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Patterns of carbonate chemistry in mangroves of the Northern Persian Gulf

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ABSTRACT

The mangroves located in the Northern Persian Gulf are reeling from anthropogenic pressures including from intense industrial activities (Pars Special Economic Energy Zone-PSEEZ). Given the unique geographical location of these mangroves, understanding the initial basis of seawater carbonate chemistry is key to link with global patterns of coastal ocean carbonate dynamics. In this study, water samples were collected from pre-designated stations representing the mangrove forest and nearshore water namely Nayband, Mel-e-Gonzeh and Bardestan of the Persian Gulf in September of 2016. Based on extensive carbonate chemistry measurements, the results show that the pCO_2 at the Nayband site (13217.9±5841.5 μatm) was significantly higher than the other two sites (Mel-e-Gonzeh: 416.4±49.3 μatm and Bardestan: 294.3±95.0 μatm) while pH (6.92±0.18) was significantly lower than the two other sites (Mel-e-Gonzeh: 8.18±0.02, Bardestan: 8.26±0.04). The observed increase of pCO_2 and decrease of surface water pH at the Nayband site compared to other two sites may have due to the emission of CO_2 originating from oil and gas refining facilities located PSEEZ. Moreover, surface water in Nayband was undersaturated with respect to aragonite (Ω_{arg}<1) and supersaturated (Ω_{arg}>1) in case of the Mel-e-Gonzeh and Bardestan sites. This study although preliminary provides much-needed baseline information to address issues of changing carbonate chemistry and can help towards understanding the basis of coastal ocean acidification.

1. Introduction

Mangrove ecosystems distributed along the coasts and estuaries in tropical and subtropical areas (Soeprobowati et al., 2022). The rates of primary production in mangroves are known to be equal to tropical humid evergreen forests and coral reefs (Alongi, 2014). Mangroves sustain wide array of economically and ecologically important biological diversity (Getzner and Islam, 2020; Ghosh et al., 2022) including important species of fisheries. Hence, mangroves form the basis of sustainable blue economy. Most importantly, mangroves contribute to global climate mitigation efforts through CO_2 sequestration as part of carbon cycle (Saderne et al. 2018).

At a global scale, increasing trends of global warming and resulting change in climate are affecting long-term survival of mangrove ecosystems due to multiple stressors such as rise in sea level, ocean currents, increased storminess, increased temperature, changes in precipitation and increased CO_2 (Alongi, 2015). These factors are inter- related and spatially variable across inter-regional scales. Over the past two-and-a-half centuries, continuous and increased use of fossil fuel burning as well as land-use changes associated with human activities have resulted in an increase in atmospheric CO_2 concentrations from 280 ppm to about 423 ppm in 2023 [National Oceanic and Atmospheric Administration (NOAA), 2023]. Therefore, the changing carbonate chemistry (and resulting changes in pH- ocean acidification) due to anthropogenic increase of atmospheric concentration of CO_2 is expected to exhibit variabilities across local, regional and global scales.

When anthropogenic CO_2 is absorbed by seawater, chemical reactions occur that reduce seawater pH, concentration of carbonate ion ($[CO_3^{2-}]$), and the saturation states of the biominerals aragonite (Ω_{arg}) and calcite (Ω_{cal}) in a process commonly referred to as ocean acidification (OA). As oceans become less basic, the ability of biological communities such as marine calcifiers to form calcite and aragonite skeletons decreases (Leung et al., 2022). In general, surface seawater is supersaturated with respect to calcium carbonate minerals (i.e., Ω> 1; see Feely et al., 2009). When carbonate saturation states in seawater drop below saturation (Ω=1), whether the reason for the decline in saturation is due to ocean acidification or other natural processes, carbonate biominerals in shells and skeletons may begin to dissolve, and the water is generally termed as "corrosive".

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Newton et al., 2015) has identified and recognized particular gaps in understanding of carbonate chemistry for coastal and inshore waters across regions globally (León et al., 2018). This gap in knowledge has raised questions regarding potential consequences of OA for near-shore ecosystems such as mangroves. To be able to accurately predict future impacts of OA on biological communities and across biotopes in near-shore coastal environments, it is absolutely necessary to understand the present conditions and the variability of seawater carbonate chemistry in these environments (Wahl et al., 2016; Knor et al., 2024). Such information would be ultimately critical towards developing robust science-based policy frameworks for OA across regional seas and oceans.

The Persian Gulf (PG) is a Northwest to Southeast oriented basin adjacent to the northwestern Indian Ocean, with water surface area of approximately 24,0000 km^2 (Reynolds and Michael, 1993). It is one of the largest marine habitats and home to rich biodiversity including ornamental fish, edible and non-edible fish as well as marine turtles, dolphins and sharks, and harbors the mangrove communities as the only coastal vegetative habitat (Kor and Mehdinia, 2020; Van Lavieren et al., 2011). According to Van Lavieren et al. (2011) up to three quarters of the total mangroves in the Gulf region are located along the Iranian coast. Mangrove in the region is already affected by climate change as well as anthropogenic factors, e.g., dredging, residential building construction, tourism, oil extraction, shipping, and marine pollution (Halpern et al., 2008; Zahed et al., 2010; Sharifinia et al., 2019; Kor and Mehdinia, 2020). Sixty percent of the world's oil reserves are in this Gulf, hence construction of oil rigs, refineries, oil transit [approximately 35,000 tankers crossing the Strait of Hormuz (Naji et al., 2017)] and resulting release of industrial effluents (Sharifinia et al., 2019) as well as untreated sewage (Sheppard et al., 2010) are considered to be the major contributors to this pollution. The oil and gas exploration and processing activities in this region also results in intense CO_2 emission at different timescales. Moreover, the PG is characterized by its high seawater temperature and salinity, and the flexibility of its coastal ecosystems to global warming is of growing interest regionally and globally. This high salinity and temperature might render the PG a very favorable ecosystem for calcification, and therefore resistant to OA. The warm and saline water naturally tend to have a more basic pH and can be less corrosive to calcareous skeletons. Therefore, changes in chemistry of the CO_2 and acidity may impacts coastal ecosystems. There are a few studies addressing changes in the carbonate chemistry of seawater in mangrove ecosystems in some parts of the world (Saderne et al., 2019; Borges et al., 2003; Bouillon et al., 2007; Call et al., 2015; Camp et al., 2016; Ray et al., 2018; Rosentreter et al., 2018; Sippo et al., 2016; Land et al., 2019). However, such studies have not been conducted in the Persian Gulf, while being one of the critical research needs for identifying future changes in the Persian Gulf mangrove ecosystems.

