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ORIGINAL ARTICLE

Elemental distributions in the marine sediments off Doha, Qatar: role of urbanisation and coastal dynamics

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Abstract

This research investigates the present status and decadal variability of element distributions in the marine sediments off Doha, on the east coast of Qatar. Twenty elements were considered from 11 sediment sampling stations and 3 dust sampling stations by grouping them into major elements, toxic elements, and other trace elements. The results show elevated concentrations of certain toxic and trace elements, including Ba, Be, Co, Cr, Cu, Fe, Mg, V, Zn, Mg, and Ti, in the nearshore region, primarily influenced by the settling of dissolved elements under weak hydrodynamic circulations in the Doha Bay. The relatively higher currents in offshore enable quick advection and dispersion of the elements. On the other hand, the dust deposits have caused significant contributions to the Al, As, Mg, Ca, Sr, Fe, Zn, and Cd concentrations. Decadal variability is evident in element concentrations, which are linked to the urbanisation of the capital city in the State of Qatar. The Cu, Ni, V, Zn, and Cd concentrations indicate a notable increase in recent years compared to the last two decades, with values of about 20.7, 17.9, 25.0, 25.9, 0.66 ppm in 2022. In contrast, a few other elements fluctuate between the decades/years. The results pointed out the increased elemental concentrations in the bay due to the vast expansion of infrastructure facilities in the vicinity of Doha Bay in recent years. The Geoaccumulation Index resulted in a slight pollution of Cd, while other elements are unpolluted. The Degree of Contamination reveals low degree of contamination of sediments, and the Pollution Load Index illustrates no significant pollution in the sediments off Doha.

Keywords Marine geochemistry · Toxic elements · Trace elements · Shamal winds · Dust deposits · Arabian Gulf · Doha Bay

Introduction

Metals in sediments have significant roles in marine life through their interactions with overlying water (Burden et al. 2002). They reach the marine environment through natural and anthropogenic sources and tend to deposit in the bottom sediments (Zhang et al. 2019). Even though sediments perform as ultimate sinks for heavy metals, they do not always adhere to sediments as they move to the water column through several remobilization processes under suitable conditions (Allen 1995). They recycle through chemical and biological mediators within the water column and then contribute to bioaccumulation (Wang and Chen 2000) and biotransfer (Al-Ansari et al. 2017; Elsayed et al. 2020) in the food web. Enriching metals in marine sediments is controlled by local hydrography, redox conditions, and biological activity (Smrzka et al. 2019). Heavy metals are one of the major anthropogenic pollutants in the marine environment, which accumulate mostly in oxides, clay, and sulphides (Ruilian et al. 2008). Metals such as Cd, Cu, Ba, Ni, and Zn are recognised as significant marine contaminants due to their inherent toxicity and prolonged persistence in the environment (Huber et al. 2016). Due to physico-chemical properties such as particle characteristics, precipitation, and adsorption, the deposited sediments are considered a major pathway of sink and transporter of heavy metals from the seawater (Al-Mur et al. 2017).

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Industrialisation and urbanisation in coastal areas have led to a significant rise in metal concentrations within the marine environment (Shriadah et al. 2004). In line with the increasing urbanisation in maritime countries, the Arabian Gulf (hereafter, the Gulf) has also witnessed a substantial rise in developments in the last few decades. This has led to changes in the coastal morphology and nearshore dynamics (Al-Dalamah and Al-Hurban 2019). Reclamation, dredging, industrial and sewage effluents, oil pollution, and hypersaline water discharges from desalination plants are anthropogenic stressors that contribute to sea degradation in the Gulf (Naser 2013; Al-Ghadban et al. 1994). These activities contribute to shifts in the Gulf's ocean circulation patterns, impacting the movement of sediments, biological matter, and energy (Bishop et al. 2017; Martín-Antón et al. 2016). Several aquatic organisms, like benthic organisms, make sediment their habitats and provide a storehouse for most of the organic and inorganic chemicals, especially toxic chemicals, which accumulate through anthropogenic as well as natural activities.

The Gulf sediments consist of primarily terrigenous materials and carbonates (Sheppard et al. 2010; Basaham 2010). Heavy metals present in the sewage effluents reach the marine sediments through discharges. In the coastal regions of GCC nations around the Gulf, wastewater discharges are identified as a major contributor to marine pollution (Naser 2013). Despite stringent sewage treatment regulations, a significant volume of untreated domestic wastewater has been directly discharged to the marine environment through sea outfalls (Al Mamoon et al. 2019a). As a result of complex hydrodynamic patterns and dust storms, terrestrial runoff, and increased anthropogenic activities, the biogeochemical processes in the Gulf are intricate, which might alter the stoichiometry of essential elements with detrimental effects (Amin and Almahasheer 2022; Elhabab and Adsani 2013).

In Qatar, outfalls are situated adjacent to the shore and directly discharge the untreated water from stormwater and non-stormwater into the sea, especially into Doha Bay (Al Mamoon et al. 2019a, 2019b). The wastewater in Qatar has been reused for irrigation purposes. On the other hand, the groundwater collection and dewatering systems have been integrated into the stormwater networks. However, there is a potential public health risk to recreational users from accumulated pollutants due to shallow depths near the stormwater discharge outlets in Doha Bay (Fig. 1). The first flush occurs during the initial stage of rainfall after a long dry period, which carries the urban runoff with high loads of contaminants, and ultimately reaches Doha Bay (Al Mamoon et al. 2019a). Consequently, slight contamination has been identified in the marine sediments of Doha Bay (Al-Naimi et al. 2015).

The morphological and biogeochemical conditions of the bay have been frequently modified in the last two decades due to population growth, urbanisation, industrial developments, transportation, anthropogenic activities, natural weathering, and other increased developments. Therefore, it is important to evaluate the present status of the elemental distributions in the marine sediments off Doha to provide a comprehensive understanding of the environmental dynamics, shedding light on both natural and anthropogenic factors influencing the element concentration. This has been attained by characterising element concentrations at 11 stations inside and outside Doha Bay, analysing their spatial variability, and assessing their decadal changes by comparing them with earlier investigations. The study analysed twenty element concentrations, which have been categorised into major elements: Aluminium (Al), Calcium (Ca), Potassium (K), Magnesium (Mg), Sodium (Na), Phosphorous (P) and Strontium (Sr); toxic elements: Arsenic (As), Cadmium (Cd), Copper (Cu), Chromium (Cr), Zinc (Zn) and Nickel (Ni); and other trace elements: Barium (Ba), Beryllium (Be), Cobalt (Co), Iron (Fe), Manganese (Mn), Vanadium (V) and Titanium (Ti). Earlier studies (Al Naimi et al. 2015; Al Mamoon et al. 2019a) assessed the above metals and found contaminated levels in a few of them. For a useful comparison, these elements have been considered in the present investigation. Due to bioaccumulation, toxicity, biomagnification, and non-biodegradability, certain elements are considered major environmental contaminants. In addition, rapid industrialization and economic growth in recent years, there has been a significant increase in elemental concentrations in marine sediments (Mashiatullah et al. 2013; Sharifuzzaman et al. 2016; Cardoso et al. 2001). With the help of historical data obtained from the literature, the present study assessed the decadal variability of element concentrations off Doha. The study also critically evaluates the exceedance of element concentrations compared with various sediment quality standards.

The paper has been organised as follows: Sect. 2 describes the features of the study area; Sect. 3 briefs the data collection and method of analysis; Sect. 4 highlights important results and their discussions, and Sect. 5 concludes the interpretations.

