FISEVIER

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul



Baseline

Status of trace metals in surface seawater of the Gulf of Aqaba, Saudi Arabia



Ahmed A. Al-Taani ^{a,*}, Awni Batayneh ^b, Yousef Nazzal ^b, Habes Ghrefat ^b, Eslam Elawadi ^b, Haider Zaman ^c

- ^a Department of Earth and Environmental Sciences, Faculty of Science, Yarmouk University, Irbid 21163, Jordan
- ^b Department of Geology and Geophysics, King Saud University, PO Box 2455, Riyadh 11451, Saudi Arabia
- ^c Department of Geology, Taibah University, PO Box 30002, Madinah 41477, Saudi Arabia

ARTICLE INFO

Article history: Available online 7 August 2014

Keywords: Trace element Coastal water Pollution source Gulf of Aqaba Red Sea Saudi Arabia

ABSTRACT

The Gulf of Aqaba (GoA) is of significant ecological value with unique ecosystems that host one of the most diverse coral communities in the world. However, these marine environments and biodiversity have been threatened by growing human activities. We investigated the levels and distributions of trace metals in surface seawater across the eastern coast of the Saudi GoA. Zn, Cu, Fe, B and Se in addition to total dissolved solids and seawater temperature exhibited decreasing trends northwards. While Mn, Cd, As and Pb showed higher average levels in the northern GoA. Metal input in waters is dependent on the adjacent geologic materials. The spatial variability of metals in water is also related to wave action, prevailing wind direction, and atmospheric dry deposition from adjacent arid lands. Also, water discharged from thermal desalination plants, mineral dust from fertilizer and cement factories are potential contributors of metals to seawater water, particularly, in the northern GoA.

© 2014 Elsevier Ltd. All rights reserved.

The GoA is a semi-enclosed basin located at the northern extension of the Red Sea (Fig. 1). It contains unique ecosystems and biodiversity and is habitat for one of the most diverse coral communities in the world. Only 27 km of its 180 km eastern coastline lies in Jordan, while the remaining portion, largely undeveloped, belongs to Saudi Arabia.

The Gulf is of significant strategic and economic value to all gulf-bordering states, particularly to Jordan, where it provides Jordan with its only marine outlet. Lack of significant wave activity along with the low rate of water circulation and renewal, among others, render the Gulf particularly susceptible to pollution. Thus, the impact of intense and widespread human activities from the neighboring countries, poses a potential threat to the Saudi GoA coast. Evidence of human impact has been documented (Batayneh et al., 2012; Al-Trabulsy et al., 2013; Batayneh et al., 2013a,b).

The growing concern over the potential contamination of aquatic ecosystems along the Saudi GoA has gained momentum in recent years and became a priority issue. Among other contaminants, heavy metals in seawater have received particular attention as a way of assessing the early impact of human activities on the marine environment. This is also of critical importance for

protecting aquatic ecosystems and determines the proper conditions for various uses.

The prevailing sub-tropical arid conditions of high temperatures and rare rainfall along with limited freshwater input, made the GoA of unique aquatic ecosystems. The surface water of the GoA is oligotrophic with a shallow but stable thermocline for most of the year, except during the winter, when winds drive convective mixing of deep (higher-nutrients) and surface waters. Because of a low rate of water exchange between the GoA and the Red Sea, the average residence time of water in the Gulf is relatively long about one year (Klinker et al., 1976; Paldor and Anati, 1979; Hulings, 1979). The tidal waves generated at the Strait of Tiran in the southern GoA are carried by the inflow waters from the Red Sea and propagate northwestward into the GoA (Manasrah et al., 2004), which play a role in metals distribution. Surface runoff is limited to intermittent flash floods occurring in winter, which is discharged into the Red Sea or percolated to groundwater aquifers. Groundwater is the primary source of drinking and irrigation water in the region, though evidence of salinization has been reported (Al-Taani et al., 2013; Batayneh et al., 2013a,b).