The most recent ecological characterization study including carbonate chemistry within mangrove ecosystems was performed by Saderne et al. (2019) on the central Red Sea coast, Saudi Arabia, which is similar to the Persian Gulf in terms of environmental conditions (temperature, salinity, lack of freshwater run-off, and nutrient limitation). The present study is a baseline study aiming at characterizing the carbonate chemistry parameters including total alkalinity (TA), dissolved inorganic carbon (DIC), pH, CO_2 partial pressure (pCO_2), aragonite saturation (Ω_{arg}), salinity, dissolved oxygen (DO), temperature, nitrate and silicate in three mangrove ecosystems of the northern PG (Nayband, Mel-e-Gonzeh, and Bardestan) and additional nearshore stations as a reference site for comparison. The primary purpose of this research is to investigate the spatial variations of the carbonate chemistry in the northern coasts of the Persian Gulf in order to establish a regional framework for OA monitoring. By examining this region's unique characteristics, including its proximity to the largest natural gas field in the world (PSEEZ) and the presence of Nayband mangrove forest, we aim to provide valuable insights into the potential influence of anthropogenic CO_2 emission from PSEEZ on the carbonate chemistry of nearby coastal environments. For this purpose, we compared the Nayband mangrove with two other mangroves that are in remote locations (Mel-e-Gonzeh and Bardestan).

This study seeks to address some of the gaps in the current understanding of carbonate chemistry in the coastal ocean and act as a starting point for further studies aiming to better understand these valuable habitats which are of major economic, ecologic, scientific, and social importance.

2. Material and methods

2.1. Study sites

The mangroves in Iran occur between the northern orbits ranging from 25°19' to 27°84'. This area covers the north part of the Persian Gulf and Oman Sea, and three coastal provinces in the south of Iran (from southwest to southeast: Bushehr, Hormuzgan and Sistan & Balouchestan) (Zahed et al., 2010). These mangroves represent one of the biodiversity rich marine ecosystems across the region. To date, more than 107 species of fishes, 100 species of sea and shoreline birds, six species of prawn, and 10 species of crabs, five species of sea snake and two species of sea turtle have been reported from the mangroves of Iran (Zahed et al., 2010). In the present study, three mangrove sites namely Nayband, Mel-e-Gonzeh and Bardestan were studied (Fig. 1). The mangroves of Nayband located in the northern coast of the Persian Gulf with an area of approximately 390 ha represents the last dense and extensive complex ecosystem in the northwest Indian Ocean. However, Nayband mangroves, is facing reeling from the release of pollutants due to intense oil and gas exploration [largest natural gas field in the world and known as the Pars Special Energy Economic Zone (PSEEZ)]. In addition, changing land-use is affecting the region on a daily basis (Zahed et al., 2010). Besides, oil and gas exploration, other linked industries such as polymers, resins and adhesives, synthetic fibers and textiles, rubber and plastics, paints and protective coatings are in function within the vicinity of the Nayband mangrove (Kor and Mehdinia, 2020).

The Mel-e-Gonzeh mangroves are located along the southern section of the Mond protected area, close to Mel-e-Gonzeh village and near Omolgarm Island of Bushehr province, Iran (51°57' E and 27°84' N). The Mel-e-Gonzeh mangrove is home to *Avicennia marina* with an estimated coverage of 30 ha. The Bardestan mangrove forest consisting *Avicennia marina* is the smallest mangrove forest with an area of 1 hectare and located in the Bardestan estuary opposite to Dayer Port (Zahed et al., 2010). The sampled stations for each site along with respective coordinates are included in Table 1.

2.2. Sampling activities

The sampling activities were undertaken to measure inorganic carbonate chemistry of seawater from three mangrove sites (stations in each site were selected near the mangrove trees and additional nearshore stations as a reference site for comparison) during low tide in September 2016 (17th and 18th). The water samples were collected from a depth of 1 m using a 4-L Niskin water sampler (Hydro-Bios, Kiel, Germany).

2.3. Measurement of in situ environmental parameters

At the time of sampling, *in situ* environmental parameters such as pH_{NBS}, surface water temperature, dissolved oxygen (DO) and salinity were measured from each station using a HACH portable meter HQ40d over two consecutive days around midday (10:30–16:00). Seawater pH and temperature measurements were performed using a combined glass/reference electrode (HACH, IntelliCAL PHC101) calibrated by NBS buffers (accuracy of ± 0.02, precision of ± 0.001). Salinity was determined using a conductivity probe (HACH, IntelliCAL CDC401 with the precision of ± 0.1) calibrated by a certified reference seawater.

