Vietnam Academy of Science and Technology

Vietnam Journal of Marine Science and Technology

journal homepage: vjs.ac.vn/index.php/jmst

Water quality of submarine caves and marine karst lakes in Cat Ba Archipelago (Hai Phong, Vietnam)

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Received: 25 May 2024; Accepted: 16 August 2024

ABSTRACT

Submarine caves and marine karst lakes in the Cat Ba archipelago (Hai Phong) were surveyed in June and November, 2019. The results showed that the water was weakly alkaline, the dissolved oxygen concentration was very low, most of the oxygen saturation in the water was in the range of 50–70%. Water in submarine caves had higher and more stable salinity than that in marine karst lakes, however, the dissolved oxygen concentration was lower than that in lakes. The self-purification of water was better in the rainy season. The water was polluted by ammonium in the rainy season in Ang Vem, Ba Man, Ba Mat and Ang Gay lakes. There is no evidence of organic contamination but the high nitrate and phosphate concentration had been recorded. The presence of H_2S gas in the water had begun to affect organisms.

Keywords: Submarine caves, marine karst lakes, water quality, Cat Ba Archipelago.

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https://doi.org/10.15625/1859-3097/18632

INTRODUCTION

Karst is a type of landscape developed on highly soluble rocks (e.g., limestone, dolomite, gypsum, halite) as a result of dissolution, corrosion, subsidence, and/or collapse, characterized by the presence of distinctive hydrological and morphological features [1]. Submarine cave and marine karst lake are types of karst landscape. For most of this landscape, access requires climbing over the surrounding cliffs.

Submarine caves are often dark, poorly lit, confined spaces. They are often home to unknown biodiversity as well as home to communities with low tolerance. Submarine caves are also targets that need to be protected in order to maintain the functional integrity of the habitat [2]. Geologically, the development of submarine caves is also governed by hydro-geochemical conditions. Hydrogeochemical modeling experiments show that the pH of the mixture of groundwater and seawater must be lower than about 7.6 to initiate the dissolution of carbonate rocks that can lead to marine cave formation [2].

The area of Cat Ba Archipelago has undergone many processes of subsidence, sea advance and mountain formation - the sea recedes, the rise and fall of the tectonic plates and karst erosion lasting about last 20 million years that forming submarine caves and marine karst lakes when the area is flooded due to sea level rise [3]. The research on the biological and environmental characteristics of submarine caves and marine karst lakes in the Cat Ba Archipelago is still quite limited. The first study in the framework of cooperation between Italian and Vietnamese scientists in 2003 conducted in 4 caves and lakes (Hang Luon, Me Cung, Bu Xam and Hang Du I) in Ha Long Bay - Cat Ba area recorded water temperature up to 36^{o}C in September 2003, along with the disappearance of medusa and anemones during this period [4, 5]. Research by Nguyen Dang Ngai et al., (2016) [6] in 3 underground caves namely Hang Sang Cave, Hang Toi Cave, Qua Bang Cave and 3 marine karst lakes Ang Du, Ang Dau Be, Ang Qua Bang in July 2014 showed that the caves and the lake had a rather high concentration of dissolved oxygen, up to 9.03 mg/L; however, the pH value was quite low (from 7.30 to 7.88). Low concentration of mineral nutrients (Dissolved Inorganic Nitrogen from 114.16 to 163.89 µg/L; phosphate from 15.84 to 18 µg/L) and organic matter (COD values ranged from 1.83 to 1.96 mg/L) were recorded here.

There are many submarine caves and marine karst lakes in Cat Ba Archipelago, some caves and lakes also have cultural and tourist values. Most of the submarine caves and marine karst lakes have not been exploited so they are still very unspoiled and difficult to access. These submarine caves and marine karst lakes have their own physicochemical and water quality characteristics that define their typical ecosystems. Due to the fact that, this paper presents the overall water quality of submarine caves and marine karst lakes in the Cat Ba Archipelago, make basic for further research on other ecological and geological characteristics as well as researches on culture, tourism, conservation.

MATERIALS AND METHODS

Study area and time

The submarine caves and marine karst lakes studied here belong to the sea area of Cat Ba Archipelago, Hai Phong City, Vietnam.

Caves are a characteristic of the eroded karst mountains. The characteristic submarine caves is lack of light. The light that penetrates deep into submarine caves depends on many factors such as: the width of the cave entrance, the depth of the cave and the clarity of the water.

Marine karst lakes are sub-ecosystems isolated from the outside environment. This difference that defines a characteristic biome of saltwater lakes.