Area of study

Qatar lies in the central part of the Gulf (Fig. 1). It is a subtropical, arid region with an extremely hot summer (May-September) and a moderately cold winter (November-March). Qatar experiences a relatively low annual precipitation of 70 mm, which usually occurs during the winter season (Projects 2019). Doha Bay is a semi-enclosed,

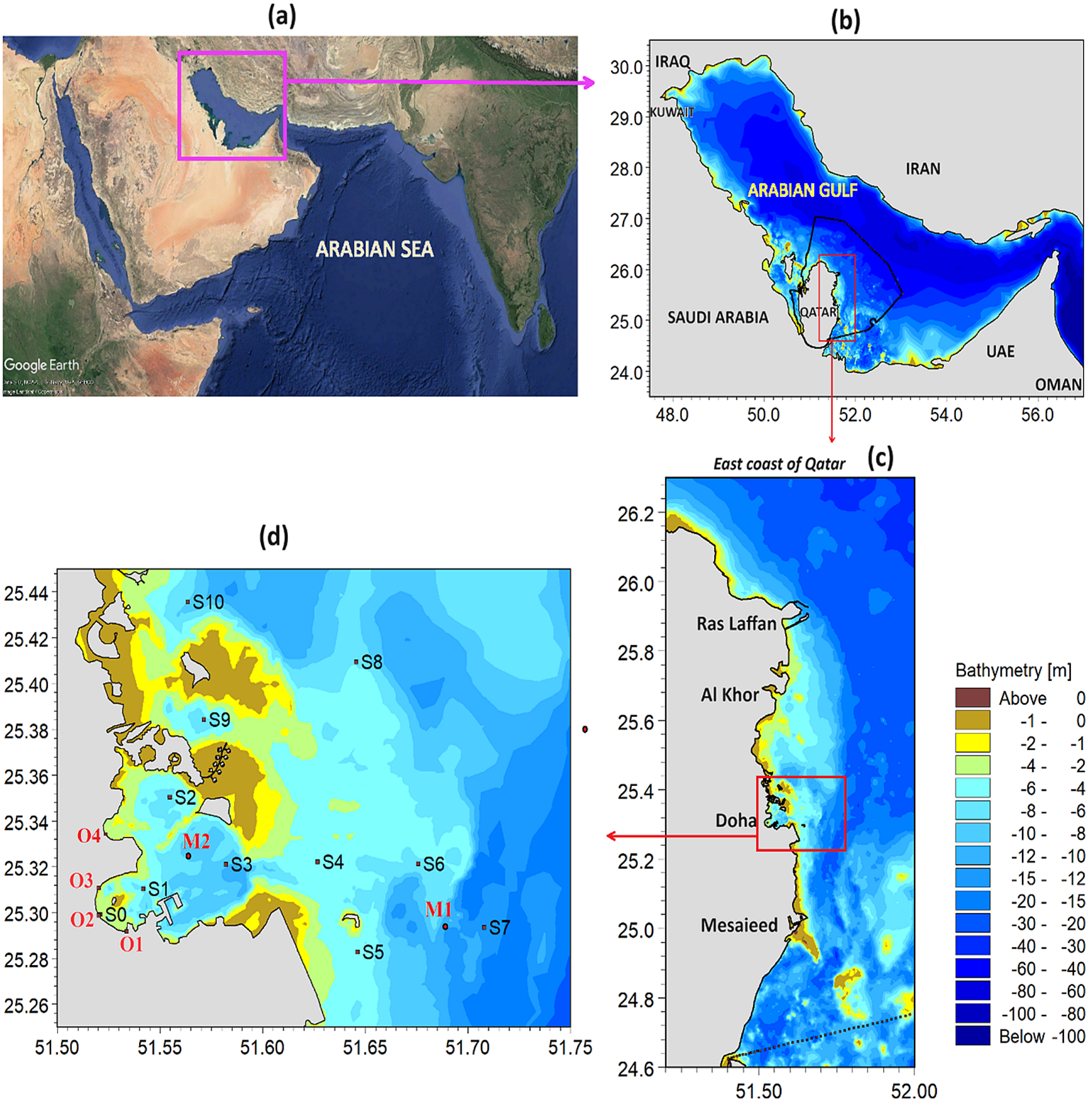


Fig. 1 (**a**) Map of the Arabian Gulf connecting the Arabian Sea, (**b**) bathymetry of the Arabian Gulf and the Exclusive Economic Zone of Qatar (marked by a polygon), (**c**) the bathymetry of the east coast of Qatar and (**d**) the sampling and mooring locations in the Doha Bay and offshore

shallow water body in the central Gulf, adjacent to Doha, the capital city of the State of Qatar. The adjacent regions of the bay are The Pearl and Lusail on the north and Hamad International Airport on the south. The bay is approximately 9 km long, and its maximum width is about 8 km. In the present study, we consider a domain that consists of Doha Bay, The Pearl, and part of Lusail and their offshore regions (17 km × 17 km). Doha Bay, in general, has poor flushing characteristics and very high evaporation rates (Price 1992). Restricted exchange with offshore waters impacts adversely on the physical, chemical, biological, and geochemical characteristics of Doha Bay (Al-Naimi et al. 2015). The seabed of the bay is mostly silty or muddy (Al Mamoon et al. 2020).

The temperature (during the summer) and salinity in the bay are generally higher, which strengthens the growth of harmful microorganisms. The average seawater temperature in the offshore regions of Doha during summer and winter is about 31 °C and 23 °C, respectively, while the salinity is about 40 and 40.6, respectively (Al-Ansari et al. 2022). Effluent discharges, coastal development activities, and dredging add up particles in the bay (Yigiterhan et al. 2018). There are four marine outfalls along the shores of the bay, namely, Souq Waqif (O1), Rumailah (O2), Tennis Court (O3) and Diplomatic Area (O4) (Fig. 1). The Souq Waqif outfall is located adjacent to the Doha Harbour; the Rumailah outfall is close to Al-Bidda Park; the Tennis Court is along the Khalifa International Tennis and Squash Complex; and the Diplomatic Area is between the West Bay and Katara Cultural Village (Al Mamoon et al. 2019a, 2020).

Within the shallow regions of Doha Bay, the currents are generally low, of the order of 0.1–0.2 m/s (Lecart et al. 2024), while they are of the order of 0.3–0.6 m/s in the Doha offshore (Hanert et al. 2023). Higher waves generally occur along the east coast of Qatar during shamal and nashi wind events (Aboobacker et al. 2021a); however, the bay remains relatively calm because of fetch limitations and the obstruction created by its orography.

Data and methods

Sediment samples were collected using Van Veen Grab from 11 stations off Doha (Fig. 1) during June 2022. For this purpose, the boat owned and operated by the Environmental Science Center (ESC) of Qatar University was utilised. The nearshore station (S0) is very close to the Rumailah outfall (O2), while station S3 is in the mouth of the bay. The stations S9 and S10 are close to The Pearl, an artificial island, north of Doha Bay. The collected samples were carefully transferred into acid-cleaned glass jars. They were freeze-dried under clean conditions for 3 days, grinded at -80 °C, and homogenised using the metal-free tool. The samples were taken to the Hot Block system for total acid-digestion and they were diluted thereafter. Further, the analysis has been conducted using the US EPA 6010D method, which uses the Inductively Coupled Optical Emission-Mass Spectrometer (ICP-OES) to analyse trace elements, and establishes certain standards for quality control (QC) in terms of calibration validity, linear dynamic range (LDR), and method detection limits (MDLs). A subset of dried and homogenised samples (250 ± 10 mg) was transferred into each tube, followed by the addition of reagent grade 3 mL HNO_3 (Honeywell Fluka 65%) and 9 mL HCl (Honeywell Fluka ≥ 30%) (Aqua regia) to each sample. The temperature of the HotBlock was adjusted carefully, and then tubes were placed on the HotBlock in a fume hood with loose caps at 95 °C for 30 min. After that, 3 mL of HF (ARISTAR 48%) was added to each sample, and the temperature was increased to 135 °C for 1 h. Then, the temperature was increased to 150 °C untill approximately 1 mL of the sample was left. 1 mL of trace metal grade H_2O_2 oxidizer (Riedel-de Haën 30%) was added, and the samples were continued to be heated at 150 °C till 1 to 2 mL of the sample was left.