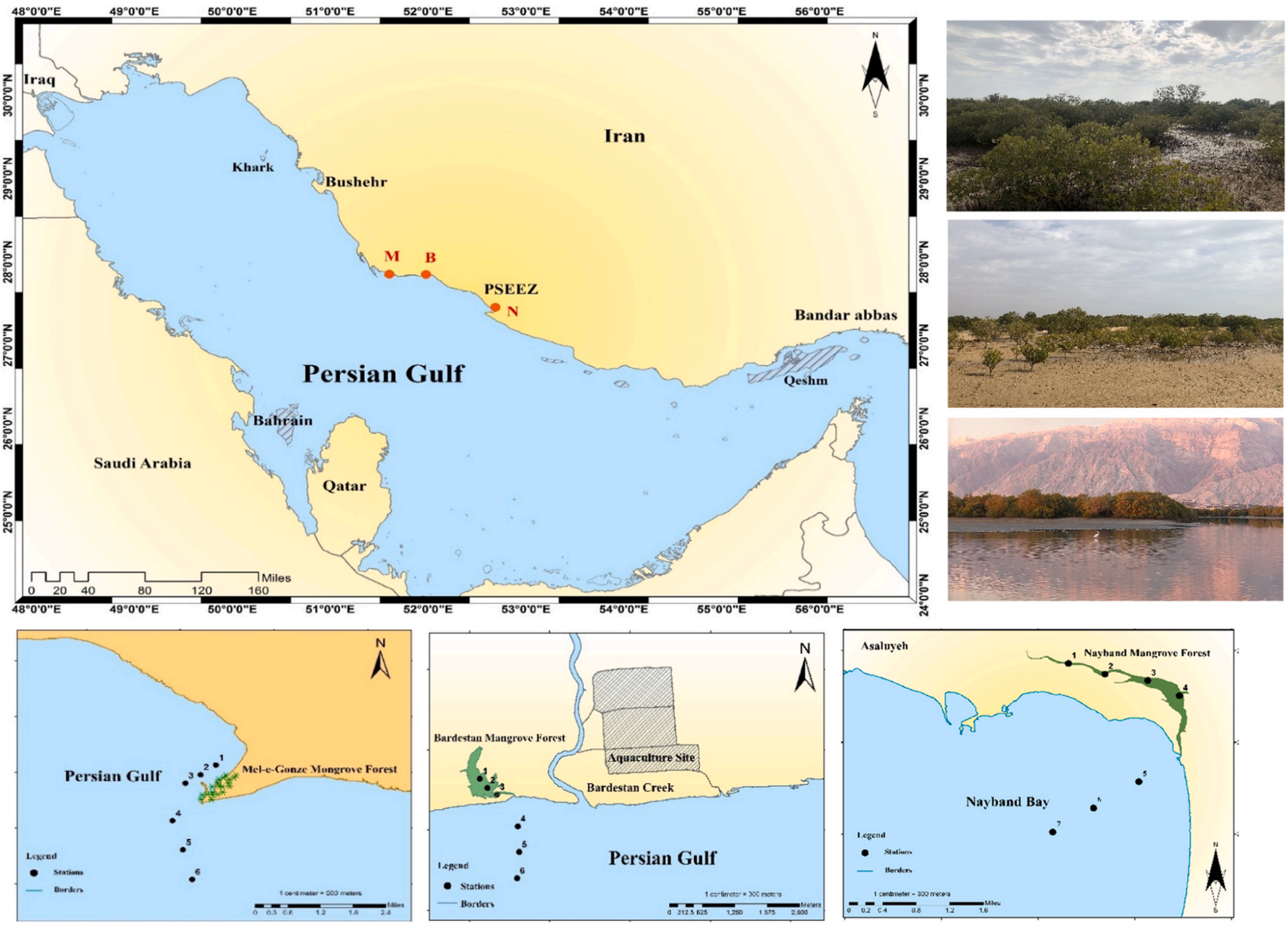

Fig. 1. The selected mangroves along with their location in the Northern Persian Gulf, M: Mel-e-Gonzeh, B: Bardestan, and N: Nayband mangrove forests.

Table 1
Sampling and measuring locations in the Persian Gulf.

Duration of study	Coordinates	Station name	Study site
18 Sep. 2016	27.464 N; 52.655 E	N1	Nayband (N)
	27.462 N; 52.661 E	N2	
	27.461 N; 52.668E	N3	
	27.447 N; 52.674 E	N4	
	27.442 N; 52.667 E	N5	
	27.438 N; 52.659 E	N6	
	27.433 N; 52.652 E	N7	
17 Sep. 2016	27.852 N; 51.584 E	M1	Mel-e-Gonzeh (M)
	27.849 N; 51.580 E	M2	
	27.846 N; 51.576 E	M3	
	27.835 N; 51.572 E	M4	
	27.826 N; 51.575 E	M5	
	27.817 N; 51.578 E	M6	
17 Sep. 2016	27.842 N; 51.960 E	B1	Bardestan (B)
	27.840 N; 51.961 E	B2	
	27.839 N; 51.963 E	B3	
	27.833 N; 51.966 E	B4	
	27.829 N; 51.966 E	B5	
	27.825 N; 51.966 E	B6	

Dissolved oxygen was measured using a calibrated dissolved oxygen optical sensor (HACH, IntelliCAL LDO101 luminescent/optical dissolved oxygen probe). The climatologic factors such as wind speed and direction, relative humidity, air temperature, and cloudiness, were obtained from the I.R. of Iran meteorological organization (http://www.irimo.ir) during the study period, which extended from 17/09/2016–18/ 09/ 2016.

2.4. Sample analysis

Water samples for determining dissolved inorganic nutrients were immediately filtered by syringe filters (0.45 μm, cellulose acetate), collected in 125 mL high-density polyethylene bottles and quickly frozen until further analysis (Grasshoff et al., 2009). Water samples for determining total alkalinity (TA) were collected in 500 mL glass bottles and 100 μL of a saturated mercury (II) chloride ($HgCl_2$) solution were added to stop the biological activities (Dickson et al., 2007). Samples were stored at 4 °C until laboratory analysis. Dissolved inorganic nutrients were determined using spectrophotometric techniques (ROPME, 1999) with a UV–Vis spectrophotometer (Analytikjena, Specord 210). Repeatability (relative standard deviation) for determination of orthophosphate and silicate in seawater were better than 5 and 10 %, respectively.