In the Cat Ba area, there has been no investigation on the number of submarine caves and marine karst lakes. There are not many submarine caves in Cat Ba while there are about 26 large and small marine karst lakes scattered on islands and island clusters, the largest lake is about 28 hectares.

The study scope of the article is submarine caves and marine karts lakes located within the boundaries of the Cat Ba Biosphere Reserve. For marine karts lakes: only natural lakes with closed shorelines, an area of over 1,000 m^2, and not too difficult to access were surveyed. For submarine caves, only caves that were completely submerged or flooded at high tide, with a width of the cave entrance over 3 m and a depth of over 20 m from the cave entrance were surveyed.

Submarine caves

Of the 6 submarine caves selected for survey, they are all caves with 2 doors (pine caves) that connected between the lake and the bay. Water is circulated regularly according to the tide. For the caves connect to large lakes, the flow through the cave is quite strong. The bottom of the cave is usually rock, sand or gravel. The longest cave is Hang Toi Cave (270 m long) followed by Luoi Liem Cave (180 m long), and the shortest is Ang Ha Cave, 70 m long. Most of the caves are flooded at high tide, when the tide is low, the ceiling of the cave is exposed. Particularly, Qua Bang Cave is completely submerged at low tide.

Marine karst lakes

Among the 27 surveyed marine karst lakes, in terms of water exchange and shoreline tightness, there are two main types:

Closed lake: there are 10 lakes (Ang Xanh, Ba Mat, Ba Trai Dao, Bong Tron, Ca Hong Nho, Ca Vuoc, Cap Do, Lom Bung, Trat Sao, Van Ha). There is no doors or openings to the outside in these lakes, but they still exchange water with the outside environment through small openings or capillaries. The daily amount of water exchanged with the sea is not significant, so the lake usually has a low salinity of 10–15‰ in the rainy season and may be higher than that in the outside in the dry season due to water evaporation (Fig. 1).

Figure 1. Lom Bung lake (left) and Hang Sang cave (right) [*Photo by* Nguyen Dang Ngai (2019)]

Lakes connected to the sea: there are 17 lakes, these lakes usually connect to the sea through submarine caves or large trenches. The water is exchanged daily with the sea according to the rise and fall of the tide. Depending on the size of the lake and the width of the inlet, the daily water exchange is about 30–90%, so the salinity and biomes are similar to the outside.

The time for water quality survey of submarine caves and marine karst lakes: the first time was in June 2019 which typical for the rainy season; the second time was in November 2019, typical for the beginning of the dry season. The survey location of marine karst lakes and submarine caves at Cat Ba is shown in Figure 2.

Methods

Sampling

Water samples in submarine caves and marine karst lakes were collected at the surface layer using Niskin bottle. The sampling method was in accordance with TCVN 5998-1995 (ISO 5667-9:1992) - Water quality - Sampling - Seawater sampling guidelines [7]. Preservation

of samples was in accordance with TCVN 6663-3:2016 (ISO5667-3:2012) - Water quality - Sampling - Preservation and handling of water samples [8].