The sides of the tubes were rinsed consecutively with 1 mL HNO_3 and 25 mL of double-distilled deionized (DDI) water. The digested solutions were placed back onto the HotBlock in the fume hood at 150 °C, and boiled to reduce the acid volume until the solution became clear (~ 15mL). The sides of the Teflon tubes were rinsed again with 1mL HNO_3, and the samples were transferred to volumetric glass flasks, followed by rinsing the sides of the Teflon tube with DDI water. The final volume was brought up to 25 mL by adding DDI water. The analysis employs the ICP as a high-temperature excitation source for the samples. The samples were ionized, aerosolized, vaporized, and finally atomized. The charged coupled detector monitors the spectra lines at specific wavelengths as dispersed by the spectrometer, and accordingly the concentrations are determined. The instrument with CRM, PACS3 was used, and analysed the metal concentration with a recovery percentage of 71–124%.

Surface dust deposits from flat concrete surfaces (Corniche area) near the outfall were collected using a clean brush and dustpan and stored in clean plastic bags for the metal analysis. The collected dust samples then underwent a drying process in a controlled, clean environment and were homogenised using plastic (metal-free) tools. Total acid digestion was carried out on a Hot Block in acid-cleaned Teflon tubes (Yigiterhan et al. 2018). Following the digestion process, the samples were filtered and subsequently transferred into acid-cleaned volumetric flasks. Further, the analysis of metals was carried out using a PerkinElmer-Optima 7300DV ICP-OES.

The grain size distribution of the marine sediment samples was carried out using the Mastersizer 3000 laser diffraction particle size analyzer. The samples were sieved using a 2 mm sieve. Then, the intensity of scattered light was measured when a laser beam was passed through a dispersed particulate sample, and thus the particle size was estimated.

Time series current data were collected at an offshore location (M1, 14 m depth) and a nearshore location (M2, 8 m depth) using an Acoustic Doppler Profiler (ADCP) and a Recording Current Meter (RCM), respectively. These have been analysed to obtain representative current patterns inside and outside the bay. The data at M1 was available during 06 Jun-14 Sep 2022, while that at M2 was available only for a shorter period (06–09 Feb 2023). In this study, we presented the current data for a period of 48 h to illustrate the diurnal variations and to discuss their possible links with the deposition of heavy metals.

Statistical analyses have been carried out to assess the level of contamination through the Geoaccumulation Index

(Igeo), Contamination Factor (C_f), Degree of Contamination (C_{deg}) and Pollution Load Index (PLI), considering toxic and trace elements As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Fe, Mn, Ni, V, and Zn. Igeo is used to assess sediment contamination, and it is defined as (Muller 1981):

$$Igeo = log2\left[\frac{C_n}{1.5 \times B_n}\right]$$

Where C_n is the concentration of elements and B_n is the elemental geochemical background values (Turekian and Wedepohl 1961). The level of pollution is determined as unpolluted (Igeo < 0), unpolluted to moderately contaminated (0 < Igeo < 1), moderately polluted (1 < Igeo < 2), moderately to strongly polluted (2 < Igeo < 3), strongly polluted (3 < Igeo < 5), and extremely polluted (Igeo > 5).

The C_f determines the contamination status, which is the ratio of element concentration to the geochemical background values (Hakanson 1980), as given below.

$$C_f = \frac{C_n}{B_n}$$

Then the contamination status is defined as low contamination ($C_f<1$), moderate contamination ($1<C_f<3$), considerable contamination ($3<C_f<6$), and high contamination ($C_f<6$).

Table 1 Statistics of element concentrations in seabed sediments of 11 stations off Doha

Elements	Concentration (ppm)			
	Min	Max	Mean	Standard Deviation
Al	2,989 (S6)	9,803 (S1)	6,500	2,515
As	1.17 (S5)	4.11 (S9)	2.56	1.04
Ba	7.35 (S6)	105 (S0)	27.7	28.3
Be	0.010 (S4)	0.21 (S0)	0.085	0.062
Ca	121,044 (S0)	276,781 (S8)	232,753	44,840
Cd	0.33 (S0)	0.66 (S3)	0.52	0.099
Co	0.33 (S8)	1.77 (S0)	0.99	0.53
Cr	2.44 (S8)	33.2 (S0)	13.3	9.73
Cu	0.11 (S6)	20.7 (S0)	4.82	5.88
Fe	232 (S8)	4,580 (S0)	1,972	1,473
K	500 (S5)	3,366 (S9)	2,050	1,103
Mg	3365 (S8)	22,218 (S0)	9,719	5,239
Mn	2.80 (S8)	63.0 (S0)	28.2	21.3
Na	13,091 (S5)	19,559 (S9)	16,314	2,409
Ni	4.34 (S8)	17.9 (S7)	11.4	5.65
P	105 (S0)	393 (S7)	226	76.4
Sr	559 (S0)	5,368 (S5)	3,383	1,277
V	1.85 (S8)	25.0 (S0)	8.46	6.77
Zn	0.23 (S6)	25.9 (S0)	6.98	7.37
Ti	20.1 (S6)	388 (S0)	186	138

The pollution can also be assessed in combination of all the elements in condieration through C_{deg} and PLI.

The C_{deg} is calculated by adding all the C_f: $C_{deg} = \sum_{k=1}^{n} C_f$ where n is the total number of elements. $C_{deg} < 7$ indicates a low degree of contamination; $7<C_{deg}<14$ indicates a moderate degree of contamination; $14<C_{deg}<18$ indicates a considerable degree of contamination; and $C_{deg}>28$ indicates a very high degree of contamination.

PLI is calculated as:

$$PLI = (C_{f1} \times C_{f2} \times \ldots . C_{fn})^{1/n}$$

where $C_{f1}, C_{f2}, \ldots, C_{fn}$ indicate the contamination factors of each element in consideration. The PLI > 1 is an indication of pollution.

Results and discussion

Distribution of metals in marine sediments off Doha

The seabed sediments collected during June 2022 reveal varying distributions of metals. Table 1 shows the statistical analysis of metals collected from the 11 stations off Doha. The spatial variations are well pronounced in most of the metal concentrations. The listed toxic elements (Cr, Cu, Zn) and other trace elements like Ba, Be, Co, Fe, Mn, V, and Ti show higher concentrations at station S0 compared to other stations. This station is within 50 m of Rumaila Outfall (Fig. 1d). Three outfalls discharge groundwater from the city, including storm and non-storm waters, into the bay (Al Mamoon et al. 2020). Thus, a partial contribution of some of the metals through the outfalls is envisaged. Moreover, low current speed and high residence time in the bay (Hanert et al. 2023) may allow the accumulation of metals in sediments, either from the sources of outfall or from dust deposition. The distribution of heavy metals in an aquatic ecosystem is heavily influenced by sediment grain size (Al Naimi et al. 2015). The grain size analysis indicates that the sediment at station S0 is mostly silty (with 72% silt, 25% sand, and 3% clay), while offshore stations are mostly sandy (50–100%), indicating the depositional behaviour of the land-based and offshore sources (Table 2). Due to the high particle size of sandy sediments, there is a lower accumulation of contaminants within the sediments (Wang et al. 2017).