The total alkalinity (TA) was determined by potentiometric open-cell titration (Dickson et al., 2007, SOP03b) using a digital 715 Dosimat titrator (Hydro-bios). Non-linear least-squares fitting of titration data at the pH range of 3.0–3.5 were used to calculate TA. The precision of TA measurements was determined to be better than ± 3.5 μmol/kg (0.15 %) by titrating 10 subsamples of a secondary standard of seawater collected from the Persian Gulf to monitor the reproducibility of the system. The accuracy of the TA measurements was evaluated by analyzing certified reference materials (CRM, batch#182, A.G. Dickson, Scripps Institution of Oceanography, La Jolla, CA, USA). Carbonate chemistry of seawater was characterized based on pH_{NBS}, TA, temperature and salinity (and dissolved phosphate and silicate where they were measured), the CO2SYS software version 2.3 (Pierrot et al., 2006), and stoichiometric dissociation constants defined by Mehrbach et al. (1973) and refit by Dickson and Millero (1987).

2.5. Statistical analyses

The SPSS (version 22) software was utilized for statistical analysis of the obtained data. The distribution of data was attained using the Kolmogorov-Smirnov test. The non-parametric Mann-Whitney U-test and the Spearman test were used to determine the statistical difference and the correlation between the parameters, respectively. Arcmap10 GIS software was used to plot the map.

3. Results

During the study period, the wind speed and direction were 6 m/s and 160° to 180°. The relative humidity ranged between 57 % and 82 % and the recorded air temperature ranged from 29.6 to 36.4 ºC. The measured surface water temperature, salinity, dissolved oxygen and pH in studied stations are represented in Fig. 2.

The surface water temperature is the most important factor to maintain the growth, reproduction, survival, and distribution of organisms in the physical environment (Langford, 1990). Average measured temperature of nearshore water in the Nayband, Mel-e-Gonzeh and Bardestan sites, were 34.73, 32.53 and 34.57 °C, respectively. Average water temperature in the Nayband, Mel-e-Gonzeh and Bardestan mangrove, the recorded values were 36.05, 36.97 and 37.23 °C, respectively. The maximum temperature deviation of the mangrove stations from the nearshore water was 4.44 °C at the Mel-e-Gonzeh. The mean water temperatures at the mangrove stations were higher than the nearshore stations at three study sites. The surface water temperature showed a positive correlation ($p<0.01$) with pH at all of the studied sites.

Average nearshore water salinity in the Nayband, Mel-e-Gonzeh and Bardestan sites, were 37.10, 37.43 and 36.73, respectively. Average salinity of the Nayband, Mel-e-Gonzeh and Bardestan at the mangrove stations were 40.03, 40.70 and 39.70, respectively. The water salinity in mangrove stations showed a positive deviation from the corresponding values of the nearshore water in the range of +2.93 to +3.27. The higher salinity at mangrove stations is probably due to the lower depth at the mangrove stations which increases evaporation.

The average DO in the nearshore water of the Nayband, Mel-e-Gonzeh and Bardestan sites, were 7.68, 6.71 and 7.81 mg/L, respectively. Average DO at mangrove stations of the Nayband, Mel-e-Gonzeh and Bardestan were 7.95, 11.06 and 8.41, respectively. The DO showed a negative correlation ($p<0.01$) with temperatures and salinity ($p<0.01$) at all of the nearshore stations. This is due to the fact that, the higher water temperature, resulting in lower concentrations of DO (Fatema et al., 2015). Salinity and temperature affect the chemical conditions in the water, particularly the DO levels. In general, the solubility of oxygen in water is inversely correlated with temperature and salinity (CCME, 1999). The statistical analysis shows that the mean DO at the mangrove stations was significantly higher than the nearshore stations ($p<0.05$) at the three study sites, that might be due to the production of oxygen through photosynthesis by mangrove trees and release this oxygen into the surface water.

The pattern of pH in the Nayband mangrove ranged from 6.74 to 7.27 during the study period, with the lowest value recorded in stations closest to the mangrove (6.74). The average pH of surface water in the Mel-e-Gonzeh site was 8.16 and 8.18 in the nearshore water and mangrove stations, respectively. At Bardestan, the average pH of surface water was 8.17 and 8.26 in the nearshore water and mangrove stations, respectively. The observed spatial variation of carbonate chemistry parameters [pH (NBS scale), TA, DIC and pCO_2] at different stations at the three mangrove ecosystems are shown in Figs. 3–5. Incidentally, the average of TA, DIC, and pCO_2 at mangrove stations (N1 to N4) in the Nayband ecosystem was significantly ($p<0.05$) higher than the nearshore stations (N5 to N7). Also, the average of pH at the mangrove stations was significantly lower than the nearshore stations ($p<0.05$). This could be due to the smaller distance between the mangrove stations and the oil facilities.

In Figs. 4 and 5 average of TA, DIC and pCO_2 at the nearshore stations was found to be significantly higher than the mangrove stations ($p<0.05$). The mean pH at the Bardestan mangrove stations was significantly higher than the nearshore stations ($p<0.05$). The average pH in the Mel-e-Gonzeh did not show significant differences across different stations representing the mangrove and coastal region.