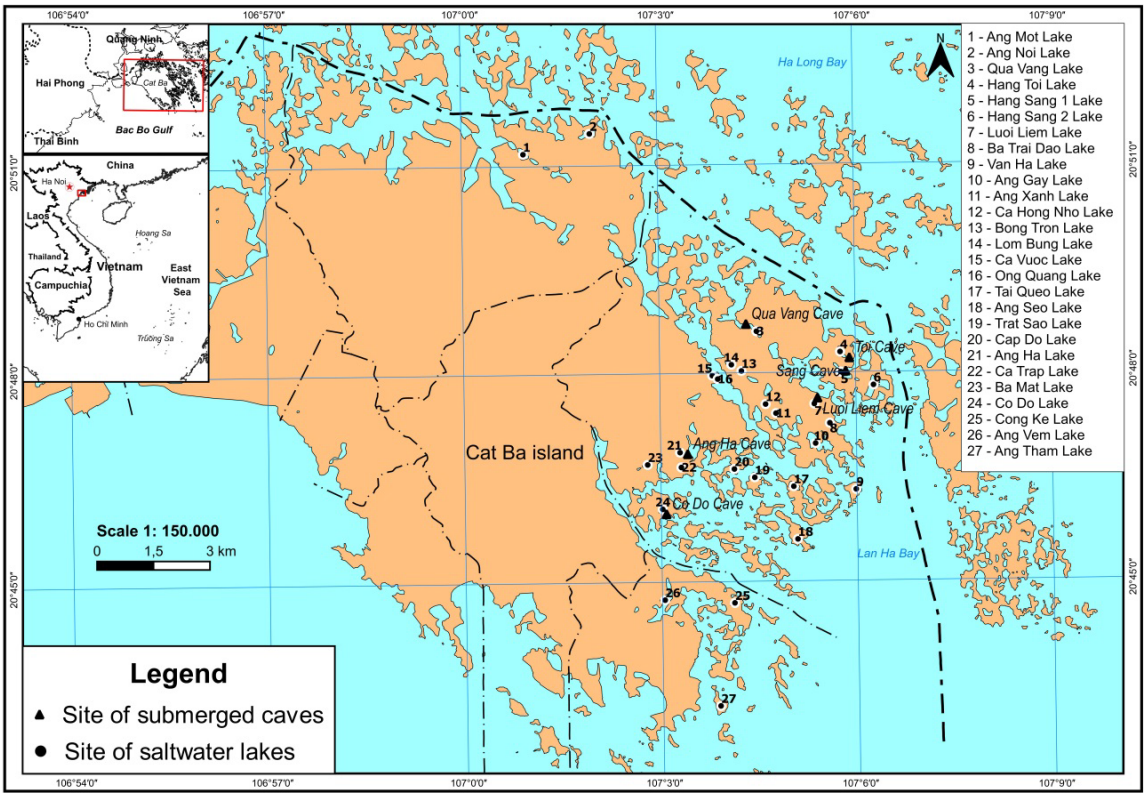

Figure 2. Location map of survey points

Water samples were collected at the surface layer of the middle of the lake/cave. Diving or wading to the sampling location and wait for the water surface to return to a static state before collecting samples. We collected 1 to 2 water samples for each lake/cave. For lakes with large depth and area (Ang Ha lake, Bong Tron lake), we collected samples in both surface and bottom water layers. A total of 38 water samples in the rainy season, 2019 and 30 water samples in the dry season, 2019 were collected in submarine caves and marine karst lakes in Cat Ba area.

Measure the parameters at situ: Water temperature, pH were measured by a portable pH meter; salinity was measured with a hand-held refractometer; DO was measured by DO meter YSY-55. Samples of mineral nutrients (N-NO_2^-, N-NO_3^-, P-PO_4^{3-}, Si-SiO_3^{2-}, N-NH_4^+), organic maters (expressed by BOD_5, COD) and S^{2-} were collected, fixed with chemicals and kept refrigerated at 4°C until analysis in the laboratory.

Analysis in the laboratory

Biochemical oxygen demand (BOD_5) was determined by Winkler method, unit mg/L, according to the guidance of TCVN 6001-1:2008.

Chemical oxygen demand (COD) was determined by oxidation of organic maters by Potassium Permanganate ($KMnO_4$) in alkaline medium, unit mg/L [9].

Nutrients: Nitrite (N-NO_2^+), nitrate (N-NO_3^-), ammonium (N-NH_4^+), phosphate (P-PO_4^{3-}), silicate (Si-SiO_3^{2-}) determined by colorimetric method on spectrophotometer DR3900 (HACH, USA), according to the guidance of TCVN 6178:1996 [10], EPA 352.1 [11], SMEWW 4500-

NH3 B&F:2017; SMEWW 4500-P.D:201717 and SMEWW 4500-SiO2 C:2017 [12].

The concentration of NH_3 gas was calculated from the results of ammonium analysis according to the formula of Thurston, et al., (1974) [13] based on temperature, pH and salinity.

Total sulfide was determined by volumetric method based on iodine measurement, according to the guidance of TCVN 4567:1988.

Data processing

Analysis, synthesis and evaluation of data: using Vietnam's national technical regulation on sea water quality (applying coastal water) and relevant ASEAN water quality criteria to evaluate the data [14–16]. The calculating and processing statistical data on Excel software is also used in this article.

RESULTS AND DISCUSSION

The survey results on the water quality of submarine caves and saltwater lake in Cat Ba Archipelago in 2019 were presented in Table 1 (June, 2019, the rainy season) and Table 2 (November, 2019, the dry season).

