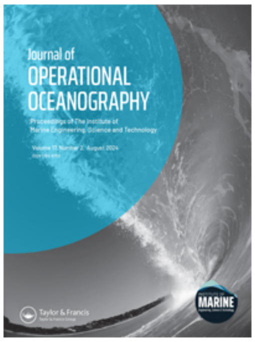

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Nutrient regimes in a semi-enclosed marginal sea: The Persian Gulf

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ABSTRACT
In this study, the results of hydrochemical measurement aboard the RV Kavoshgar Khalij Fars in the Persian Gulf (PG) in September 2018, May, and November 2019 are discussed. Nitrate, nitrite, ammonium, phosphate, and silicate concentrations, salinity, temperature, dissolved oxygen, and pH in the water column of a 1000-km transect in the PG were studied to determine the present status of nutrient regimes of this region. Nitrate, phosphate, and silicate were more concentrated at the bottom layer and showed a maximum just below the thermocline in summer and autumn. Seasonal distribution of nutrient ratios (N:P, N:Si, Si:P) indicates P limitation in autumn, N limitation in spring, P limitation and poor Si in summer throughout the upper layer. The results of this study do not infer eutrophication in the upper layer of the PG waters in autumn and summer.

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1. Introduction

The Persian Gulf (PG) is a shallow (36 m mean depth), Mediterranean-type marginal sea, and through the Strait of Hormuz connects to the Gulf of Oman (GO). Main river entrances (formed by the Arvand river also known as Shatt Al Arab, Mond, Hillah, and Hendijan rivers) are placed at the northern end of the PG, mainly on the Iranian side (Reynolds 1993).

Throughout the last decades, extreme environmental alterations have happened in the PG ecosystem due to human and natural pressures. The marine PG ecosystems have experienced severe anthropogenic pressures, such as dredging, urban development, pollution releases, and predominantly nutrient enrichment from sewage inputs. Seawater nutrient content enrichment has been associated with increasing algal blooms occurrence and increasing organic matter in the PG (Linden et al. 1990; Sheppard et al. 2010).

The chemical components of seawater modulate the functioning of the biotic compartments of marine ecosystems. In particular, the concentrations of the major nutrients (nitrate, nitrite, ammonium, phosphate and silicate) sustain the primary producers. Community structure and succession of phytoplankton reveal the ecosystem environmental situations, among which the nutrients accessibility plays an essential role (Dugdale 1967; Ryther and Dunstan 1971; Smayda 1980). If the nutrient supply is lower than the phytoplankton uptake, the concentration of nutrients decreases and limits further phytoplankton growth (Tilman et al. 1982). The community composition of phytoplankton, season, and position determine the limiting nutrient concentrations (Fisher et al. 1992). Nutrient supply fluctuations are frequently reflected in their elemental ratios (Yin et al. 2001). Therefore, nutrient ratios can use as indicators of the state of nutrient loading or forecast productivity (De Pauw and Naessens-Foucquaert 1991). These nutrient ratios (nitrate, phosphate, and silicate) are beneficial for predicting the abundance and accumulations of phytoplankton. To understand the phytoplankton ecology, the capability to recognise limiting nutrients plays a significant role. Furthermore, measurements of nutrient ratios in the water basin and their influence on the phytoplankton community can indicate potential growth limitations.

The inventory of the existing literature shows that little information is available on the hydro chemical conditions in the Persian Gulf marine system. The first chemical investigations of inorganic seawater constituents on the Iranian side of the Persian Gulf performed in the 1964–65 cruise of the R.V. Meteor (Dietrich et al. 1966). Brewer and Dyrssen (1985) studied hydrographic characteristics, nutrient distributions, alkalinity, and total CO_2 in the Persian Gulf on R.V. Atlantis II Cruise in February and March 1977. Umitaka-Maru performed three cruises in the winter of 1993–1994 to investigate the physical, chemical, and biological situations of the ROPME Sea Area (RSA) (Hashimoto

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et al. 1998; Yoshida et al. 1998). ROPME Oceanographic Cruise in winter of 2006 provided substantial baseline information about the spatial variation of physicochemical factors, chlorophyll *a,* and nutrients concentrations in the RSA (ROPME 2006). Our recent winter cruise in the PG and the GO led to more recent oceanographic information for the region (Ghaemi et al. 2021). Hydrographic characteristics, nutrients, and Chl-*a* measured in January 2018. But the studied area was limited to the eastern and western sides of the Hormuz Strait. Seasonal distribution of hydrographic parameters and nutrients neglected as well. Seasonal patterns of nutrients in this region are not publicly accessible till now.

Aside from these widespread works, sparse studies have been limited to shallow regional waters and concentrated on local environmental matters during the last few years. The distribution of hydrographic parameters and nutrients in the UAE waters from October 1993 to September 1994 studied by Shriadah and Al-Ghais (1999). Al-Yamani et al. (2006) investigated the physicochemical parameters, nutrients, Chl-*a*, and the primary productivity at six stations from March 1997 to April 1998. During the winter of 1987, Emara (2010) surveyed the southern part of the Persian Gulf and the Gulf of Oman. Sharidah (2006) studied the nutrient distributions in waters of an 800-km transect in the UAE (along with the PG and GO) from 1994 to1995.

These previous observations leave open questions about limiting nutrients in the PG. Our best information on nutrient limitation comes from Grasshoff's (1975) and Brewer and Dyrssen's (1985) studies. Grasshoff (1975) suggested that silicate may be the limiting nutrient for primary productivity in the PG. Brewer and Dyrssen (1985) showed nitrate concentrations were below the limit of detection, and so nitrogenous nutrients seemed to be limiting in the PG.

However, to the best of our knowledge, there are no studies on the seasonal variability of nutrients in the PG. In this paper, we report the nutrient results of a large-scale investigation based on three research cruises conducted in the Persian Gulf in September-October 2018 (PGE1803), May 2019 (PGE1901), and November 2019 (PGE1902) on the RV Kavoshgar Khalij Fars (Persian Gulf Explorer). The objective of this study was to understand the spatial and seasonal distribution of nutrient concentrations and determine the limiting nutrient in this region.