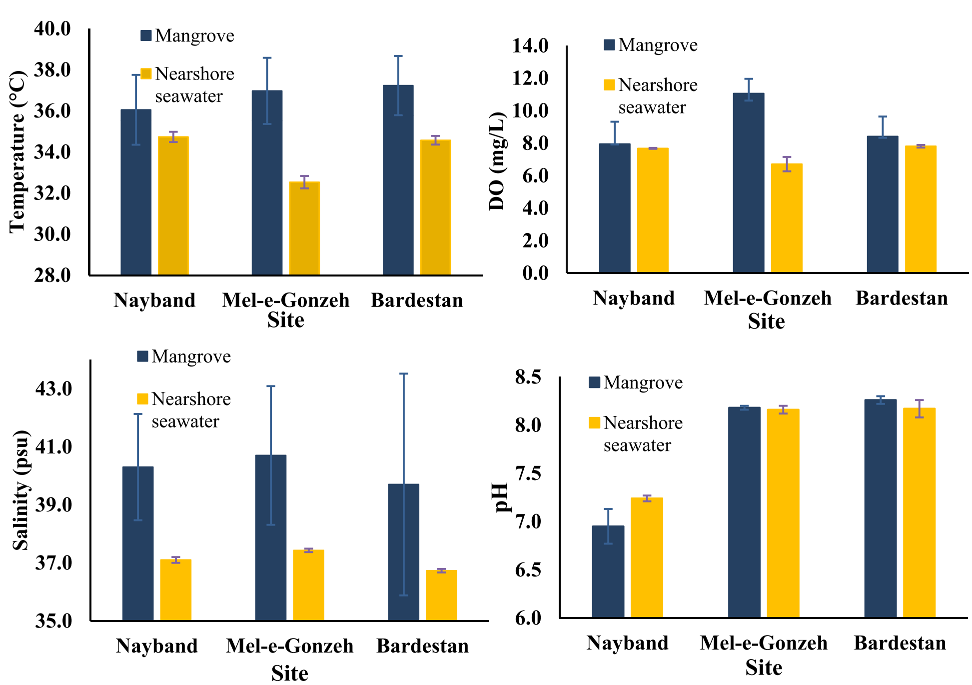

Fig. 2. Surface water temperature, dissolved oxygen, salinity, and pH in the mangrove forests and the nearshore water of the study sites. yellow color nearshore water; blue color: mangrove forest.

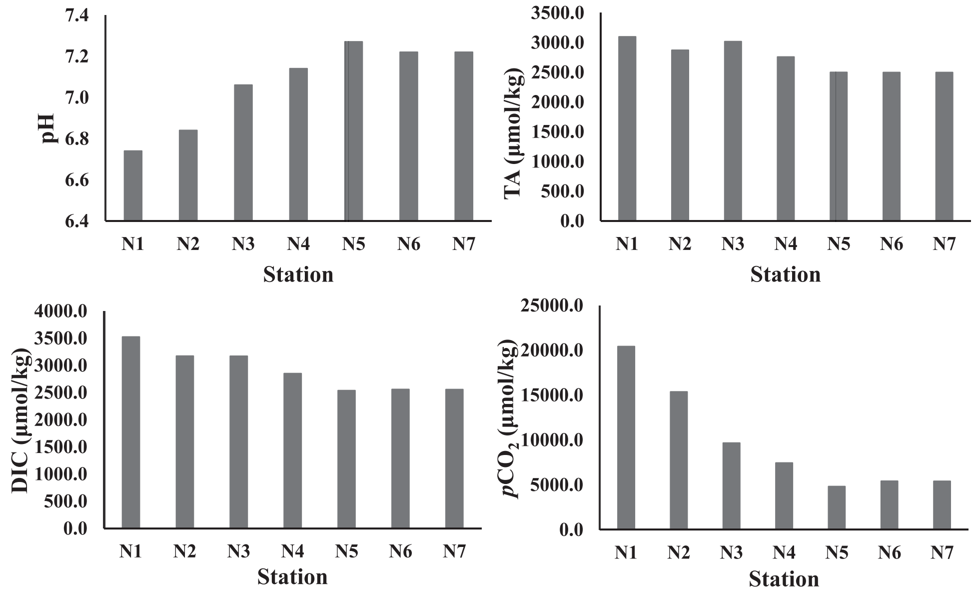

Fig. 3. Spatial variation of pH (NBS scale), TA, DIC and pCO_2 at different stations in the Nayband.

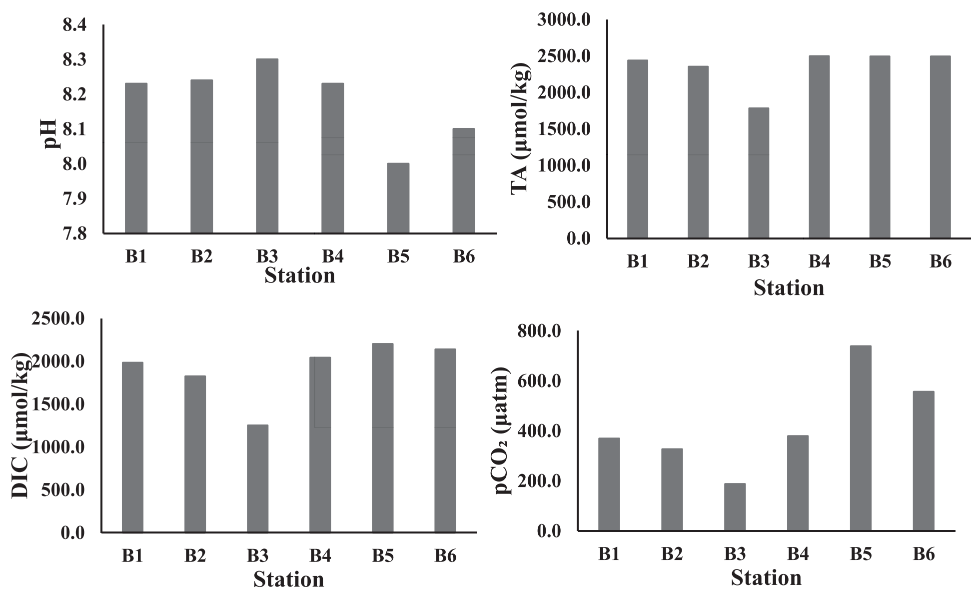

Fig. 4. Spatial variation of pH (NBS scale), TA, DIC and pCO_2 at different stations in the Bardestan.