The geologic outcrops in the study area include (in ascending order): the Proterozoic metamorphic basement which is unconformably overlain by Sharik Formation of conglomerate and sandstone (Fig. 1). These rocks are also unconformably overlain by sandstone, conglomerate, limestone and gypsum of Musayer Formation (Early Miocene). Nutaysh Formation (Middle Miocene) of

^{*} Corresponding author. Tel.: +962 779610469; fax: +962 7211117. E-mail address: taaniun@hotmail.com (A.A. Al-Taani).

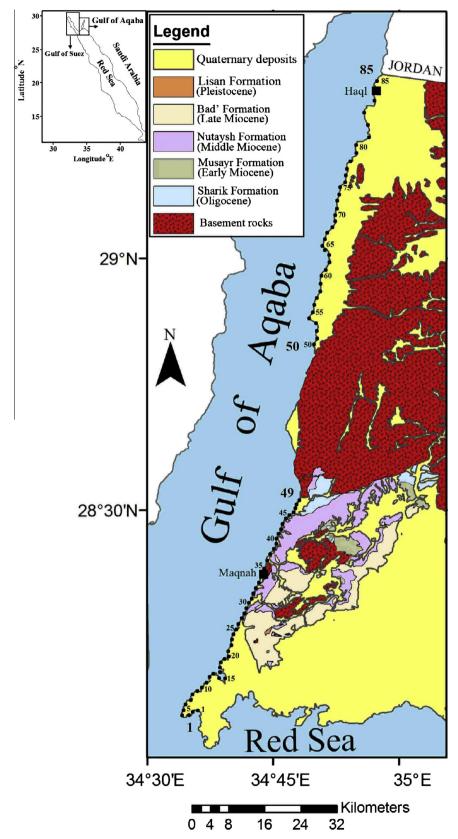


Fig. 1. Geologic outcrop location and sampling sites. The sampling sites are numbered as shown in the figure, beginning the sampling at the lower end of the GoA, and ending at the Jordan-Saudi Arabia border.

marl, gypsum, sandstone, conglomerate, marl and limestone overlies Musayer Formation. Bad Formation of Middle Miocene to Late Miocene marine evaporites consisting of gypsum and anhydrite and shallow to marginal marine sediments overlies Nutaysh Formation. Lisan Formation of Pliocene to Pleistocene age forms the youngest rocks in the study area and consists of alluvial sands and gravels (Clark, 1986).

While several publications have investigated the water quality of the Jordanian GoA (e.g., Hulings and Kirkman, 1982; Abu-Hilal and Badran, 1990, 2001; Abu-Hilal and Al-Najjar, 2004; Al-Rousan et al., 2007; Batayneh et al., 2012, 2013b), only a few have been devoted to assess seawater conditions along the Saudi part of the GoA (Al-Trabulsy et al., 2013; Batayneh et al., 2013a,c). However, none has surveyed the trace elements levels in seawater along the coastline of the Saudi GoA.

This study is designed to assess the current status and spatial distribution of trace elements along the Saudi GoA coast and to identify potential sources of contamination. This evaluation helps develop effective coastal management guidelines and strategies for better management of coastal activities. This is of particular concern, as this portion of the GoA is expected to become an important area in terms of marine waterways, tourism and various commercial and industrial activities.

Eighty-five surface seawater samples were collected along the Saudi GoA coast in January 2013 (Fig. 1). Unfiltered samples were collected in 1-liter pre-acidified polyethylene containers, kept in an icebox (at 4 °C) and transported to the water laboratory for subsequent chemical analyses. Water temperature, total dissolved solids (TDS), redox potential (Eh), and dissolved oxygen (DO) were directly measured in-situ. Trace elements were measured with Inductively Coupled Plasma Mass Spectrometer (ICP-MS): ELAN 9000 (Perkin Elmer Sciex Instrument, Concord, Ontario, Canada). Triplicate samples were collected and analyzed. In addition, 32 rock and 85 sediment samples along the coastal area were collected and measured for trace metals. The sediment samples were ground, sieved through 2 mm sieve and transferred to plastics bags. 200 mg of samples were placed in a dry and clean Teflon digestion beaker, and 6 mL of HNO₃, 2 mL HCl and 2 mL HF were added to the Teflon beaker. Samples were digested on the hot plate at 120-150 °C for approximately 40 min. The resulting digest was filtered through Whatman filtered paper No. 42. The filtrate was transferred to volumetric flask and the volume was adjusted to 50 mL with deionized water. A blank digest was carried out in the same way. 500 mg of rock-powdered samples were placed in a dry and clean Teflon digestion beaker and 2 mL of HNO3 and 6 mL HCl were added. Samples were digested, filtered and diluted with deionized water similar to soil samples. Total metals contents were measured by ICP-MS. The results of rock and sediment samples were averaged and divided into two groups: the northern and southern samples.