Hydrochemical characteristics

Water temperature: In the rainy season (June 2019), due to coincident with Summer time, the water temperature at the surveyed points was quite high, ranging from 27.7 to 34.9^{o}C, with an average of 31.0^{o}C. The highest temperature of 34.9^{o}C was recorded in the bottom water layer of Bong Tron Lake where the surface-bottom temperature difference was up to 3^{o}C. The high surface-bottom difference was related to the water exchange of caves and lakes with the outside. Due to the low water exchange, heat is retained in the water layers of the cave, especially the bottom water layer. In the dry season (November 2019), the water temperature in surveyed points ranged from 24.4 to 27.3^{o}C, with an average of 25.8^{o}C, lower than that of the rainy season. The temperature difference between the survey points was not clear in this season.

pH of water: pH in submarine caves and marine karst lakes in Cat Ba area fluctuated quite large, especially in the rainy season. The survey results in 2019 recorded pH values in the range of 7.59–8.41 units, the average in the rainy season was 8.08, the average in the dry season was 8.09. Most of the water samples obtained had a pH in the range of 8–8.2.

Salinity: Salinity of the water in surveyed points ranged from 10 to 26‰, an average of 23‰. The lowest salinity was at Ba Mat Lake. The difference in salinity between the caves and lakes was due to the influence of tides and the amount of fresh water added to the caves during the rainy season. With lakes of great depth such as Bong Tron, Ang Ha, the difference in salinity of water between the surface and the bottom is quite large, up to 11‰ in which the deeper to the bottom the higher salinity.

In the dry season, the salinity of water increased higher, but the range was also quite large, from 15–31‰, the water was brackish to saline. The survey results in two seasons show the salinity of lakes of Cong Ke, Ba Mat and Ca Vuoc was lowest.

Organic matter consumes oxygen

Dissolved oxygen (DO): The dissolved oxygen content in the water of the surveyed caves and lakes was quite low, ranging from 3.07 to 6.31 mg/L in the rainy season (June 2019), an average of 4.25 mg/L; and from 4.0 to 6.12 mg/L in the dry season (November 2019), an average of 4.89 mg/L. Thus, up to 93% of samples in the June and 53% of the samples in the November had DO values lower than the limitation of technical regulation of Viet Nam for aquatic life conservation (QCVN 10:2015/BTNMT) (5 mg/L) (Fig. 3). The oxygen saturation of water was mostly in the range of 50% to 70%, some lake have only 47% oxygen saturation (at Ang Tung Gau lake - June 2019), but some lakes had oxygen saturation reach to 97% as at Ang Gay lake (June 2019).

Table 1. Measurement and analysis results of water quality in submarine caves and marine karst lakes in Cat Ba Archipelago in June 2019

Parameters		Temp.(^{o}C)	pH	DO (mg/L)	Salinity (‰)	N-NH_4^+ (µg/L)	N-NH_3 (µg/L)	N-NO_2^- (µg/L)	N-NO_3^- (µg/L)	P-PO_4^{3-} (µg/L)	Si-$Si_2O_3^{2-}$ (µg/L)	S^{2-} (mg/L)	BOD_5 (mg/L)	COD (mg/L)
Cave (*n* = 4)	Aver. value	31.2	8.09	4.22	25	40.71	4.83	12.32	131.70	17.54	1570.4	1.67	2.69	3.41
	Min	30.2	8.06	3.67	25	26.60	3.07	5.82	92.74	13.99	1309.1	1.41	2.40	2.88
	Max	32.1	8.12	5.09	26	50.12	6.66	16.56	176.49	23.54	1868.3	2.06	2.96	3.65
Lake (*n* = 34)	Aver. value	31.1	8.08	4.26	23	66.58	8.17	9.98	134.93	17.93	1397.5	1.10	2.69	3.68
	Min	27.7	7.59	3.07	10	22.73	2.63	3.79	30.72	7.42	370.1	0.16	1.49	2.08
	Max	34.9	8.41	6.31	26	213.99	27.89	25.54	1256.30	80.12	3703.7	2.19	3.66	5.09

Table 2. Measurement and analysis results of water quality in submarine caves and marine karst lakes in Cat Ba Archipelago in November 2019

Parameters		Temp.(^{o}C)	pH	DO (mg/L)	Salinity (‰)	N-NH_4^+ (µg/L)	N-NH_3 (µg/L)	N-NO_2^- (µg/L)	N-NO_3^- (µg/L)	P-PO_4^{3-} (µg/L)	Si-$Si_2O_3^{2-}$ (µg/L)	S^{2-} (mg/L)	BOD_5 (mg/L)	COD (mg/L)
Cave (*n* = 6)	Aver. value	25.7	8.14	4.14	31	40.58	3.84	9.16	70.08	26.16	801.3	0.42	1.64	2.57
	Min	25.0	7.95	4.01	31	25.06	2.39	4.47	61.82	19.79	523.9	0.19	1.24	2.34
	Max	26.2	8.23	4.51	31	58.67	6.39	18.20	80.17	34.87	1105.0	0.75	2.08	2.92
Lake (*n* = 24)	Aver. value	25.8	8.08	5.08	26	49.99	4.06	9.92	92.69	23.82	994.1	0.28	1.47	2.55
	Min	24.4	7.81	4.00	15	23.25	1.37	4.55	60.87	15.90	509.0	0.06	1.05	1.56
	Max	27.3	8.41	6.12	31	95.68	9.26	28.54	265.64	35.44	1871.5	0.50	2.22	3.25