4. Discussion

The present study is crucial in understanding the carbonate chemistry dynamics of the mangrove ecosystems located in the northern sector of the Persian Gulf. Also, the potential influence of anthropogenic CO_2 emission on the carbonate chemistry of the mangrove ecosystems has been studied. The Nayband mangrove is a perfect test bed to carry on such experiments because of its proximity to highly industrialized city of Asaluyeh, South Pars Especial Economic Zone (the direct cause of carbon dioxide emission) and presence of about 390 ha of mangroves. On this background the present study conducted to evaluate the alteration of carbonate chemistry in three mangrove forests (Nayband, Mel-e-Gonzeh, and Bardestan) situated on the coasts of the Persian Gulf.

The higher salinity at the mangrove stations relative to the nearshore stations (see Fig. 2) is probably due to the lower depth at the mangrove stations which increases evaporation. Typically, in the PG, the salinity gradually decreases in the seaward direction as the bottom depth increases (Reynolds and Michael, 1993). But average salinity showed no significant differences between three study sites (Fig. 2). Generally, the changes in the salinity in the brackish water habitats such as estuary, backwater, mangroves and coastal waters are due to the influx of freshwater from river, by land runoff caused by monsoon or by tidal variations. Higher values could be attributed to high degree of evaporation with decreased freshwater inflow and land drainage (Srilatha et al., 2012). These mangroves exist in an extreme environment under an arid climate with hypersaline conditions (38.1–43.3), and without direct riverine input.

The statistical analysis shows that the mean DO at the mangrove stations was significantly higher than the nearshore stations ($p<0.05$) at the three study sites, that might be due to the production of oxygen through photosynthesis by mangrove trees and release this oxygen into the surface water. In aquatic systems, oxygenation is the result of an imbalance between the process of photosynthesis, degradation of organic matter, reaeration (Liqoarobby et al., 2021), and

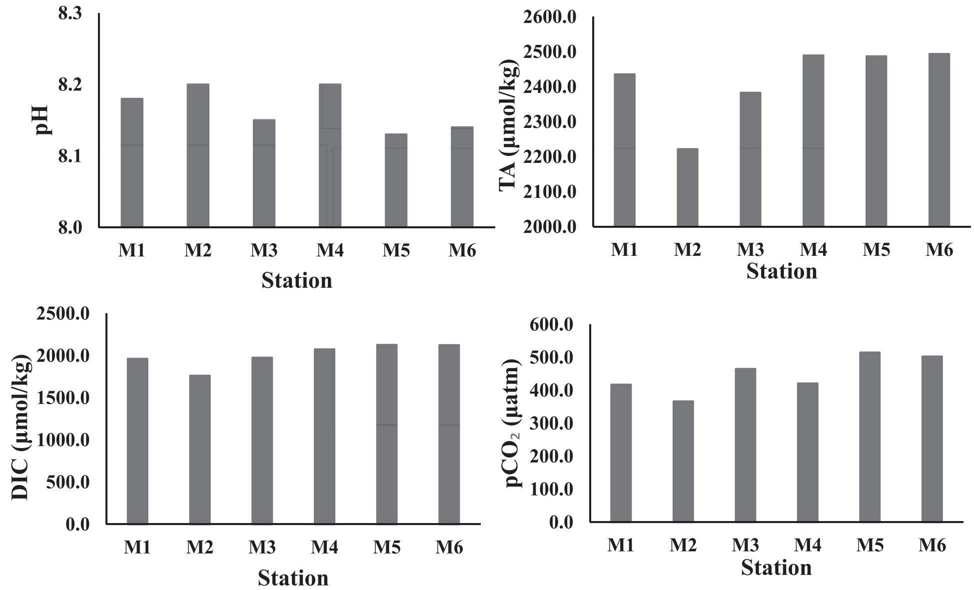

Fig. 5. Spatial variation of pH (NBS scale), TA, DIC, and pCO_2 at different stations in the Mel-e-Gonzeh.

physicochemical properties of water (ASTON and Simon, 1980).

The open ocean is known to act as net sink for atmospheric CO_2. However, the coastal zones, being transitional land-ocean zone with complex biological, physical, and chemical interactions, could act as both source or sink for the CO_2. It has been shown that waters in the coastal regions can remain supersaturated with respect to pCO_2 (Borges, 2003; Knor et al., 2024; Sarma et al., 2011; Sarma et al., 2012). From the present study, pCO_2 in the PG surface waters seems to exhibit trends towards ultimately achieving saturation in certain time intervals with respect to the atmospheric CO_2 equilibrium. Mangrove surrounding water has found to be supersaturated with respect to CO_2 due to the mangrove-derived organic carbon pool (Alongi & Mukhopadhyay, 2015; Borges, 2013; Dittmar et al., 2006).