The extremely high concentrations of some of the metals in the sediments are further confirmed by their heavy concentrations in the dust deposits. For example, the high deposition of Al is clearly evident in the marine sediments off Doha, with the highest concentration of 9,803 ppm at S1 (Table 1). The analysis of surface dust deposits (Table 3) also indicates that the Al concentration is considerably high

Table 2 Grain size distribution of sediments of 11 stations off Doha

Station	Sand (%)	Silt (%)	Clay (%)	Sediment type
S0	24.7	72.2	3.11	Sandy silt
S1	70.3	28.3	1.36	Silty sand
S2	40.9	56.4	2.73	Sandy silt
S3	66.7	31.4	1.87	Silty sand
S4	98.6	1.43	0	Sand
S5	100	0	0	Sand
S6	100	0	0	Sand
S7	51.9	45.7	2.47	Silty sand
S8	100	0	0	Sand
S9	29.5	66.2	4.35	Sandy silt
S10	72.1	26.6	1.3	Silty sand

Table 3 Concentration of elements from surface deposits near the outfalls

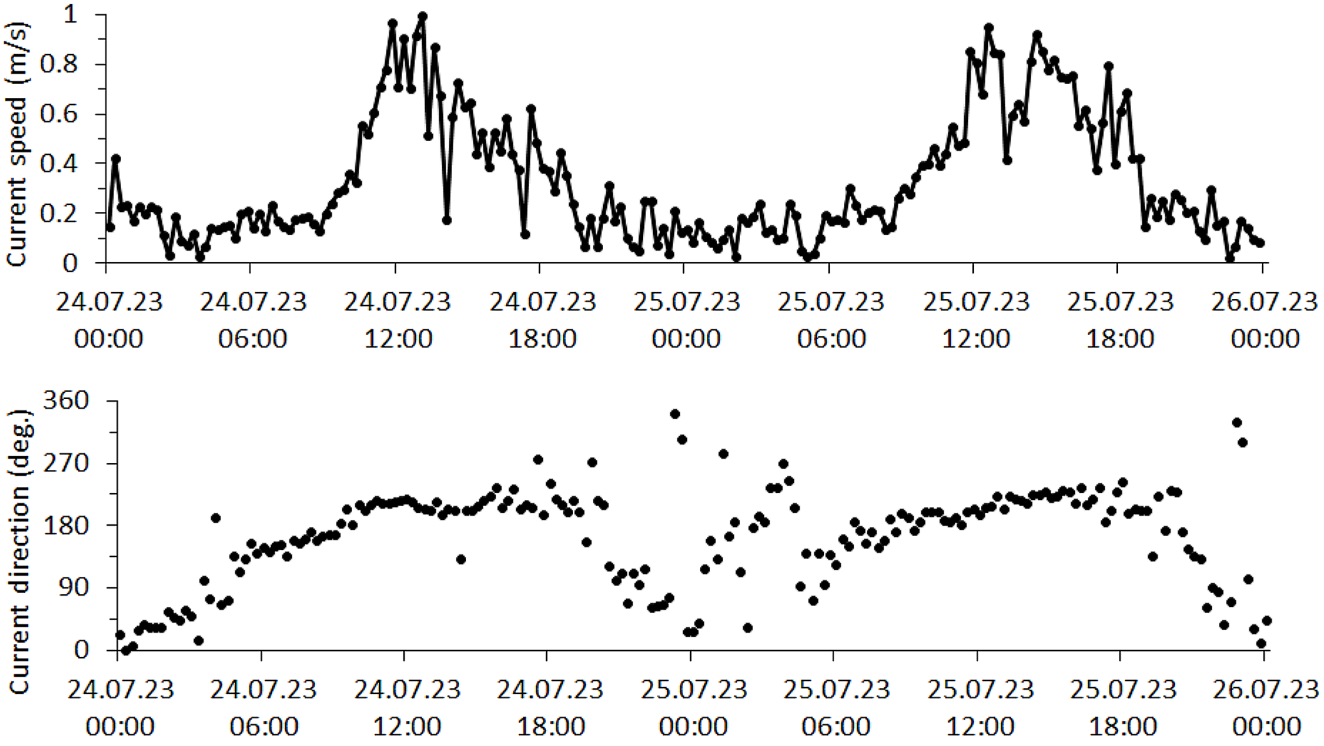
Elements	Concentration (ppm) at stations		
	O1	O2	O3
Al	23,929	14,321	12,660
As	3.45	2.30	1.60
Ba	239	153	91.1
Be	0.44	0.25	0.20
Ca	58,180	65,724	73,917
Cd	0.04	0.03	0.01
Co	2.00	1.27	2.41
Cr	32.8	28.1	40.3
Cu	7.67	8.44	11.6
Fe	7,710	5,792	7,125
K	10,668	7,421	5,672
Mg	8,062	16,028	23,126
Mn	166	122	165
Mo	0.98	0.21	0.65
Na	6,929	10,702	7,465
Ni	18.4	15.1	21.4
P	82.6	84.1	189
Pb	0.46	5.43	0.00
Sr	867	970	1,028
V	27.8	22.1	27.5
Zn	15.4	24.8	108
Ti	1,053	702	780

(23,929 ppm), mainly driven by the dust transported by strong shamal winds (Yigiterhan et al. 2020). Similarly, the As concentration in the sediment is the highest at S9 (4.11 ppm). The surface dust deposit indicates a concentration of up to 3.45 ppm onshore. The highest concentration of Ca in surface dust deposits in the vicinity of the outfalls is 73,917 ppm. This is consistent with the previous investigations of dust concentrations in Qatar (Yigiterhan et al. 2020). The dust reaching the seawater ultimately adds the particles into the seabed sediments, and this is evident from the highest concentration of Ca (276,781 ppm) observed at S8. Calcium is the major element concentration in Qatar's outdoor dust. The highest concentration of Ca in the sediment also indicates the degradation or bleaching of calcified organisms, including corals, outside Doha Bay. The recent decade has witnessed considerable degradation in the coral communities in Qatar (Burt et al. 2023).

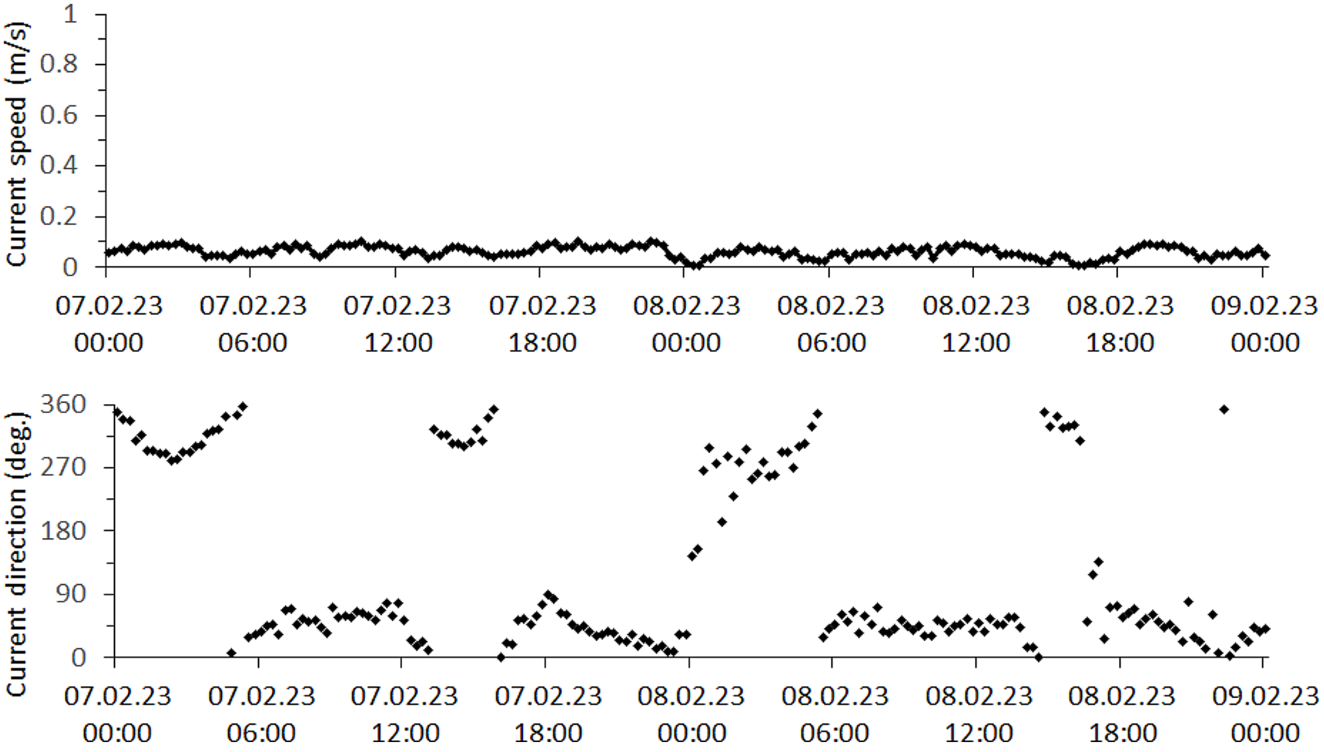
The K concentration in the sediments off Doha varies between 500 and 3,366 ppm (Table 1). In the oceanic crust, due to the presence of basalts, the concentration of K is generally elevated (White and Klien 2014). The marine sediment may contain approximately 18,000 ppm of K (Plank 2014). Compared to this, the K concentration off Doha is relatively low. The maximum observed concentration of Mg in the sediment is 22,218 ppm at S0, and in the dust samples, it is 23,126 ppm (Table 3). These results show that dust has significantly contributed to the elevated concentration of Mg in the marine sediments off Doha. However, long-term deposition through the outfalls may also add Mg to the seabed sediments in the vicinity of the outfalls. Yigiterhan et al. (2018, 2020) reported that the Mg concentration in the Qatari dust is about 1.9 times higher than that in the upper continental crust. The highest observed Na concentration in the sediments is 19,559 ppm at S9. The dust supplies a Na concentration of 10,702 ppm to the seawater (Table 3). This indicates that the dust contributes to the elevated Na concentration in the sediments off Doha. Another major process of sodium enhancement in sediments is ion exchange, when clays absorb Na in exchange for Ca that is released into the ocean water. There are also minerals with crystal structures that absorb sodium from the sea water (Buick et al. 1995).