The low amount of dissolved oxygen in water is a characteristic feature of marine karst lakes and submarine caves due to the limitation of water exchange. Surveys on dissolved oxygen content in marine karst lake in Bai Tu Long National Park area in 2018 also recorded low DO values, ranging from 4.72 to 5.43 mg/L [17]. It is quite different from Ighiu kart lake (Romania) according to research by Radu et al., 2012, in which dissolved oxygen concentration in lake water was quite high, from 8.13–10.33 mg/L; this was due to the low temperature (8–20°C) increasing dissolved oxygen in water [18].

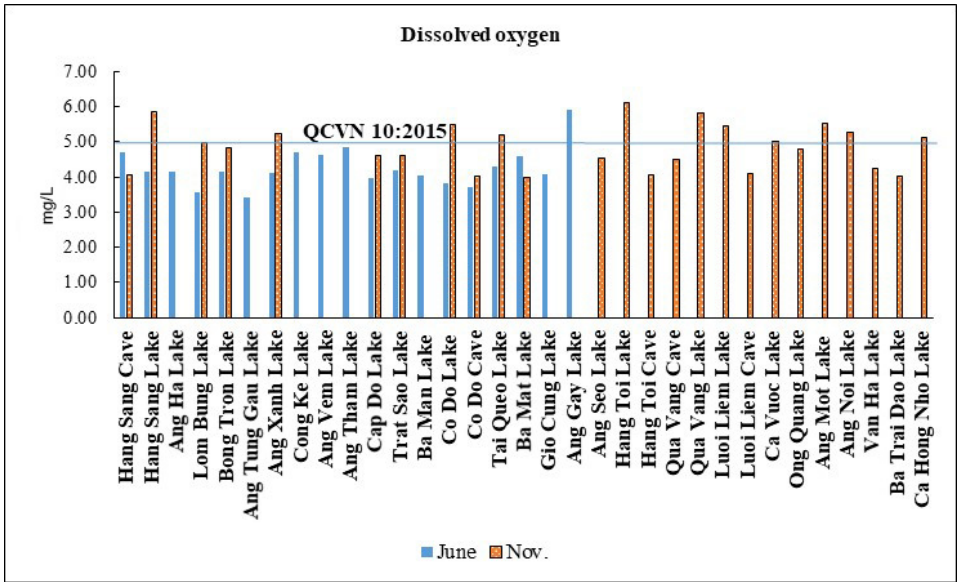

Figure 3. Dissolved oxygen concentration in water of submarine caves and marine karst lakes in Cat Ba area in 2019

Biochemical Oxygen Demand (BOD_5). The biochemical oxygen demand in the water of submarine caves and marine karst lake in Cat Ba area ranged from 1.49 to 3.66 mg/L, the average value in the rainy season was 2.57 mg/L; the average one in the dry season was 1.51 mg/L. In the rainy season (June 2019), the chemical oxygen demand of water was higher than that in the dry season (November 2019), related to organic waste sources from tourists in Summer time. Areas with higher biochemical oxygen demand in water than other sites are Ang Ha, Lom Bung, Co Do and Ang Gay lakes.

Chemical Oxygen Demand (COD). COD value in the water of submarine caves and marine karst lake in Cat Ba area ranged from 1.56 to 5.09 mg/L, an average value in the rainy season was 3.55 mg/L and in the dry season was 2.55 mg/L. In the rainy season, the chemical oxygen demand was about 1.4 times higher than that in the dry season. Areas with higher COD value than others were Ang Ha, Lom Bung, Co Do and Ang Gay lakes.

Vietnam does not regulate the limit value of BOD_5 and COD for coastal seawater, so the limit values of BOD_5 and COD for surface water has been applied (QCVN 08:2015/BTNMT). The survey results in 2019 showed that the water of the submarine caves and lakes was not polluted by organic matter, the observed values were all within the permissible limits (grade A1 for protection of aquatic life: BOD_5 and COD values in water are less than 4 and 10 mg/L, respectively).