The results (see Figs. 3–5) showed that, the average of alkalinity at Nayband mangrove stations was significantly higher than Mel-e-Gonzeh and Bardestan mangrove stations, respectively ($p<0.05$). This may be due to presence of denser mangrove forest in the Nayband (390 ha) site compared to the Mel-e-Gonzeh (30 ha) and Bardestan (1 hectare) sites (Chakraborty et al., 2013). Chakraborty et al. (2013) studied acidification of Sundarbans mangrove estuarine system and analyzed the role of mangrove vegetation in regulating the trend of acidification in that geographical locale. They just examined spatio-temporal variations of surface water pH in the eastern sector of mangrove dominated Indian Sundarbans. Their study revealed a slow pace of acidification of estuarine water of eastern Indian Sundarbans (0.026 unit/decade) compared to the estuaries of western Indian Sundarbans (0.04 unit/decade). This may be primarily due to presence dense mangrove forest in the eastern part of Indian Sundarbans. Also, total alkalinity showed no significant difference at the nearshore stations in these study sites. Previous literature has highlighted the mangrove forest can release alkalinity to the nearby coastal ocean and those alkalinity export has the potential to increase coastal ocean pH and may counteract coastal acidification on a local scale (Sippo et al., 2016). However, we have identified that pH in the Nayband site (in spite of larger area and higher alkalinity) was significantly ($p<0.05$) lower than Mel-e-Gonzeh and Bardestan in both mangrove and coastal stations. This may be due to presence of oil and gas facilities nearby the Nayband site and thus it affected by oil and gas activities and their pollution. In fact, the high pCO_2 values within this area lower surface water pH and in spite of higher alkalinity, cannot counteract coastal acidification. Doney et al. (2007) determined that in coastal regions fossil fuel combustion and agricultural practices produce increased atmospheric inputs of strong acids and bases to the coastal ocean that can further reduce the pH by as much as an additional 50 %.

Distributions of pH (NBS scale), TA, DIC, pCO_2 and Ω_{arg} at the three study sites and stations (mangrove and nearshore) are shown in Table 2.

In the surface waters of Mel-e-Gonzeh and Bardestan sites, the pH ranged from 8.13 to 8.20 and from 8.00 to 8.30, respectively and the pCO_2 ranged from 366.5 to 515.0 and from 187.4 to 738.7, respectively. The entire surface waters of the Mel-e-Gonzeh and Bardestan sites were supersaturated with respect to aragonite ($\Omega_{arg}>1$), and ranged from 4.19 to 4.97 and from 3.49 to 5.49, respectively. A similar amplitude of Ω_{arg} of 4.1±0.6 were found in the central Red Sea mangrove systems with salinities above 30 (Saderne et al., 2019). The mean (± SD) pH_T, DIC, TA, and pCO_2 were 7.95±0.26, 2069±132 µmol/kg, 2438±91 µmol/kg, and 493±178 µatm (Saderne et al., 2019). In contrast, the surface waters of Nayband had markedly lower pH and Ω_{arg} values and higher pCO_2 (6.74–7.27, 0.32–0.82, and 4929.6–20412.4 µatm, respectively) than the Mel-e-Gonzeh and Bardestan sites. So, the surface waters in the Nayband site were undersaturated with respect to aragonite ($\Omega_{arg}< 1$), as a result, carbonate biominerals in shells and skeletons may begin to dissolve. These highly corrosive waters with pH values <7.27 and Ω_{arg} <0.8 might be due to presence of oil and gas facilities (PSEEZ) nearby the Nayband site and increasing CO_2 levels of the atmosphere and other greenhouse gases. Some studies have reported high level of PAH's and heavy metals in the Nayband mangrove swamp (Zare-maivan., 2010; Amini et al., 2013; Dehghani et al., 2014; Kamalifar et al., 2016). Nayband mangrove also receives high quantity of human source sewages from industrial establishments of the PSEEZ (Parvinnia et. al., 2009). However, since there are no high-quality, long-term, carbon times-series measurements in this region, it is not possible to directly determine the increase of anthropogenic CO_2 in this area. To this date, an anthropogenic carbon signal owing to rising atmospheric CO_2 has not clearly been reported in any near shore marine environment as the likely time of emergence surpasses the present duration of observations (Sutton et al., 2019). However, temporal declines in seawater pH that exceed those of the open ocean have been reported for some systems including coral reefs (Cyronak et al., 2014), but have typically been attributed to the influence of processes other than rising atmospheric CO_2 (Cyronak et al., 2014).

Based on this initial dataset, it seems that there is non-dependency of total alkalinity on salinity. In the mangroves representing Nayband, Mel-e-Gonzeh and Bardestan, the role of mangrove porewater or sediments which are rich in bicarbonate, silicate, and phosphate can influence carbonate chemistry such as total alkalinity production in shallow

Table 2
The range and average of pH (NBS scale), TA, DIC, pCO_2 and Ω_{arg} at the three study sites and stations (mangrove and nearshore).

Study site	Station	pH	TA (μmol/kg)	DIC (μmol/kg)	pCO_2(μatm)	Ω_{arg}
Nayband	**mangrove**	6.74–7.14 (6.92 ±0.18)	2757.0–3097.0 (2935.5 ±151.4)	2849.9–3522.7 (3177.7 ±274.3)	7441.1–20412.4 (13217.9 ±5841.5)	0.32–0.75 (0.53 ±0.21)
	nearshore	7.22–7.27 (7.24 ±0.03)	2495.9–2499.0 (2497.5 ±1.57)	2536.0–2556.6 (2549.5 ±11.7)	4929.6–5542.4 (5204.2±342.3)	0.72–0.82 (0.75 ±0.06)
***p*-value** (Differences between mangrove and nearshore)		0.05	0.05	0.05	0.05	0.05
Mel-e-Gonzeh	**mangrove**	8.15–8.20 (8.18 ±0.02)	2221.7–2435.7 (2346.8 ±111.5)	1761.9–1975.9 (1900.1 ±119.9)	366.5–465.0 (416.4±49.3)	4.64–4.97 (4.86 ±0.18)
	nearshore	8.13–8.20 (8.16 ±0.04)	2487.1–2493.9 (2490.2 ±3.5)	2075.1–2124.0 (2108.8 ±29.3)	421.1–515.0 (479.7±51.1)	4.19–4.79 (4.44 ±0.31)
***p*-value** (Differences between mangrove and nearshore)		0.05	0.05	0.05	0.05	0.05
Bardestan	**mangrove**	8.23–8.30 (8.26 ±0.04)	1781.8–2436.8 (2190.1 ±356.1)	1250.8–1982.9 (1685.9 ±385.1)	187.4–369.1 (294.3±95.0)	4.25–5.49 (4.99 ±0.65)
	nearshore	8.00–8.23 (8.11 ±0.11)	2492.1–2496.2 (2493.6 ±2.2)	2041.1–2201.1 (2126.5 ±80.5)	379.2–738.7 (558.0±179.7)	3.49–5.23 (4.35 ±0.88)
***p*-value** (Differences between mangrove and nearshore)		0.05	0.05	0.05	0.05	0.05