The concentration of Sr is the highest at S5 (5,368 ppm), which is an offshore region (Table 1). Sr is enriched in dust and seabed deposits (Yigiterhan et al. 2018). The concentration of Sr in the dust sample reaches up to 1,028 ppm (Table 3). There is spatial consistency among all the stations, except at S0. The Sr concentration is the lowest at S0 (559 ppm). This is because of the limited sediment transport in the vicinity of S0 under weak hydrodynamic conditions. Among the stations, the highest concentration of titanium (Ti) is observed at S0 (388 ppm), which is near the outfall. The effluents from the aerospace and automotive industries, stormwater runoff, sewage effluents, and manufacturing processes may have caused the deposition of titanium (Hauser-Davis et al. 2020**).** The presence of organic matter and the low availability of phytoplankton in the region may have contributed to the moderate concentration of phosphorous (P) in the sediments. The highest concentrations of Ba, Cr, and V are 105, 33.2, and 25 ppm, respectively, at S0, which are also coming from various industrial sources through the outfalls.

Trace metals such as Fe, Mn, Co, Cu, Cd, Ni, and Zn are essential micronutrients for primary producers and play a critical role in marine biogeochemical cycles (Seo et al. 2022). However, they are highly toxic at high concentrations. The anthropogenic sources of Co are related to oil



(a) Currents at offshore (M1)



(b) Currents inside the Bay (M2)

Fig. 2 Typical current speed and direction in the offshore region (**a**) and inside the Bay (**b**) spills, boat traffic, and industrial wastes (Vetrimurugan et al. 2016). Co and Zn are the most frequent contaminants in agricultural activities, pesticides, industrial wastes, and anthropogenic inputs, including sewage sludge discharges, domestic discharges, and antifouling paints, that accumulate in marine waters (Looi et al. 2013). We find these elements in the marine sediments off Doha in definite concentrations. The Co concentrations measured off Doha are lower than those found in the central and northern parts of the Gulf (Sara et al. 2022), and on Amazonian oceanic beaches (Vilhena et al. 2021). The Mn concentration in the sediment reaches up to 63 ppm, while in the surface dust deposit, it reaches up to 166 ppm. This indicates that dust is the main source of Mn in the marine sediments off Doha. This is consistent with the observations of Yigiterhan et al. (2020), in which they identified atmospheric dust as the main source of a few heavy metals in suspended particulate matter sampled in the Exclusive Economic Zone of Qatar. Compared to other coastal regions, including the northern part of the Gulf and along the southeast coast of India, the Mn concentration measured off Doha is relatively low (Ahmed and Abdel-Moati 2003; Bramha et al. 2014). Cadmium is considered a highly toxic element. The Cd concentration in Doha Bay is 0.33–0.66 ppm, which is consistent with the measured values in Toulon Bay, France (Layglon et al. 2022) and is within the threshold limits. When we compare the recent research conducted north of Doha (Lusail), the concentrations of Co, Cd, Ba, V, Mn, and Ni are found to be higher, and those of Cu, Cd, and Al are lower (Afzal et al. 2023), but As and Fe are consistent.

The concentration of toxic elements like Cu, Zn, Cd, and Ni in the marine sediments off Doha is relatively lower than those measured along the Red Sea coast (Saleh 2021), the Sea of Oman (Agah et al. 2016), the east coast of India (Brahma et al. 2014), and the Mediterranean Sea (Zohra and Habib 2016). However, the concentrations of Cu, Fe, Co, Cr, Mn, Ni, and Zn are relatively higher compared to those reported along the northeast coast of Qatar (Basaham and Al-Lihaibi 1993). The concentrations of Cu and Ni measured at Halul Island, Qatar (SARC 1994), are consistent with those measured off Doha. The increased levels of Zn and Cd could be attributed to the dust found in the Gulf (Yigiterhan et al. 2018).

The semi-enclosed and shallow coastal settings of Doha Bay reduce the severity of easterly waves generated by nashi winds (Aboobacker et al. 2021a). Although strong, northerly shamal winds have little influence in the bay due to fetch limitations. Therefore, the waves experienced in the bay do not feel the bottom in most cases, and thus the re-suspension is not vivid. The measured currents indicate the current speeds are very low (below 0.15 m/s in most cases) inside the bay, while those offshore are of the order of 0.6–1.0 m/s during high wind or spring tide conditions (Fig. 2). The mean current speed in the bay is 0.06 m/s, while that offshore is 0.33 m/s. The current directions within the bay are predominantly W/NW during flood tide and NE/E during ebb tide. Whereas the current directions in the offshore fluctuate between NNE and SW, which do not follow the tidal patterns precisely, as the currents are dominated by winds. Although the data represent two different seasons, seasonal variations in current speeds are not robust between M1 and M2 compared to the changes that occurred due to the bathymetric effects. It is evident that the winter experiences higher winds compared to the summer (Aboobacker et al. 2021b), but that is not reflected in the current speeds at M2. In general, the low hydrodynamic and weak wave conditions within the bay together enable high residency for the contaminants entering the bay through the outfalls. Although limited concentrations of the elements are consumed by the organisms due to biogeochemical interactions, a good quantity still remains in the surface sediments. This may lead to contamination of sediments and water in the long run unless control measures are taken to minimise the heavy metal discharge through the outfalls.

Temporal variability of elemental distributions off Doha

The variability of the element concentrations off Doha has been assessed by comparing the present values (maximum values) with those of earlier studies spread over more than 2 decades (3 of them with approximately 10–11 years intervals). This includes the data from 2000 to 2001 (De Mora et al. 2004), 2012 (Al-Naimi et al. 2015), 2016 (Al Mamoon et al. 2019a), and 2022 (the present study). A few parameters, which were not studied in the earlier works, have been ignored in the comparison. The results indicate that there is decadal variability in the elemental concentrations off Doha, with relatively higher concentrations in all the parameters during 2022 compared to 2012 (Al-Naimi et al. 2015). The concentrations of toxic elements Cr, Cu, Ni, and Zn have increased to 124%, 223%, 107%, and 75%, respectively, during this decade (Fig. 3). The highest concentrations of Cr, Cu, and Zn are found at Stn. S0, close to the Rumailah outfall. Compared to 2000–2001 (De Mora et al. 2004), the concentrations of Cr and Ni in 2022 have decreased by 19% and 24%, respectively, while the concentration of Cu has increased to 158%. These differences indicate that the concentrations of elements in surface sediments off Doha have been significantly modified over the decades. The higher increment in these element concentrations in the present day is attributed to their accumulation over the years through the continuous discharges at the outfalls. The concentration of Cu has shown a marginal exceedance over the