The BOD_5/COD ratio of the water in the rainy season reached 70–83% while in the dry season it reached 45–77%, this shown the self-purification of water in submarine caves and marine karst lakes was better in rainy season, related to the water exchange of the natural system.

Mineral nutrients

Nitrite ($N\text{-}NO_2^-$): Nitrite is a nutrient for plants but a poison for animals [19]. In water of submarine caves and marine karst lakes in Cat Ba, the nitrite concentration in water ranged from 3.79 to 28.54 µg/L, an average of 10.75 µg/L in the rainy season and 28.54 µg/L in the dry season. In general, in the rainy season, the nitrite concentration in water was higher than in the dry season, however, there are some sampling points with high nitrite content in the dry season such as Lom Bung, Bong Tron, Luoi Liem lakes.

Nitrate ($N\text{-}NO_3^-$): The analysis results showed that the nitrate content in the water of submarine caves and marine karst lake ranged from 30.72–1,256.30 µgN/L, an average of 99.99 µgN/L in the rainy season and 160.87 µg/L in the dry season. The highest nitrate value was recorded at Hang Sang Lake in the rainy season, indicating local pollution there. The source of nitrate discharge in the area is mainly from domestic and tourist wastewater.

In addition to Hang Sang 3 lake, some sampling points have quite high nitrate content in water such as Cap Do lake (in dry season - 265.64 µgN/L), Ba Mat lake (in rainy season - 203.58 µgN/L), Ba Trai Dao lake (in dry season - 173.12 µgN/L).

Vietnam does not regulate the permissible limit for nitrite and nitrate in coastal seawater, but compared with ASEAN criteria for conservation of aquatic life, the permissible limits for nitrite and nitrate in water are 55 and 60 µgN/L, respectively. Compare to these, all of the water samples surveyed have nitrite concentration lower than this value, so the water was still safe with nitrite. However, 85% of samples in the rainy season and 100% of the samples in the dry season had higher nitrate content than the permitted level.

Phosphate ($P\text{-}PO_4^{3-}$): The phosphate concentration in water of submarine caves and marine karst lakes ranged from 7.42 to 80.12 µgP/L, the average value in the rainy season was 19.24 µgP/L and in the dry season is 15.90 µgP/L. The increasing trend of phosphate concentration in the dry season was observed at most of the monitoring points except at Bong Tron and Ba Mat lakes. Most of the water samples had phosphate concentration in the range of 10–30 µgP/L, some lakes with higher phosphate concentrationwere Ang Vem (in rainy season - 80.12 µgP/L), Ba Mat (in rainy season - 65.79 µgP/L), Ang Noi (in dry season - 35.44 µgP/L) and Luoi Liem Cave (in dry season - 34.87 µgP/L).

Compared with the permissible limits regulated in QCVN 10:2015 for coastal seawater (200 mg/L), the water of submarine caves and marine karst lakes in Cat Ba area was not contaminated with phosphates. However, compared with ASEAN criteria for conservation of aquatic life (45 µgP/L for coastal estuary), there were two samples collected in June (the rainy season) with values higher than the permissible limit, namely at Ang Vem and Ba Mat lakes.

Silicate ($Si\text{-}SiO_3^{2-}$): The silicate concentration in the water of submarine caves and marine karst lakes in 2019 ranged from 370–3,704 µgSi/L, the average concentrtaion in the rainy season was 1,369 µgSi/L; and in the dry season was 509 µgSi/L. In general, in the rainy season, the silicate concentration increased, the value was about 1.7–2.7 times higher than that in the dry season. However, there were some points that tend to increase the silicate content in the dry season, such as Lom Bung and Cap Do lake. In the rainy season, Ang Xanh lake was the point with the lowest silicate content in water (476 µgSi/L) and Ang Vem lake was the highest silicate concent in water - 2,248 µgSi/L. In the dry season, Tai Queo lake was the point with the lowest silicate content in water (509 µgSi/L) and Ba Trai Dao lake was the point with the highest silicate content - 1,872 µgSi/L.

The existence of gases in water

In an oxygen-deficient environment, there are present of harmful gases such as H_2S and NH_3 in submarine caves and marine karst lakes.

Ammonium ($N\text{-}NH_4^+$) and Ammonia gas ($N\text{-}NH_3$):

According to Boardman et al., (2004) [20], animals still functioned well and developed normally when the concentration of ammonia (non-ionic form ie NH_3) < 0.05 µg/L. When the concentration of ammonia gas exceeds 50 µg/L,

it can be toxic to fish and other organisms, even causing death. The ASEAN criteria stipulates that the permissible limit for NH_3 gas in water is 70 µg/L for coservation of aquatic life.