2. Methods

Seawater samples were collected in the Persian Gulf as a part of 'The Persian Gulf and Gulf of Oman Oceanographic Monitoring Program'. Three cruises in summer (September 16–29, 2018), spring (May 2–13, 2019), and autumn season (November 8–18, 2019) on the RV Kavoshgar Khalij Fars sampled 15 stations in the Persian Gulf (Figure 1). The samplings were carried out on 15 stations (st1 to st15) during cruises PGE1803 (September 2018) and PGE 1901 (May 2019) and 11 stations (st1 to st11) during cruise PGE1902 (November 2019). Water samples were collected at the surface, 10, 25, 50, 100 m, and even lower, where applicable (in triplicate). The deepest sample were collected at 180 m at station 14. Using a calibrated luminescent DO sensor (Hach IntelliCal LDO101, USA) dissolved oxygen (DO) concentrations were measured. To check the accuracy of the oxygen sensor, the Winkler iodometric titration method was used to determine oxygen at some stations (Grasshoff et al. 1999). Seawater pH was measured on desk using a combined glass/reference electrode (HACH portable metre HQ40d) calibrated by NBS buffers (accuracy of ± 0.02, precision of ± 0.001). Salinity and temperature profiles were recorded using a CTD probe (Idronaut, Ocean Seven 316, Italy). A Rosette water sampler equipped with twelve 1.7-liter bottles (Hydro-Bios, Kiel, Germany) was used for collecting the seawater samples. For nutrients (nitrite, NO_2^-; nitrate, NO_3^-; ammonium, NH_4^+; phosphate, PO_4^{3-} and silicate, $Si(OH)_4$) measurements, water samples were filtered by 0.45 µm syringe filters (cellulose acetate, Sartorius, Germany), collected into new, sterile high-density polyethylene bottles, and rapidly frozen for subsequent analysis with three replicates at any depth (Grasshoff et al. 1999). Dissolved nutrients were determined by spectrophotometric techniques (Moopam 1999) with a UV-Vis spectrophotometer (Analytikjena, specord 210, Germany). As a component of instrumental quality control, artificial seawater is used to establish baseline characteristics. Sodium chloride solution (39 g/L) has been used as artificial seawater. This water is then used as both the wash solution and for the preparation of working standards.

The precisions of the method employed in this work were determined by estimating the relative standard deviation values for replicate analysis of selected samples. Precision (relative standard deviation) for the laboratory analysis of nitrate, nitrite, ammonium, phosphate and silicate in seawater were better than 2, 5, 10, 3 and 5%, respectively. Inter-laboratory tests were also performed for several samples to confirm the accuracy of the methodology and results.

For analysing the data and plotting the distribution maps and sections, Ocean Data View (ODV) programme (version 5.1.7) was used (Schlitzer 2020).

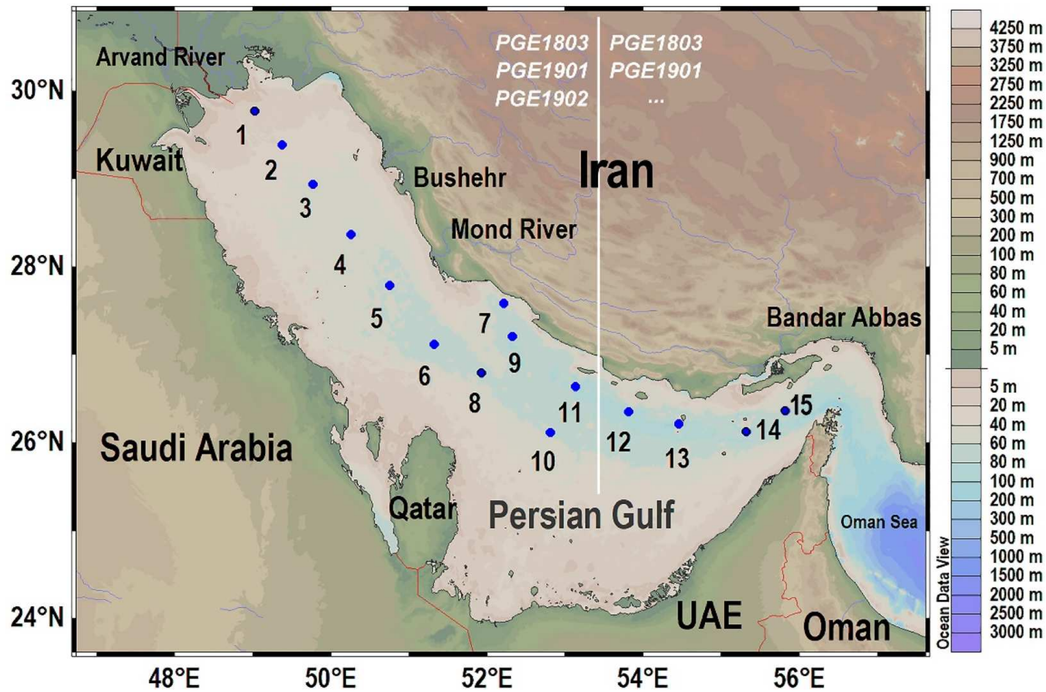

Figure 1. The map of sampling stations in the PG. Water samples were collected in stations 1–15 during cruises PGE1803 and PGE1901, and 1-11 during cruise PGE1902 (2018–2019).

3. Results and discussion

3.1. Physicochemical characteristics

The statistics of temperature (T), salinity (S), dissolved oxygen (DO), oxygen saturation (DO sat.), and pH of water samples during cruises PGE1803, PGE1901, and PGE1902 in the Persian Gulf are shown in Supplementary Information Table S1. The results for temperature, salinity and dissolved oxygen are presented in Ghaemi et al. (2022).

The highest mean upper layer temperatures, 32.88 ± 1.17°C, were recorded in the summer of 2018, while the lowest one, 23.96 ± 1.68 °C, was recorded in the spring of 2019 (Table S1).

The mean salinity values in the upper layer were 39.18 ± 0.98, 39.84 ± 0.43, and 38.88 ± 3.12 in summer, autumn, and spring, respectively (Table S1).

The temperature-salinity diagram for water samples collected from the PG is shown in Figure 2. Potential density anomalies higher than 29.0 (up to 29.57) were observed in samples obtained during May 2019 in the northwest of the PG while the PG surface waters during summer showed the lowest measured densities in this study ($\sigma_0 < 23$ kg/m^3).

The pH values revealed wide variations, ranging from 7.87 to 8.23, 7.98 to 8.25, and 7.85 to 8.22 during summer, spring, and autumn, respectively (Table S1). The minimum value observed at station 4 at 50 m depth in summer (pH = 7.88) and autumn (pH = 7.85). The mean pH in summer, autumn, and spring were 8.14 ± 0.075, 8.18 ± 0.02, and 8.17 ± 0.05 in the upper layer, while in the bottom layer was 7.96 ± 0.03, 7.96 ± 0.06, and 8.09 ± 0.05. The decomposition of organic matter followed by CO_2 production is the leading cause of lower pH values in the bottom layer (Gobler and Baumann 2016).

It is also important to note that a substantial decrease in oxygen amount to reach values less than 2 mg/L and associated with low pH waters (7.84–7.94). Moreover, they are characterised by the high concentration of phosphate, nitrate, and silicate released during organic matter respiration, accompanied by dissolved oxygen consumption and carbon dioxide (CO_2) production. Under the photosynthetic zone, in situ processes like organic matter oxidation tend to decrease the oxygen value (Richards 1965). Nutrient concentrations in a water basin are closely related to their immobilisation and regeneration, which correlate with DO (Grasshoff 1975; Emara 2010).