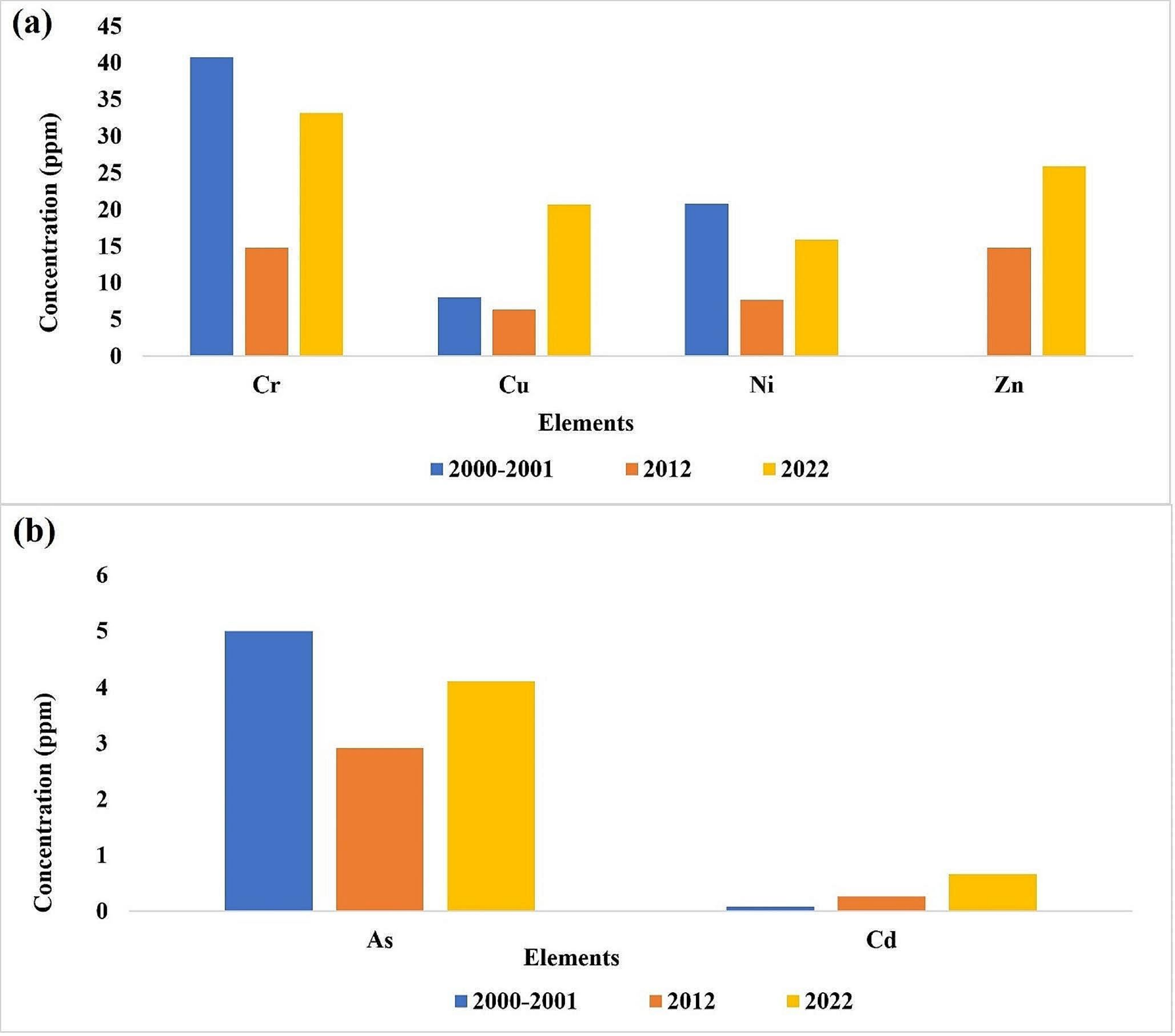


Fig. 3 Variation of Cr, Cu, Ni and Zn (top), and As and Cd (bottom) concentrations in sediments during the last two decades

US EPA threshold of 18.7 ppm (US EPA 1996), while it is within the limits of TEL (Mac Donald et al. 1996), and PEL (CCME 1995). The observed concentrations of Cr, Zn, and Ni are within the internationally recognised standards (Mac Donald et al. 1996; ADS 2018). The highest As concentration was observed during 2000–2001 compared to other years. The leaching of industrial wastes and domestic sewage contributed to the As concentration (Mahboob et al. 2021). Whereas, the concentrations of As and Co obtained are below the threshold limits of 7.24 ppm and 10 ppm, respectively, as per the Canadian interim sediment quality guidelines (ISQG) (Ccrem 1987). The Cd concentration progressively increased from 2000 to 2022, from 0.08 to 0.66 ppm (de Mora et al. 2004; Al Naimi et al. 2015); however, it is below the effective range low (ERL) of 1.2 ppm (Abu Khatita 2011). Domestic sewage, industrial wastes, ship paints, and fertilisers are the most frequent sources of Cd contamination (Watts et al. 2017).

The maximum concentrations of Al fluctuate among different years, with the highest observed values during 2016 and the lowest value in 2012 (Fig. 4). Compared to 2016 observations (Al-Mamoon et al. 2019b), Al concentrations are low in 2022. Dust contributes to the higher levels of Al found in the sediments of the bay due to extensive construction activities in Qatar prior to the FIFA 2022 World Cup. Nonetheless, the Al concentrations obtained off Doha are far below thresholds such as PAHDC of 32,206 ppm (Abu Khatita 2011) and lower than those obtained off the Dammam coast (Mahboob et al. 2021). Compared to 2012

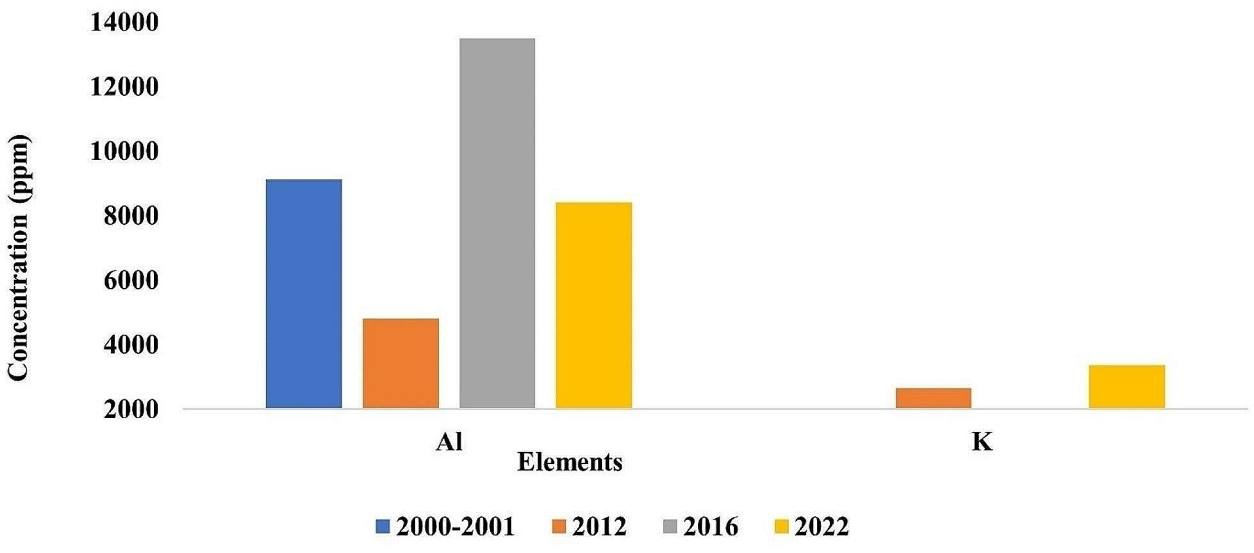


Fig. 4 Variation of Al and K concentrations in sediments during the last two decades

observations (Al Naimi et al. 2015), K concentration is slightly higher in 2022.