The survey results show that the concentration of NH_3 gas in the water ranged from 1.37 to 27.89 µgN/L, the average concentrations in June and November were 8.65 and 4.01 µgN/L, respectively. In general, the concentration of NH_3 in the water of submarine caves and marine karst lakes of Cat Ba does not affect the growth and development of aquatic organisms due to the water was weak alkaline. However, it should be noted that some lakes show high ammonium concentration in water were Ang Vem, Ba Mat, Ang Gay (Fig. 4), at these concentrations, if the pH and water temperature increased (due to an increase in water temperature in the summer plus an increase in the photosynthesis of phytoplankton), ammonia gas concentration would increase and be toxic to aquatic organisms.

In the rainy season, the concentration of ammonia in the water was higher than that in the dry season, about 2.1 times on average. The increase in NH_3 concentration in the rainy season was due to the temperature of the water in submarine caves and marine karst lakes increased in the rainy season, leading to a change in the balance between NH_4^+ ions and NH_3. In addition, this was also the time of high tourists in the area.

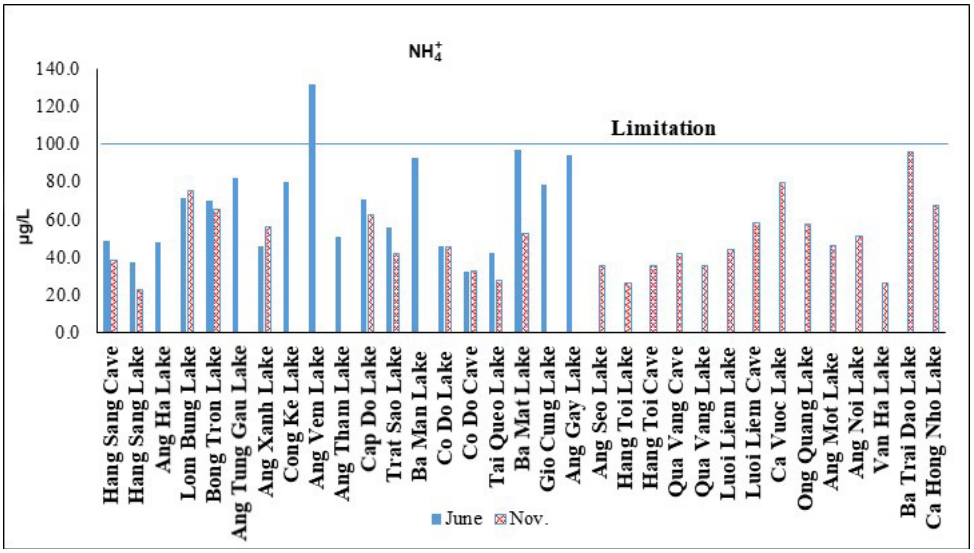

Figure 4. Ammonium concentration in water of submarine caves and marine karst lakes in Cat Ba area in 2019

Hydrogen sulfide gas (H_2S):

The surveyed results showed that the total sulfur content in the submarine caves and marine karst lakes of Cat Ba was quite high, ranging from 0.16 to 2.19 mgS/L, the average contents in the rainy season (June 2019) and in the dry season (November 2019) were 1.15 mgS/L and 0.06 mgS/L, respectively. An increase in the value of total sulfur in the rainy season has also been detected in the areas of the salty lakes of Cat Ba National Park [17]. The correlation between dissolved oxygen concentration and sulfide concentration in water was a weak positive correlation in the rainy season (correlation coefficient 0.24) and a weak negative correlation in the dry season (correlation coefficient -0.02).

According to research by ANZECC & ARMCANZ (2000) [21], in environmental conditions of submarine caves and marine karst lakes with temperature of 25 to 30°, pH from 7.5 to 8.5 and average salinity about 25‰, the concentration H_2S gas only accounts for 1–5% of the total sulfide (average 3%). Thus, in Cat Ba area, the concentration of H_2S gas in water of submarine caves and marine karst lakes ranged from 4.8 mgS/L to 65.7 mgS/L, the

average contents in June and November were 34.5 mg/L and 9.3 mg/L. The toxicity study of ANZECC & ARMCANZ (2000) is as follows:

Marine Molluscs: The EC_{50} of H_2S in 48hoursfor*Mytilus edulis* is 1.5 mg/L.