The mean water column DO saturation (%) in summer, autumn, and spring were 75.14 ± 30.10, 72.14 ± 29.72, and 95.35 ± 13.85, respectively. The hypoxic conditions were found in autumn 2019 in the western PG at the depths of ≥50 m, which is in accord with the layer of maximum phosphate (0.73–1.20 μmol/kg), nitrate (12.69–19.15 μmol/kg), and silicate (8.27–17.47 μmol/kg) which could be resulted from organic matter mineralisation (Emara 2010). Hypoxia in the Persian Gulf and

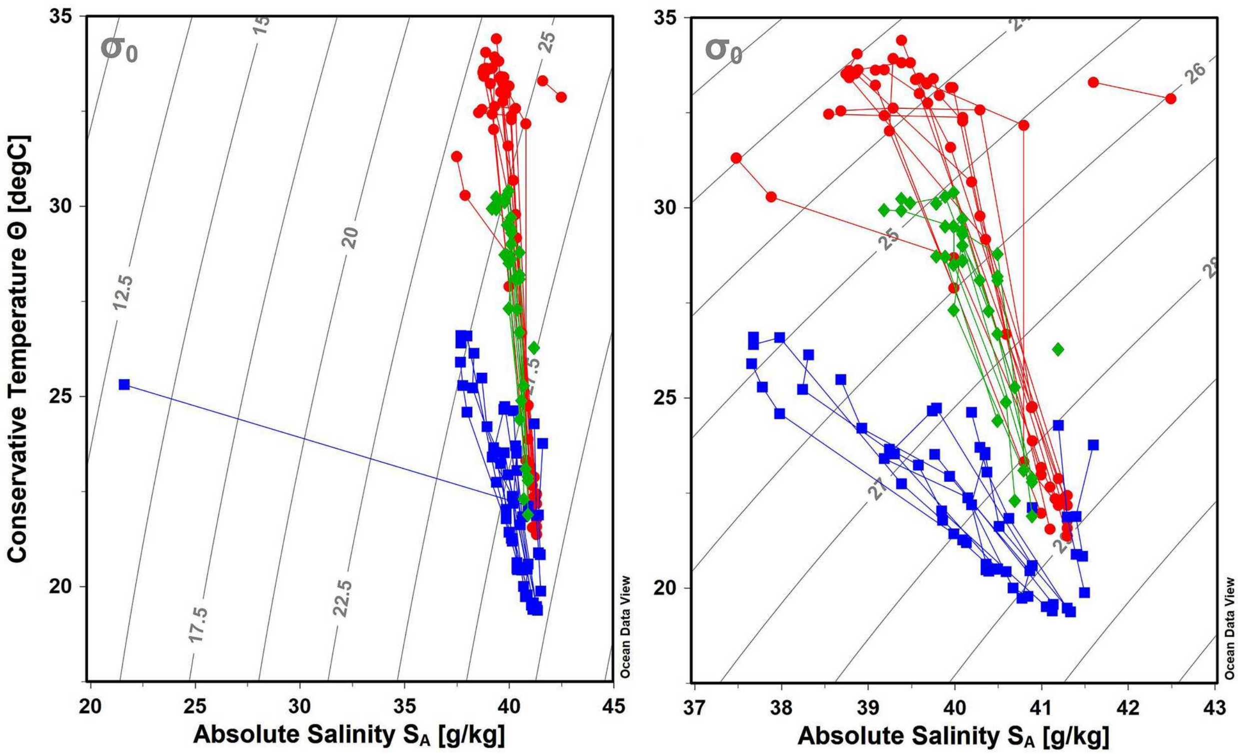

Figure 2. Temperature-salinity diagram, inclusive of isopycnals, depict the water samples collected from the Persian Gulf during cruises PGE1803, PGE1901, and PGE1902 (conducted in 2018 and 2019). Red circles: PGE1803, blue squares: PGE1901 and green diamonds: PGE1902. The right panel illustrates the data subsequent to the exclusion of the surface sample taken at station 1 during PGE1901.

the Strait of Hormuz in a wider scope has been published by Saleh et al. (2021). Lachkar et al. (2022) reconstruct the evolution of DO in the Persian Gulf from 1982 through 2010 and discover its controlling factors.

3.2. Spatio-seasonal variation of nutrient concentrations

Nitrogen, primarily in the form of nitrate (NO_3), nitrite (O_2), ammonia (NH_4), and phosphorous, mainly phosphate (PO_4), are essential elements for primary production.

Vertical profiles of nitrate, nitrite, ammonium, phosphate, and silicate for the PG region are show in Figures 3–5. The range of phosphate, silicate, nitrite, nitrate, and ammonium concentrations (all in μmol/kg) for three cruises were: 0.00–2.11; 0.02–42.87; 0.00–4.38; 0.00–46.23; and 0.00–1.52, respectively (presented in Supplementary Information Table S2).

The seasonal variations of nutrient concentration in the water column followed a robust seasonal trend, with higher concentrations in the summer 2018 (Figures 3–5). In the Persian Gulf, input of nutrients from the Gulf of Oman occurs by sub-surface inflow of nutrient-rich water that peaks in summer (Grasshoff 1976). According to Shriadah (2006), nitrate and phosphate showed higher concentrations during the summer of 1996 than in the winter of 1995 in the Persian Gulf and the Gulf of Oman off the United Arab Emirates. Also, this observation may be the result of increased biological activity during the summer.

We found that the concentration of nitrate, phosphate, and silicate was higher at the bottom layer than in the upper layer and showed a maximum just below the thermocline in summer and autumn. These increases with depth in the PG waters might be because of regeneration from organic matter in bottom layers, release from sediments, and dissolution of SiO_2 particulates (Chester 1990; Shriadah 2006; Quigg et al. 2013). During ROPME Oceanographic Cruise (ROPME 2006), a similar trend for concentrations of nitrate and silicate was observed in the upper and bottom water layers. Shriadah and Al-Ghais (1999) sampled 24 stations along the UAE coasts monthly during October 1993-September 1994. The distribution patterns did not show a significant difference between surface and bottom layers due to the shallowness of the region, water column turbulence, and the effects of sewage discharge.

Ammonia concentration was often low in most of the water column in spring and autumn (Figures 4 and 5).