coastal water. The pCO_2 values showed site specific trends with the Bardestan mangrove showing lesser value compared to the Nayband mangrove. Globally, similar trends have been reported from other coastal ecosystems such as from New South Wales, Australia (4000–6000 μatm; Maher et al., 2015), Brazil (2674 μatm; Noriega and Araujo, 2014), Changjiang, China (642–1445 μatm; Zhai et al., 2007), and Papua New Guinea (465–2565 μatm; Borges et al., 2003). The observed higher pCO_2 values in particular for the Nayband mangroves (~4929–13217 μatm) indicate the possible role of heterotrophic microbial CO_2 generation from benthic sediment and water column. Incidentally, mangrove creek water has already found to exhibit oversaturation with CO_2 and hence are a net source of CO_2 to the atmosphere (Borges at el., 2003). The major global factors that affect the carbonate chemistry include: organic matter production and degradation that result in the consumption and release of carbon dioxide; oxidation and reduction reaction that involves the consumption and production of protons; carbonate mineral formation and dissolution reactions that cause consumption or release of carbonate and bicarbonate ions. In the mangroves of the Persian Gulf, many of these factors could be in interplay and warrant further investigations.

The results of this study showed that there is a linear relationship between alkalinity and salinity in coastal stations in the three studied sites (Nayband, Mel-e-Gonzeh and Bardestan), while there is no linear relationship between alkalinity and salinity in the stations distributed throughout the mangrove forests. Alkalinity exhibits a linear relationship with respect to salinity in the surface waters of oceans, but in coastal and estuarine systems, due to the mixing of fresh water resources, lateral alongshore current, upwelling and biological activities, they can be diverted from linearity (Cai et al., 2010).

There is a large gap in terms of data focusing on the carbonate chemistry and acidity baselines in the mangrove located on the Persian Gulf. Thus, the actual response of the Persian Gulf mangrove ecosystems to global climatic changes remains an enigma for scientists. It will be speculative at this point to provide a comprehensive and reliable regional forecast of long-term change in the carbonate chemistry, largely due to non-availability of reliable information. What is required is a comprehensive, long-term, study to assess the carbonate chemistry patterns and factors affecting its changes, sources and sinks, and the impacts of these changes. It is clear from the data generated in the present study that the current status is ecologically unsustainable and calls for a concerted effort from scientists, regulators and politicians to enact legally binding policies to protect these economically important marine ecosystems.

5. Conclusions

In this paper, the carbonate chemistry parameters including TA, DIC, pH, pCO_2, temperature, salinity and Ω_{arg} in the surface waters of three mangrove ecosystems on the northern coasts of the Persian Gulf (Nayband, Mel-e-Gonzeh and Bardestan) have been investigated. Our findings revealed that the studied parameters exhibited considerable spatial variations. We have identified that the average of alkalinity at the Nayband mangrove stations was significantly higher than the Mel-e-Gonzeh and Bardestan mangrove stations that may be due to presence of denser mangrove forest in the Nayband site compared to the other two sites.

The observed increase of pCO_2 and decrease of surface water pH at the Nayband site compared to the other two sites was related to the emission of CO_2 originating from oil and gas facilities (PSEEZ) adjacent to the Nayband mangroves; but it might be limited to specific periods throughout the year and could have the opposite effect in the future. However, the existence of other carbonate producers in the studied mangroves could be an affecting factor in an acidifying environment, which was not addressed in this study.

Previous literature has highlighted the mangrove forest can release alkalinity to the nearby coastal ocean and those alkalinity export has the potential to increase coastal ocean pH and may counteract coastal acidification on a local scale. However, we have identified that the Nayband mangrove (in spite of larger area and higher alkalinity) affected by oil and gas activities and their pollution and so cannot counteract coastal acidification.

The entire surface waters of the Mel-e-Gonzeh and Bardestan sites were supersaturated with respect to aragonite (Ω_{arg}>1), but the surface waters in the Nayband site was undersaturated with respect to aragonite (Ω_{arg}< 1). The results showed that there is a linear relationship between alkalinity and salinity in the coastal stations in three studied sites, while there is no linear relationship between alkalinity and salinity in the stations distributed throughout the mangrove forests.

The results reported herein address some of the gaps in the current understanding of carbonate

chemistry and act as a starting point for further studies aiming to better understand these valuable habitats which are of major economic, ecologic, scientific, and social importance. It highlights the extreme variability in carbonate chemistry conditions experienced by mangrove ecosystems of the region, an essential consideration for future ecological researches. To have a more precise perspective about the carbonate system in the study area measurements and samplings should be performed in a better temporal and special resolution including annual and seasonal data. This research group is continuing its monitoring program in the mangrove ecosystems by improving the accuracy and precision of measurements (e.g., by direct measuring of pH in total hydrogen ion scale, DIC and pCO_2) to prepare for a part of the critical research needs for the future necessary protective measures in the Persian Gulf. It is clear that additional measurements in the mangrove ecosystems are needed to document and monitor for further changes as anthropogenic CO_2 continues to rise in the future.

CRediT authorship contribution statement

Maryam Ghaemi: Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Punyasloke Bhadury:** Writing – review & editing, Validation, Conceptualization. **Sara Gholmipour:** Investigation.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: This research was funded by the Iranian National Institute for Oceanography and Atmospheric Science (INIOAS).

Data Availability

Data will be made available on request.

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