Sea urchin: The EC_{50} of H_2S in 48 hours for *Strongylocentratus purpuratus* is 3 mg/L.

Marine crustaceans: LC_{50} of H_2S in 48to 96 hours for 3 species, *Palaemonetes pugio, Rhepoxynius abronius* and *Eohaustorius estuarius* is from 24 to 112 mg/L.

Thus, with the concentration of H_2S in water of the study area of 4.8–65.7 mg/L, it also has a certain effect on aquatic organisms, especially in the rainy season. However, further studies are needed because it is only preliminary studies on the existence of H_2S gas in these caves and lakes, or the organisms in these caves may be adapted to these environment conditions.

General assessment

In general, the water quality in submarine caves and marine karst lakes was quite similar to the waters around Cat Ba archipelago according previous publication by the same group of authors in 2020 except for lower dissolved oxygen concentration, higher and more stability salinity in submarine caves and marine karst lakes [22]. For the group parameters of pollutants (heavy metals, organochlorine and organophosphorus pesticides, PCBs, oil and grease, cyanide, etc.), due to lack of research conditions, there are no data for evaluation and comparation. The water quality characteristics in submarine caves and marine karst lakes in Cat Ba archipelago was quite similar to the water quality in another research of the same objects in the Ha Long Bay - Bai Tu Long area [17].

In the world, research on water quality in submarine caves and marine karst lakes is limited, almost studies focuses on the formation of submarine caves and marine karst lakes [23–25]. The study of Mackenzie et al., (1995) on water quality of some saline lakes but the salinities of the water was very high, from 70 to more than 100 psu, and the studied parameters of water quality was different from our study [26]. In the study by Radu et al., (2012) [18] on water quality at Ighiu limestone lake (Romania), the lake was freshwater so the characteristics of water quality were much different from saltwater lakes with quite high DO (due to low water temperature) and high mineral nutrients. Study by Dominović et al., (2022) [27] in a marine lake in the central Adriatic (Lake Rogoznica) showed a lack of dissolved oxygen in lake water. Due to the lack of water quality data for these objects, the comparison is quite lame and needs more attention and research in the future. Similarly, the relationship between water quality and biodiversity of these objects also needs more studies. Regarding water quality characteristics, attention should be paid to light intensity and water clarity, especially in submarine caves. In addition, pollution factors such as pesticides, heavy metals, phenol, etc. need to be surveyed to create a baseline data set for further research. In general, these studies have contributed greatly to the economic and educational development of the Cat Ba Archipelago, especially when Ha Long Bay - Cat Ba Archipelago was recently recognized by UNESCO as a World Natural Heritage Site in September 2023.

CONCLUSION

Survey results at submarine caves and marine karst lakes in Cat Ba archipelago in 2019 showed that the water there was weakly alkaline, with pH ranging from 7.6 to 8.4. Water temperature changed seasonally, in which was especially high in summer, the highest recorded temperature was 34.9^{o}C in the bottom water layer. The salinity of the water was quite high, ranging from 10–31‰, water was brackish to saline. Water had low dissolved oxygen, most of the oxygen saturation in water was in the range of 50–70%. Although the water in submarine caves and marine karst lakes was not polluted by organic matter, the increase of organic matter in water in the rainy season was observed. Similarly, the water was not polluted by mineral nutrients of nitrogen and phosphorus but their concentration was still at an alarming level compared to ASEAN criteria. The existence of ammonia gas in the water of submarine caves and lakes does not pose a threat to organisms and ecosystems. However, the existence of H2S gas has begun

to have an impact on the growth of organisms. These are only preliminary studies on the existence of these gases, and further research is needed in the future.

Research on water quality in submarine caves and marine karst lakes in Cat Ba is quite new, not have been published in Vietnam. The submarine caves and marine karst lakes needs to be further researched in the future to supplement economic development and conservation in Cat Ba. In particular, Ha Long Bay - Cat Ba Archipelago has just been recognized by UNESCO as a World Natural Heritage Site, the number of tourists coming to Cat Ba archipelago will be very high, so the City needs make plans to exploit and preserve reasonable the Cat Ba archipelago in general and the submarine caves and marine karst lakes in particular.

Acknowledgments: The authors would like to thank the project "Research on the environment and biodiversity in some submarine caves and marine karst lakes in Cat Ba area for conservation and tourism development" for permission of publishing the data. The authors also would like to thank the project “Research on carbonate buffer systems in northeast coastal water bodies and the intrusion of atmospheric CO_2 into water bodies”, coded VAST06.04/23–24 for supporting this research.

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