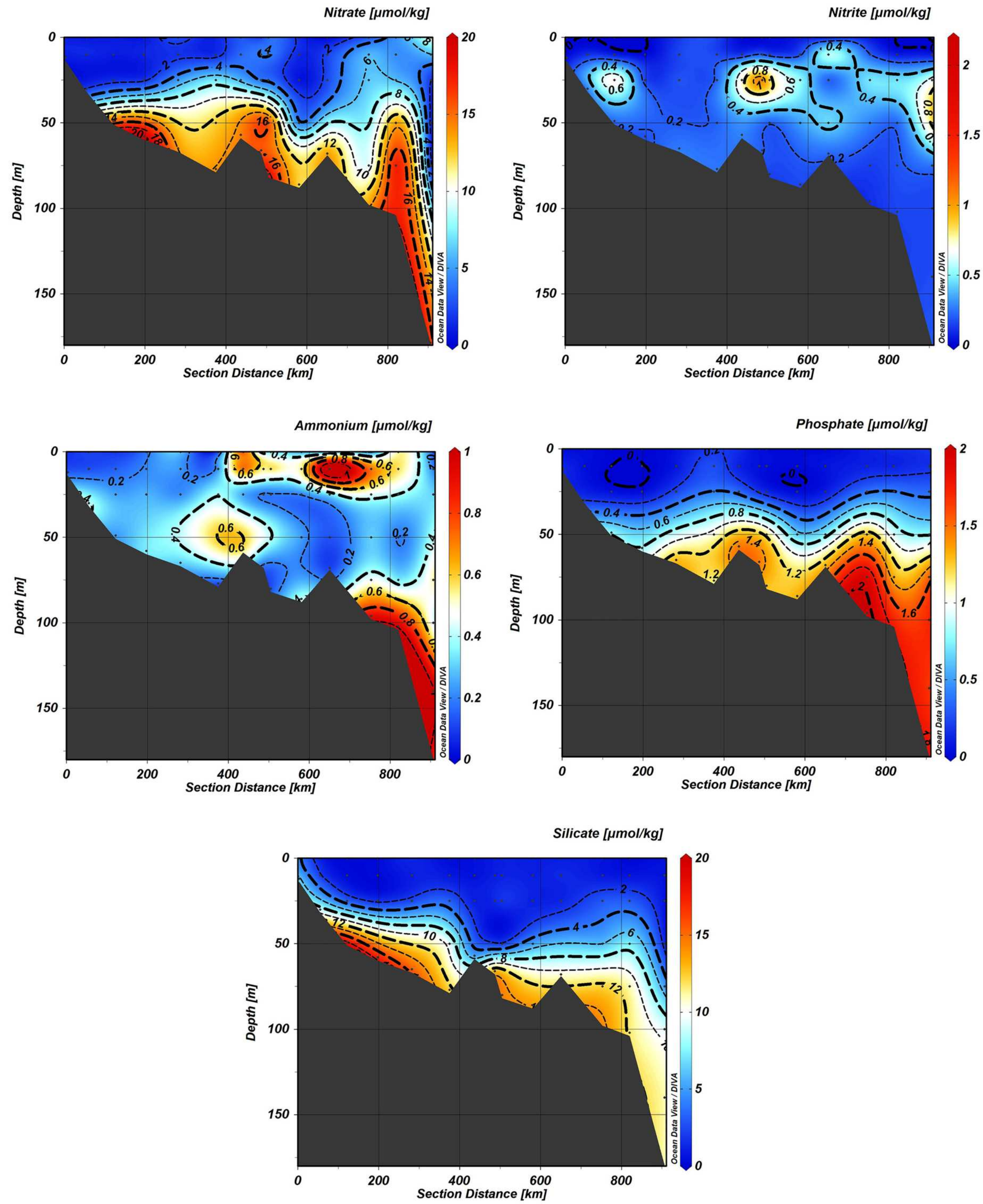

Figure 3. Profiles of nutrient concentration (in µmol/kg) throughout the study area during the cruises on summer 2018 (PGE1803).

They ranged from near zero to a maximum of 1.52 µmol/kg. According to Watson et al. (2005), ammonium concentration in oligotrophic oceans is less than one µM.

Nitrite plays an intermediate role in several biological processes within the oceanic nitrogen cycle, being the net result of different generation and consumption processes. Studies showed that in a stratified water column, the nitrite maximum concentrations are found near the bottom of the euphotic zone (Al-Qutob et al. 2002) which could be associated with phytoplankton activities. Our results clearly showed an intermediate maximum of NO_2 concentration at the depth of maximum chlorophyll a (Ghaemi et al. 2022) in summer 2018, when the water column was significantly stratified (Figure 3). Excretion of nitrite during nitrate reduction, i.e.

