep (Southern Baltic)	360.69 ± 74.14	42.48 ± 31.65	[28]
Bornholm Deep (Southern Baltic)	403.17 ± 74.14	49.15 ± 28.32	[28]
The Geum and Seomjin estuary systems (South Korea)	-	15.83–1,084.9	[27]
River, Hanoi (Vietnam)	1291.1 ± 199.92	299.9 ± 74.97	[26]
Bach Dang River (Vietnam)	95.80 ± 74.13	163.27 ± 68.30	[25]
Loch Eriboll (Northern Scottish)	72.9 ± 5.6	132.4 ± 83.9	[29]
Loch Inchard (Northern Scottish)	67.4 ± 4.0	63.1 ± 23.6	[29]
Loch a' Chàirn Bhàin (Northern Scottish)	61.4 ± 19.0	145.2 ± 64.2	[29]
Loch Torridon (Northern Scottish)	24.9 ± 3.9	108.8 ± 35.0	[29]
CW: Coastal Water	94.64 ± 21.23	36.39 ± 32.71	[30]
SYS: South Yellow Sea	108.22 ± 22.90	17.72 ± 12.10	[30]
ECS: East China Sea	76.60 ± 22.56	9.39 ± 2.08	[30]
TWC: Taiwan Warm Current	90.02 ± 13.75	15.55 ± 6.88	[30]
KC: Kuroshio Current	86.77 ± 16.70	3.95 ± 0.75	[30]
Coastal Waters	285.7 ± 5.7	-	[31]
Estuaries	329.8 ± 7.0	-	[31]

The study area's *DOC* and *POC* concentrations are higher than those in the larger sea area that stretches from the Korean Strait through the East Vietnam Sea and the East Yellow Sea. The range of DOC concentrations is 76.60 ± 22.56 µmol C/L at ECSMW to 108.22 ± 22.90 µmol C/L at SYSMW, while the range of *POC* concentrations is 3.95 ± 0.75 µmol C/L at KC to 36.39 ± 32.71 µmol C/L at CW [30], as Table 2 shows. Nonetheless, according to research findings from Northern Scotland, *POC* is less than the other three places with *POC* values greater than 100 µmol C/L and like the Loch Inchard point (63.1 ± 23.6 µmol C/L) [29]. Barrón and Duarte estimate that the *DOC* concentration in estuarine areas is around 329.8 ± 7.0 µmol C/L, while the *DOC* concentration in coastal waters is roughly 285.7 ± 5.7 µmol C/L [31]. The current values in the study area are not as high as the organic carbon concentrations reported by Barrón and Duarte at coastal and estuarine locations.

CONCLUSION

The results of the current assessment of the organic carbon in surface water in the Ha Long Bay area in 2023 are as follows: Total organic carbon (*TOC* = *DOC* + *POC*) ranges from 1.41 mgC/L to 3.04 mgC/L, with an average of 2.33 ± 0.40 mgC/L that includes *DOC* concentrations range from 1.04 mgC/L to 1.98 mgC/L, with an average of 1.59 ± 0.21 mgC/L and POC concentrations range from 0.25 mgC/L to 1.47 mgC/L, average of 0.74 ± 0.35 mgC/L. In the whole research region, the average *DOC*/*POC* ratio was 2.39 ± 2.10 in stage 1 and 7.38 ± 12.41 in stage 2; the average *POC*/Chl-*a* ratio varied from 450 mgC/mg Chl-*a* to 1,563 mgC/mg Chl-*a* and averaged 916 ± 324 mgC/mg Chl-*a*.

The research provided data on carbon concentration and its variations and fluctuations in the water environment, particularly the *POC*/Chl-*a* ratio, which shows the contribution ratio of phytoplankton biomass to carbon. Additionally, the *DOC*/*POC* ratio shows that river erosion and leaching influence the amount of carbon in Cua Luc Bay.

One of its shortcomings is the lack of oceanographic data to evaluate the weight or environmental variables impacting the transport flow and distribution of carbon in the studied area is. These are preliminary findings regarding the present state of organic carbon.

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