Decadal variability of other trace elements like Be, Ba, Co, Mn, Fe, and V is evident in the marine sediments off Doha (Fig. 5). Ba and Mn concentrations off Doha vary over the decades (Fig. 5). We observed a maximum of 105 ppm only in 2022, which is higher than the values observed by Al Naimi et al. (2015). However, it is within the limits of the Dutch standard target value of 160 ppm (Dutch Standards 2000). As Ba is an abundant metal in the earth's crust, due to the natural weathering of rocks, it accumulates in marine sediments (Fischer and Puchelt 1972). Barite is the principal component of drilling mud (around half the dry weight) (Neff 2008). The concentration of Mn in 2022 is marginally higher than that measured in 2012; however, it is lower than that of 2000–2001. Mn concentrations obtained in this region are far below threshold values such as TEL (1081 ppm) (Persaud et al. 1993). The concentration of Be obtained in 2022 is higher than that found in 2012 (Al Naimi et al. 2015). The Be can reach marine waters from treated wastewater effluents or by air by through the combustion of coal or fossil fuels (Bolan et al. 2023), however, such sources are limited in Qatar. It is reported that the highest Fe concentrations generally occur in the waters near the desert regions, including the Gulf and Red Sea (Mahboob et al. 2021; Fung et al. 2000; Boyko et al. 2019). In Doha Bay, the Fe concentration is highest in the vicinity of the Rumailah outfall, which is consistent with earlier observations (Al-Mamoon et al. 2019b). However, the year 2016 recorded the highest Fe concentration among the different years reported. This is in alignment with the elevated concentration of Al as well, due to increased development activities in the vicinity of Doha prior to FIFA 2022. Among the two decades, the highest concentrations of V and Co were observed during 2000–2001 (De Mora et al. 2004), which were higher than those observed in 2012 (Al-Naimi et al. 2015) by 38% and 62%, respectively. The observed V concentration is within the chronic benchmark for aquatic life (Buchman 2008). The authors of recent studies (Al Naimi et al. 2015; Al Mamoon et al. 2019a, 2020) reveal that the discharge from the outfall is a major contributor to the contaminants. However, further studies are recommended for a detailed investigation of metal analysis in Doha Bay sediments.

In general, the increase in concentration of a few elements in the marine sediments off Doha in recent years, as identified, is attributed to the increased developments and population growth in the State of Qatar. The ecosystem services are largely affected by such a change in metal concentrations, along with the influence of other factors in the marine environment. Land reclamation activities, which are frequently observed in the region, have been found to intensify the impacts, leading to the requirement for strategic interventions to alleviate the adverse consequences on the marine environment (Al Naimi et al. 2018). However, the State of Qatar has taken various measures to protect some of the world's most critically endangered species and supports many uniquely adapted organisms (Richer 2008). Mangrove forests are one of the best sinks for carbon and the development of coastal habitats (Gu et al. 2022). The State of Qatar has initiated a programme for large-scale forestation of mangroves along the Qatar coast.

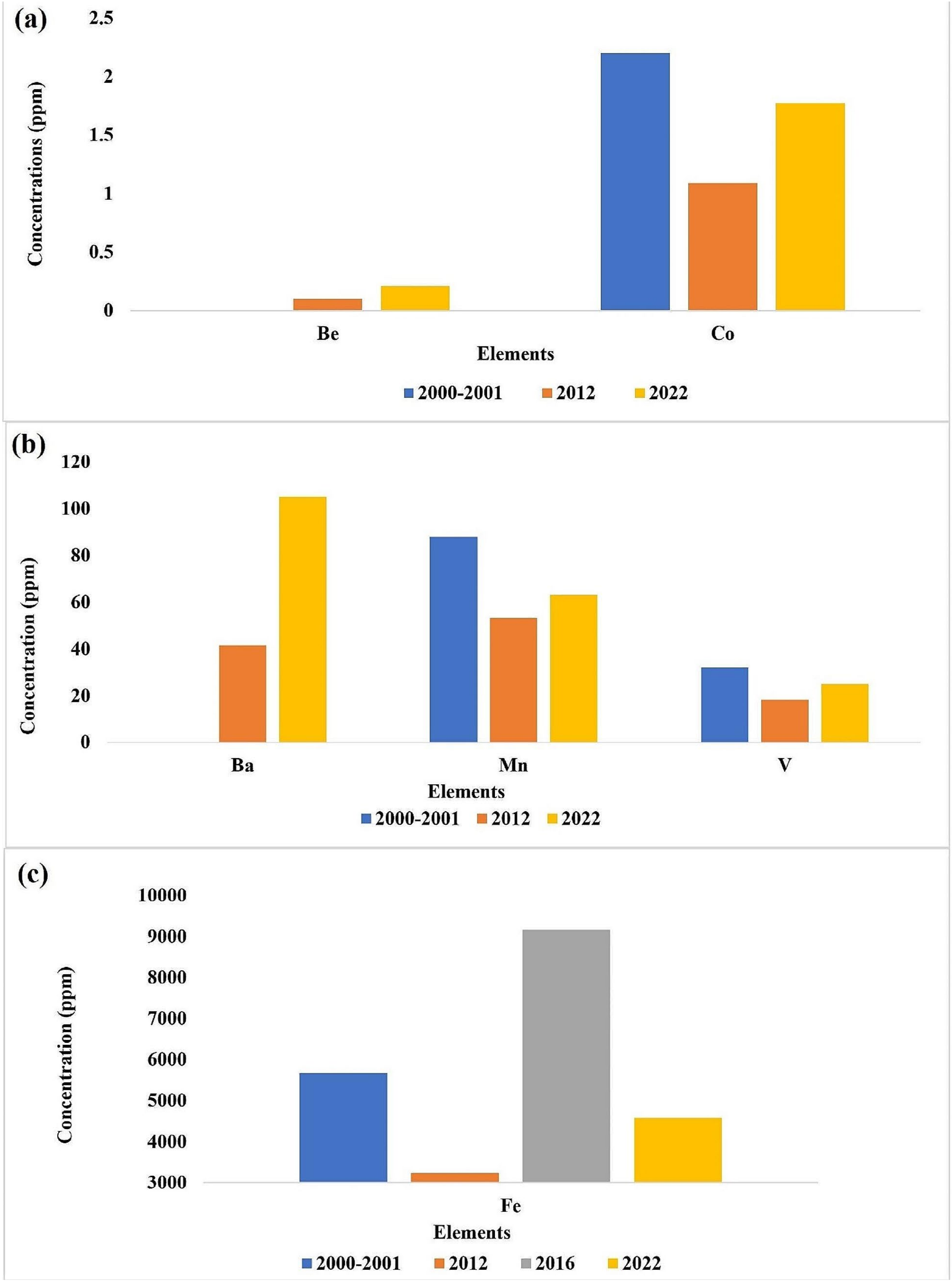


Fig. 5 Variations of Be and Co (top), Ba, Mn and V (middle) and Fe (bottom) concentrations in sediments during the last two decades

Table 4 Geoaccumulation Indices (Igeo) calculated for various elements in the sediments off Doha