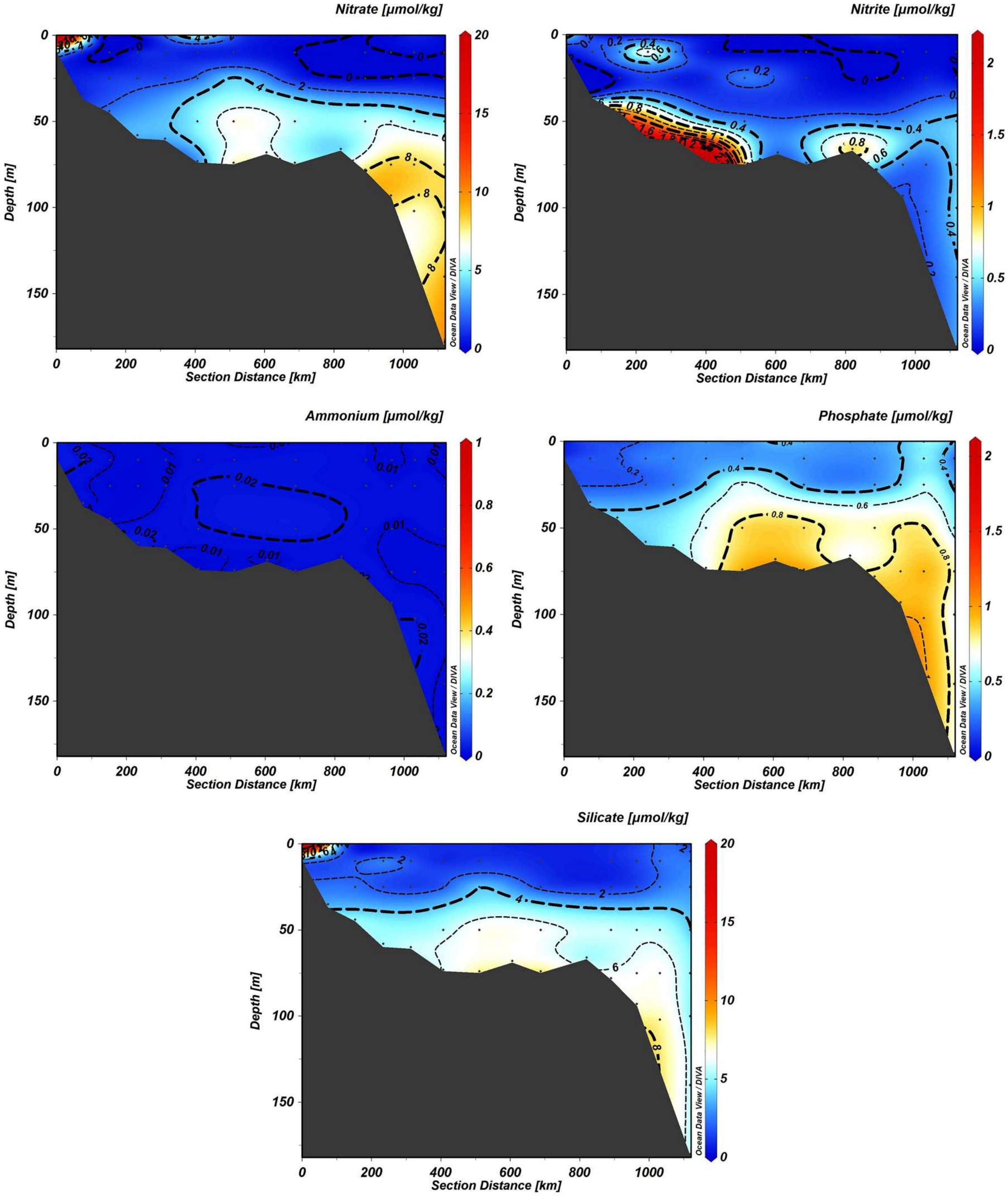

Figure 4. Profiles of nutrient concentration (in µmol/kg) throughout the study area during the cruises on spring 2019 (PGE1901).

incomplete assimilatory reduction of nitrate by phytoplankton and bacteria (Vaccaro and Ryther 1960) probably is the main source of nitrite generation in the depth of maximum chlorophyll *a*. The intermediate maximum nitrite concentration zone was not observed in spring 2019 when the water column was not effectively stratified (Figure 4). In autumn 2019 (Figure 5), NO_2 distribution pattern was more complex probably due to distinct processes in the northernmost stations compared to the southernmost open waters.

The nitrite concentrations were considerably lower than nitrate; thus, its contribution to the marine nitrogen cycle is not as crucial as nitrate (Kamykowski and Zentara 1991). Hashimoto et al. (1998) reported that nitrite concentrations in the RSA were moderately high relative to nitrate during three winter cruises. However, the results of our three cruises in the PG do not confirm this finding.

A strong peak was observed in nitrate (46.23 µmol/kg) and silicate (42.87 µmol/kg) surface concentration

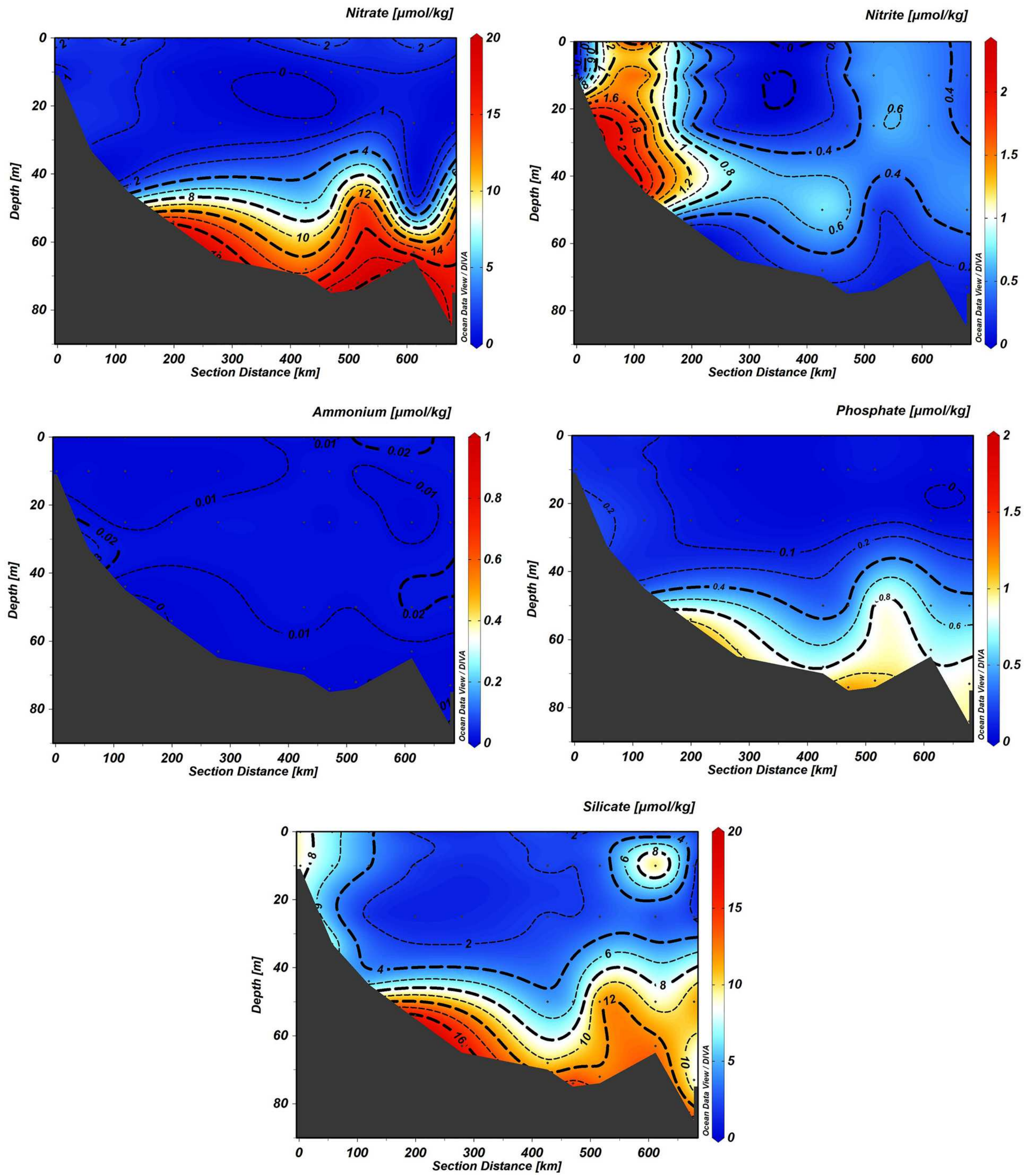

Figure 5. Profiles of nutrient concentration (in µmol/kg) throughout the study area during the cruises on autumn 2019 (PGE1902).

at station 1 (nearby to the Arvand River mouth), where surface salinity was 21.5 in spring 2019 (see Figure 4). It corresponded likely to temporary injections of nutrients following flood events. Heavy rain has happened during short timeframe, which has resulted in flash flooding in urban areas and catchments in the north-western area of the PG. Such events are known to have a 20- year return period, but their magnitude seems to be critical (Alosairi et al. 2019).

Figure 6 illustrates the silicate (µmol/kg), nitrate (µmol/kg), and salinity of water samples collected from the Persian Gulf during cruises on summer 2018 (PGE1803), spring 2019 (PGE1901), and autumn 2019 (PGE1902). The anomalous behaviour of salinity, nitrate and silicate at surface of station 1 has been shown in the scatter plot. In the plot, circle represent the surface sample of station 1 in the PGE1901 cruise.

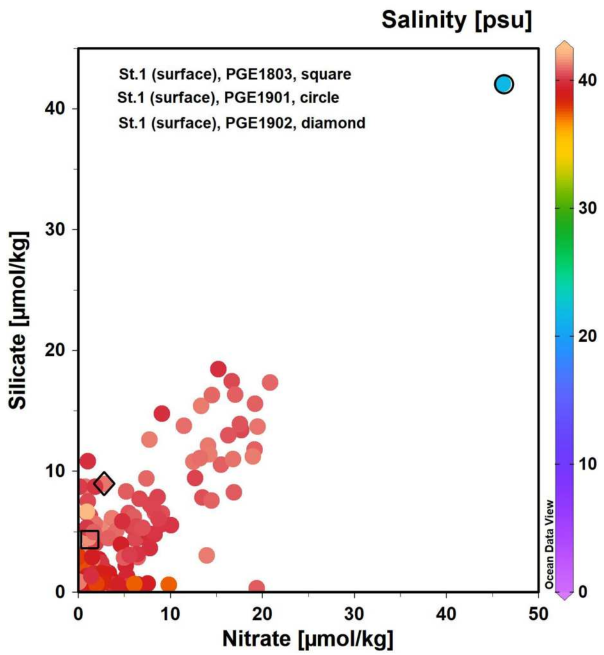

Figure 6. Scatter plot illustrating the silicate (µmol/kg), nitrate (µmol/kg), and salinity of water samples collected from the Persian Gulf during cruises PGE1803, PGE1901, and PGE1902 (conducted in 2018 and 2019). In the plot, a square, circle, and diamond represent the surface sample of station 1 in the PGE1803, PGE1901, and PGE1902 cruises, respectively.

Our findings also showed the surface concentration of Chlorophyll-*a* (a proxy for phytoplankton biomass) was highest in this station and station 5 (Mand river outlet) in spring 2019 (see Ghaemi et al. 2022). The extraordinary concentrations of nutrients and Chlorophyll-*a* at the Arvand River mouth, along with low salinity propose that river-borne nutrients supported high phytoplankton biomass.

Nezlin et al. (2007) described some sub-regions of the Persian Gulf; especially its northwestern portion near Shatt Al-Arab (Arvand River) deltaic system, impacted by intense river depletion, should be categorised as coastal waters. Brewer and Dyrssen (1985) showed silicate values were shallow in the Persian Gulf waters in February and March 1977. The highest concentration recorded was ∼ 6 µmol/kg in the outflow from the Shatt al Arab at the northern part of the PG. Jurado et al. (2007) reported the influence of freshwater discharge by comparing nitrate + nitrite distributions near the end of the rainy season in 1999 and 2000 on the southwest Florida inner shelf. During the rainy season, surface nitrate + nitrite concentrations frequently were > 2 µmol/kg at the mouth of the Shark River. During the 1999 dry season, the average nitrate + nitrite concentration was 0.3 µmol/kg at the mouth of the Shark River. Surface silicate was > 15 µmol/kg, where surface salinities were < 35. The highest silicate concentrations were found at the river mouth, for example, when Si $(OH)_4$ exceeded 40 µmol/kg in February 1999 in the Ten Thousand Island, where salinities were ca. 28. Farther offshore silicate concentrations were <1 µmol/kg at surface salinities > 35.

3.3. Comparison with previous works

The long-term trend of the nutrients in the Persian Gulf for the past three decades are unresolved. This probably arising from the differences between nutrient concentrations in the inflowing and outflowing currents and unknown roles of the local sources and sinks.

Also, the long-term nutrients changes are not so clear, presumably because of rapid uptake of nutrients by the phytoplankton. In this study, there is a significant negative relationship between phosphate, nitrate, and silicate, and Chl-*a* content in summer ($r = -0.462$ for phosphate, $r = -0.609$ for nitrate and $r = -0.454$ for silicate) and autumn ($r = -0.608$ for phosphate, $r = -0.590$ for nitrate and $r = -0.538$ for silicate). This may be related to the rapid utilisation of phosphate, nitrate, and silicate by phytoplankton.

Previous published results of nutrient's variability in different regions within the PG are based on data collected in specific regions and time periods providing general overviews (Table 1). However, these studies cannot be accurately compared, because systematic analyses (regular sampling network) of spatial/temporal variability of nutrients remain poorly quantified. Nevertheless, a general comparison with the previous studies in the region (see Table 1) showed increases in mean nitrate, phosphate and silicate distribution on a decadal scale. Earlier studies conducted during January and December 1993, and December 1994 by Hashimoto et al. (1998) reported higher amounts of nitrate, phosphate, and silicate along the Iranian coast of the Persian Gulf, due to the north–south slope and river inputs. El Samra and El Gindy (1990) reported lower nutrients ranges between September 1985 and 1986 in the southern PG as compared with our summer 2018 survey. However, these researchers did not survey the deeper parts along the coasts of Iran where higher concentrations were anticipated.

Therefore, commenting on the long-term process of nutrient changes in the Persian Gulf requires a regular monitoring programme with the cooperation among the concerned countries.

3.4. Seasonal variation of nutrient ratios

Nitrogen fixation, denitrification, phosphorus sorption, and desorption are biogeochemical processes that can

Table 1. Comparison of nutrients (nitrate, nitrite, ammonia, phosphate and silicate) variability (μmol/kg) in different studies in the region.