Stations	Elements												
	As	Ba	Be	Cd	Co	Cr	Cu	Fe	Mn	Ni	V	Zn	Ti
S0	-1.03	-0.92	-1.33	-0.13	-1.21	-0.61	-0.51	-1.19	-1.31	-0.77	-0.89	-0.74	-1.25
S1	-0.69	-1.27	-1.54	0.07	-1.26	-0.82	-0.99	-1.38	-1.39	-0.81	-1.23	-1.17	-1.34
S2	-0.81	-1.54	-1.70	0.09	-1.34	-0.89	-1.11	-1.42	-1.47	-0.84	-1.27	-1.25	-1.37
S3	-0.77	-1.54	-1.70	0.17	-1.31	-0.95	-1.07	-1.48	-1.58	-0.84	-1.32	-1.25	-1.51
S4	-1.09	-2.02	-2.65	0.03	-1.71	-1.56	-2.45	-2.13	-2.16	-1.28	-1.77	-2.12	-2.33
S5	-1.22	-2.03	0.00	-0.04	-1.88	-1.56	-2.15	-2.06	-2.32	-1.32	-1.94	-2.56	-2.47
S6	-1.15	-2.07	-2.35	0.03	-1.92	-1.69	-2.79	-2.38	-2.53	-1.36	-1.96	-2.79	-2.54
S7	-0.88	-1.51	-1.57	0.11	-1.39	-0.82	-1.13	-1.30	-1.46	-0.76	-1.23	-1.18	-1.35
S8	-1.00	-1.96	-2.35	0.02	-1.94	-1.74	-2.16	-2.48	-2.66	-1.37	-2.02	-1.98	-2.15
S9	-0.68	-1.53	-1.61	0.12	-1.34	-0.89	-1.06	-1.41	-1.55	-0.81	-1.28	-1.20	-1.40
S10	-0.78	-1.74	-1.95	0.15	-1.56	-1.10	-1.47	-1.76	-1.87	-1.00	-1.55	-1.60	-1.71

Table 5 Contamination factor (C_f), Degree of Contamination (C_d) and Pollution Load Index (PLI) calculated for various elements in the sediments off Doha

Stations	Elements Contamination factor (C_f)													C_d	PLI
	As	Ba	Be	Cd	Co	Cr	Cu	Fe	Mn	Ni	V	Zn	Ti		
S0	0.14	0.18	0.07	1.10	0.09	0.37	0.46	0.10	0.07	0.25	0.19	0.27	0.08	3.39	< 1
S1	0.31	0.08	0.04	1.77	0.08	0.22	0.15	0.06	0.06	0.23	0.09	0.10	0.07	3.20	< 1
S2	0.23	0.04	0.03	1.83	0.07	0.19	0.12	0.06	0.05	0.22	0.08	0.08	0.06	3.07	< 1
S3	0.25	0.04	0.03	2.20	0.07	0.17	0.13	0.05	0.04	0.22	0.07	0.08	0.05	3.40	< 1
S4	0.12	0.01	0.00	1.60	0.03	0.04	0.01	0.01	0.01	0.08	0.03	0.01	0.01	1.96	< 1
S5	0.09	0.01	0.00	1.37	0.02	0.04	0.01	0.01	0.01	0.07	0.02	0.00	0.01	1.66	< 1
S6	0.11	0.01	0.01	1.60	0.02	0.03	0.00	0.01	0.00	0.06	0.02	0.00	0.00	1.88	< 1
S7	0.20	0.05	0.04	1.93	0.06	0.22	0.11	0.07	0.05	0.26	0.09	0.10	0.07	3.26	< 1
S8	0.15	0.02	0.01	1.57	0.02	0.03	0.01	0.00	0.00	0.06	0.01	0.02	0.01	1.91	< 1
S9	0.32	0.04	0.04	1.97	0.07	0.19	0.13	0.06	0.04	0.23	0.08	0.10	0.06	3.32	< 1
S10	0.25	0.03	0.02	2.13	0.04	0.12	0.05	0.03	0.02	0.15	0.04	0.04	0.03	2.95	< 1

Statistics on sediment contamination

The toxic and trace elements in the sediments off Doha are mostly at an unpolluted level, as the caluated Igeo is negative, except for Cd (Table 4). At S0 and S5, the Igeo of Cd is negative, indicating no pollution. In all other stations, the Igeo of Cd is between 0.02 and 0.17, which can be referred to as slightly polluted. This is consistent with other regions, such as Izmit Bay in Turkey (Tan and Aslan 2020), but lower than that found in the Yanbu and Alwajh areas of the Red Sea (El-Sorogy et al. 2021; Youssef et al. 2020).

The C_f estimated for the toxic and trace elements, except for Cd, is less than 0.5, which is generally categorised under low contamination (Table 5). However, the C_f estimated for Cd in all the stations is in the range of 1.1–2.2, which is classified as moderate contamination. But the overall C_{deg} estimated in combination of all elements is in the range of 1.66–3.4, which is classified as a low degree of contamination. A recent study conducted in the Al-Khafji area of the Gulf reveals C_{deg} in the range of 5.7–11.0 (Alharbi et al. 2023). Such moderate levels of C_{deg} are found at Izmit Bay as well (Tan and Aslan 2020).

The PLI estimated from all the elements in consideration falls below 1, which is referred to as an unpolluted condition (Table 5). In general, the statistical analysis reveals that Doha Bay and its surroundings maintain an unpolluted status. The Igeo, C_f, $C_{deg,}$ and PLI values point towards minimal contamination for most elements analysed, indicating that these sites are generally free from significant pollution. However, Cd stands out as the primary element of concern due to its relatively higher contamination levels compared to other elements. Despite the moderate contamination factors for Cd, the measured concentrations remain lower than the SQGs, USEPA and European Community (EC) thresholds (Aikaterini et al. 2010). The alignment with the international standards demonstrates that, although Cd exhibits moderate contamination, it does not pose an immediate or significant threat to the marine ecosystem. The PLI further supports the inference that the sites are generally unpolluted. Compared to international standards, the measured Cu off Doha has shown some exceedances. However, the statistics on cotamination highlight minimal levels of Cu contamination in the sediments off Doha.

Summary and conclusions

The concentrations of major, toxic, and trace elements in the seabed sediments off Doha have been analysed, and their spatial and temporal distributions have been investigated. The study reveals elevated concentrations of certain major elements (Al, Ca, Mg, and Sr), and trace elements (As, Mn, Fe, Zn, and Cd) over the decades, which are primarily attributed to the aeolian dust brought to the marine environment by shamal winds. The maximum concentrations of the above elements measured from the recent sampling are Al (9803), Ca (276,781), As (4.11), Mg (22,218), Sr (5368), Mn (63), Fe (4580), Zn (25.9), and Cd (0.66) ppm, respectively. Al and Fe showed higher concentrations in 2016 as compared to other years due to the increased developments prior to the FIFA-2022 events. The weak currents in the bay also favour the adsorption and accumulation of elements in the seabed sediments. Compared to the last two decades, the concentrations of toxic metals Cu, Ni, Zn, and Cd are found to be higher (20.7, 17.9, 25.9, and 0.66 ppb in 2022), while, the other trace elements fluctuate between the decades/years. The temporal variability identified in the elemental concentration in the bay is an indication of the response of the water body to urbanisation in the vicinity of Doha Bay.

The comparison of elemental concentrations of the sediments off Doha with various standards indicates that most of the elements are within the threshold limits, except Cu, which has marginally exceeded the US EPA threshold of 18.7 ppm. It is important to note that the discrepancies exist among various standards for the same parameter as they are formulated based on various factors of the specific regions. As far as we know, there are no updated standards for the elemental concentration of marine sediments in Qatar. However, in the context of the physical and biogeochemical characteristics of Qatari waters, along with the sustainability, reliable standards are required to be developed for the State of Qatar, and this work is under consideration.

The Geoaccumulation Index (Igeo), Contamination Factor (C_f), Degree of Contamination (C_{deg}) and Pollution Load Index (PLI) were derived for the sediments, considering toxic and trace elements As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Fe, Mn, Ni, V, and Zn. The Igeo of Cd (< 0.18) resulted in a slight pollution, and the C_f of Cd (1.1–2.2) reveals a moderate contamination. The C_{deg} estimates indicate that the sediments off Doha have a low degree of contamination, while the PLI reveals no significant pollution. Although Cu has shown exceedances over a few international thresholds, it has not resulted in pollution, according to the statistics derived. These highlight that the present element concentrations in the sediments of the bay do not pose a significant threat to its marine ecosystem, provided proper control is needed on the anthropogenic influx of certain elements to safeguard the region from possible pollution.

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Author contributions The study conception and design are made by AVM, OZ, EMA and PV. Data collection was carried out by AVM, OZ, EMA and SD. Material preparation and analysis were performed by HVM, SD and AI. All authors were contributed to interpretation of results and discussions. The first draft of the manuscript was written by HVM and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare no competing interests.

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