Region	Measurement period	Nitrate Range (Mean)	Nitrite Range (Mean)	Ammonia Range (Mean)	Phosphate Range (Mean)	Silicate Range (Mean)	References
RSA	Jan and Dec 1993, and Dec 1994	<0.09–1.78 (0.62)	<0.09–14.3 (1.56)	0.32–2.64 (1.12)	<0.06–1.23 (0.41)	0.34–15.5 (3.65)	Hashimoto et al. (1998)
SE Inner RSA	Feb to Mar 2006	0.10–6.67 (2.65)	0.00–1.28 (0.26)	0.05–1.80 (0.52)	0.00–2.33 (0.36)	0.00–11.07 (2.62)	ROPME (2006)
Central part of the PG and GO	Jan 2018	0.14–16.03 (7.23)	0.11–2.43 (1.22)	0.001–0.01 (0.004)	0.17–1.62 (0.63)	0.73–8.03 (3.22)	Ghaemi et al. (2021)
PG	Sep–Oct 2018	0.01–21.23 (6.29)	0.0–1.93 (0.23)	0.01–1.52 (0.36)	0.0–2.11 (0.54)	0.28–19.3 (4.56)	This study
PG	May 2019	0.0–46.23 (3.77)	0.00–4.38 (0.30)	0.0–0.04 (0.01)	0.01–1.68 (0.52)	0.02–42.87 (4.01)	This study
PG	Nov 2019	0.0–19.39 (5.26)	0.01–2.09 (0.52)	0.0–0.04 (0.01)	0.0–1.21 (0.27)	1.06–18.26 (5.73)	This study
UAE territorial waters	Oct 1993–Sep 1994	0.00–0.23	undetectable −0.11	undetectable-0.85	–	0.01–0.94	Shriadah and Al-Ghais (1999)
Kuwait's Waters	Mar 1997–Apr 1998	0.0–14.1 (1.2)	0.0–0.1 (0.5)	0.0–11.4 (1.2)	0.0–5.2 (0.4)	1.19–51.3 (9.3)	Al-Yamani et al. (2006)
Southern part of the PG and GO	Feb–Mar 1987	0.17–0.54 (0.29)	–	0.14–0.45 (0.33)	0.07–0.84 (0.37)	2.14–6.26 (4.20)	Emara (2010)
UAE (along with the PG and GO)	Oct 1993–Sep 1994	ND-10.88 (1.18)	ND-3.02 (0.42)	ND-6.32 (0.84)	ND–4.22 (0.62)	1.14–28.80 (6.52)	Shriadah (2006)
Southern Gulf between Qatar and Hormuz Strait	Sep 1985 and 1986	0.16–1.25	0.04–1.13	0.07–0.45	0.11–0.56	–	El Samra and El Gindy (1990)

lead more toward nitrogen (N) or phosphorus (P) limitation in an aquatic environment (Howarth et al. 2021). There is a discrepancy about the nutrients limiting primary production in marine ecosystems (Howarth 1988). From one side, some have deduced that (e.g. Boynton et al. 1982) because N:P ratios are frequently less than the mean intracellular nitrogen to phosphorus ratio of aquatic organisms (Redfield 1934; Redfield 1963), *N* is in the shortest amount and thus limit primary production. On the other side, geochemical budgets propose that P should be the element in the shortest supply (Meybeck 1982) since atmospheric nitrogen can be fixed (Redfield 1958; Vitousek and Howarth 1991). Paul et al. (2008) have examined the seasonal variation of the nutrient ratios in the western and central portion of the Bay of Bengal during Sept–Oct 2002 and spring-inter monsoon (April-May 2003) seasons. The nitrogen to phosphorus ratios < 16 in the water column of the Bay of Bengal proposes the nitrogen limitation. In this way, atmospheric N_2 could be essential to impacting the primary production in the Bay of Bengal.

Unfortunately, there is no data on the seasonal distribution of nutrient ratios in the Persian Gulf waters. Figure 7 illustrates the average nitrogen to phosphate (N:P), nitrogen to silicate (N:Si), and silicate to phosphate (Si:P) ratios for the three seasons, indicating P limitation in autumn, N limitation in spring, P limitation and poor Si in summer, throughout the upper layer.

During autumn, the N:P ratios in the upper layer were >16:1, suggesting phosphate limitation.

In spring, the mean N:P ratios in the upper layer were <10, offering nitrogen a limiting nutrient to the phytoplankton. As reported in previous works the vast majority of the Arabian sea (Morrison et al. 1998), PG and GO (Emara 2010) is potentially nitrogen-limited mostly in spring inter-monsoon a period of high vertical stability. The relatively high values in the upper layer (N:P ratios >16:1) came from stations located close to the Arvand River, which might be due to the increased concentration of dissolved nitrogen resulting from the spring 2019 regional flood. Eyre (2000) indicated that increased concentration of dissolved nitrogen following flood events could be due to erosion and leaching of material from the catchments. Anbazhagan suggested that the addition of nitrogenous nutrients, mainly through freshwater and groundwater runoff, increases nitrogenous nutrient levels. D'Elia et al. (1986) found a seasonal variation of the nitrogen to phosphorus ratio in the Chesapeake estuary (in the United States), with the highest value of nearly 100:1 during the peak freshwater flow, late winter period and the lowest value of 1:1 during the minimum freshwater flow, late summer. These results propose that primary productivity may shift from P limitation in winter to N limitation in summer.

In summer, the high average N:Si ratios (>1) were in agreement with the previously reported values in the upwelling eastern region of the Arabian Sea during late summer in the upper 25 m (Morrison et al. 1998). About 47% of the samples from the upper 25 m have the N:Si >1 and Si:*P* < 16, indicating poor Si waters. In spring, about 22% of the samples from the upper layer

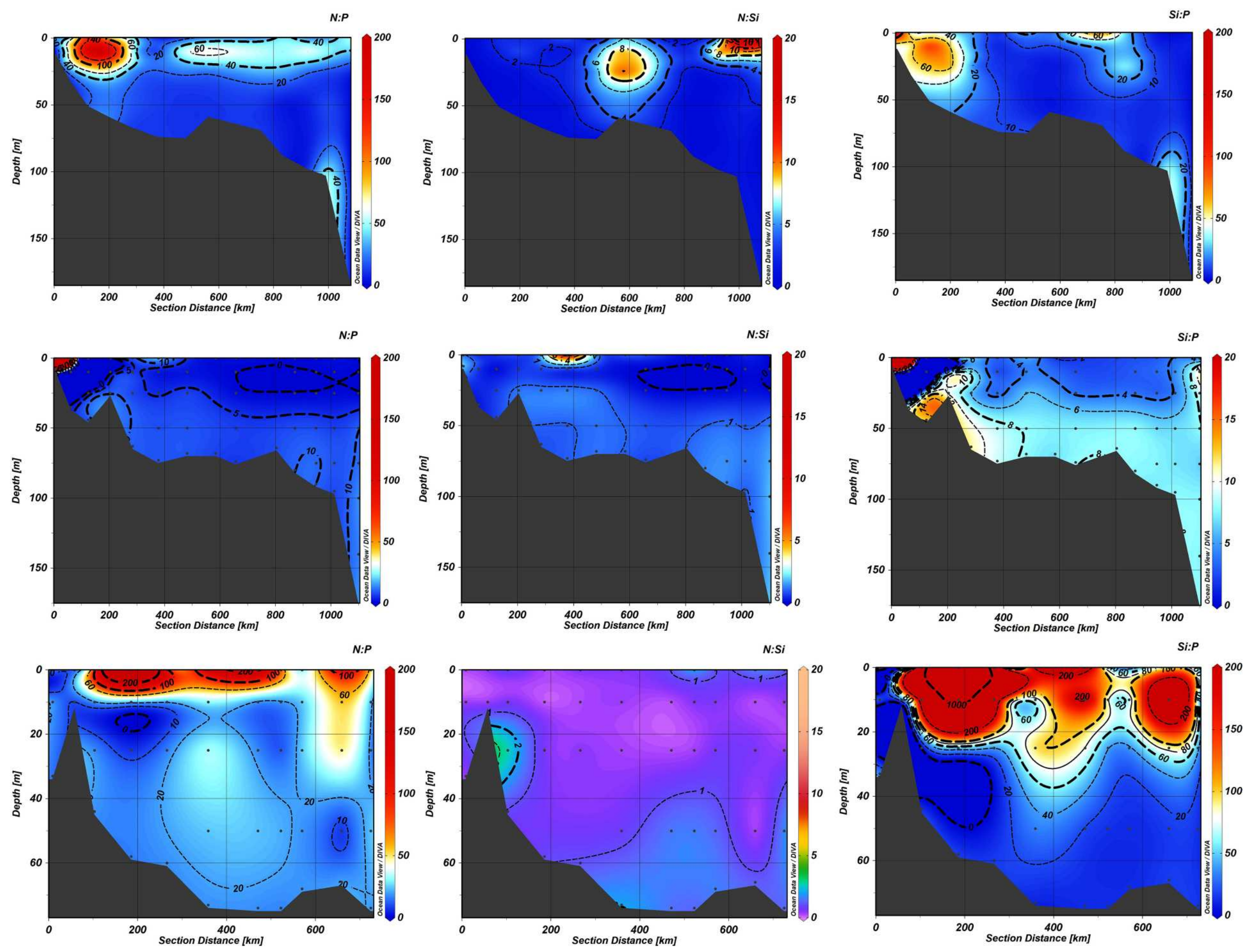

Figure 7. Patterns of N:P ratios, N:Si ratios and Si:P ratios in the PG. The first, second, and third rows show the summer (PGE1803), spring (PGE1901), and autumn (PGE1902) data, respectively.

showed the poor Si condition. According to Harrison et al. (1977), the Si:P ratio <16 is a sign of poor silica waters but does not limit the phytoplankton since the Si:P ratios were >3 throughout the water column of their study area. The silicate distribution in the world oceans is to some extent different from that of nitrate and phosphate since its pathway through the water column is different. Silicate is a nutrient essential only to siliceous-bearing plankton such as diatoms and radiolarians (Levitus et al. 1993). The shortage of silicate can limit only phytoplankton species that need it to build cell walls, mainly diatoms (Löscher 2021), whereas phytoplankton community can be scarcely affected if there is a prevalent presence of non-siliceous algal species that assimilate only of N and P. Silica is regenerated at different rates and by different processes than phosphate and nitrate and there is uncertainty about the factors that control the marine silica budget (Chester 1990, p. 552).

During summer, about 87% of the samples from the upper 25 m of water column showed the average N:P ratios higher than 16:1, indicating a deficiency of P relative to N. Tett (1990) suggested that nitrogen to phosphorus molar ratios is particularly high in the upper photic zone, where the greatest of the ocean's planktonic production happens and where nutrient deficiency is severe. Only 12 percent of open, photic zone sites had nitrogen to phosphorus ratio lower than 16. Only 3 percent had $N:P < 10$, showing substantial nitrogen limitation, 19 percent had N:P close to biological necessities ($10 < N:P < 20$), whereas 78 percent of the open ocean photic zone had N: P showing a deficiency of P or some element except N. Downing (1997) showed that the mean nitrogen to phosphorus ratios for open ocean photic zone sites was noticeably higher than 16. Oligotrophic sites had most elevated total nitrogen to phosphorus ratios. The substantial propensity for oligotrophic, open seas to have N:P higher than 16 shows that phosphorus or some nutrient other than nitrogen limits production in open seas.

The Meteor nutrient information has been argued by Grasshoff (1975). He suggested that silicate may be the limiting nutrient for primary production in the PG, and specific consideration should be paid to the dynamics of silicate circulation. According to Emara (2010), during the winter of 1987, the atomic ratios of the elements P:N:Si were 1:2.2:11.1 and 1:2.7:11.8 for the PG and GO surface waters, respectively. These ratios suggest that nitrogen was the limiting element in the PG. This finding is supported by the results of Brewer and Dyrssen (1985) and Emara (2010). Brewer and Dyrssen (1985) reported the existence of measurable phosphate at virtually all surface locations during the winter of 1977 would demonstrate that phosphate is not a limiting nutrient. The ammonia concentration was not determined, though it seems highly possible that productivity within the Gulf is limited by nitrogenous nutrients.

4. Conclusions

To date, in-situ observations and the simulated changes in productivity and nutrient supply to the PG remain to be unknown. Seasonal and spatial measurements of key physicochemical parameters and nutrient are essential to documenting ongoing changes.

To investigate the spatial and temporal changes that occurred in nutrient regimes and the limiting nutrient; samples were collected at 15 stations in the northern Persian Gulf under 'The Persian Gulf and Gulf of Oman Oceanographic Monitoring Program'.

We found that the nutrient concentrations in the PG increased slightly towards the summer months. A strong peak was observed in nitrate and silicate surface concentration close to the Arvand River mouth, where surface salinity was 21.5 in spring 2019, which corresponded likely to temporary injections of nutrients following regional flood events.

High phosphate, nitrate, and silicate concentrations were associated with low DO and pH values at depths ≥ 50 m. These findings propose high concentration of nutrients formed during the organic matter degradation and remineralization at the bottom layer below the thermocline.

Our current understanding of spatial and seasonal limiting nutrient ratios (N:P, N:Si, and Si:P) patterns within the PG waters is limited. Thus, mapping the detailed distribution of N:P, N:Si, and Si:P ratios is central to understanding regional differences in the PG ecosystem and biogeochemical processes.

The results of this study indicate a large seasonal variability in nutrient ratios in the Persian Gulf waters. While the data from spring season confirmed the previous reports in the PG (Brewer and Dyrssen 1985; Emara 2010), the widespread observation of high N:*P* values during the autumn and summer cruises, may highlight the contribution of nitrogen fixation to the nitrogen cycle in the region. Primary production seemed to be limited by inorganic nitrogen availability in spring and phosphate availability in summer and autumn. The data analysed here suggest that the N:P ratios in the upper layer are high (> 25:1) in autumn and summer, so the upper layer of the PG is considered oligotrophic. In summer and spring, about 47% and 22% of the samples from the upper 25 m showed poor Si condition, respectively.

Finally, our findings recommend that the Persian Gulf nutrient regimes and their influences on the marine ecosystems of this region should be more examined. It would be desirable to conduct systematic seasonal and annual monitoring in the PG to assess the long-term trend of nutrient concentration and the nutrient limitation in the region.

CRediT authorship contribution statement

Maryam Ghaemi: Supervision, Conceptualisation, Methodology, Investigation, Validation, Formal analysis, Resources, Visualisation, Writing – original draft, Project administration. **Samad Hamzei:** Resources, Writing – review & editing. **Abolfazl Saleh:** Writing – review & editing. **Sara Gholamipour:** Formal analysis, Resources.

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