Metals concentrations (B, Cr, Fe, Mn, Cu, Zn, Mo, As, Pb, Cr, Hg, Sr, Co) in surface seawater along with TDS, DO, temperature and Eh are presented in Table 1. Surface water temperature varied from 19.8 °C to 23.2 °C with a decreasing trend northwards to site 49 before temperatures remained relatively constant (Fig. 2 and Table 1).

The distribution of the seawater temperature is closely related to the northwards currents dragging warm surface waters from the Red Sea through the shallow Strait of Tiran to the GoA (Genin et al., 1995; Manasrah et al., 2004), where they occupied the southern end and extending their impact to the central GoA (up to sampling site 49). Evaporation of about 350 cm/year of the GoA water is compensated primarily by inflow in the upper 80 m of water from the Red Sea to the GoA (Murray et al., 1984). The average temperatures of the Red Sea are about 2 °C warmer than that of the GoA.

The near-saturated and relatively uniform DO levels of the seawaters indicate oxygenated water, where the concentrations ranged between 5.8 and 6.9 mg/L (Fig. 2 and Table 1). Eh values of surface seawater ranged between 260 and 275 mV in the southern part and between 270 and 284 mV in the northern GoA (Table 2, Fig. 2). Redox indicators suggest that the coastal water in predominantly oxidizing conditions. These oxidizing conditions are favorable for immobilization of most elements, and may contribute to the relative lower levels of some metals observed particularly in the northern samples.

The TDS of surface water showed spatial variability (Fig. 3), with average concentrations ranging between 41.9 and 42.7 g/L in the southern part and between 39.9 and 40.9 g/L from sites 50–85 (Table 1).

The higher TDS levels observed in the southern GoA are related to dissolution and leaching of the adjacent limestone and evaporite deposits (anhydrite and gypsum). Mineral dissolution primarily occurred due to wave activity and irregular flash floods, where salts (and trace elements) are transported coastward.

The atmospheric dust input from the surrounding arid region is an important source of salts (and trace metals) to seawater. The GoA is situated in a desert-belt area, bordered by the Sinai and Negev Deserts to the west and by the Arabian Desert to the east with frequent dust storm, where large fraction of the aerosols delivered to the Gulf is derived from adjacent land-masses (Chen et al., 2008), which play a significant role in modifying the chemical composition of seawater.

Atmospheric dust input to the GoA varies spatially and temporally, with an annual average deposition rate of 28 g/m²/year in Eilat city at the upper northwestern end (Chase et al., 2006) and

Table 1Temperature, TDS, DO, Eh and selected metals in surface seawater along the Saudi GoA.

S.N.		Temp.	TDS	DO	Eh	As	В	Cd	Co	Cr	Cu	Fe	Hg	Mn	Mo	Pb	Se	Zn
		(°C)	(g/l)	(mg/l)	(mV)							(µg/L)						
Southern	Mean	21.6	42.2	6.3	267.9	0.55	2335	0.017	0.248	0.928	9.190	21.849	0.061	0.224	5.561	0.138	0.314	3.992
Samples	Min	20.4	41.9	5.8	260.0	0.46	1887	0.005	0.150	0.470	4.500	11.200	0.021	0.100	0.380	0.020	0.176	1.330
(1-49)	Max	23.2	42.7	6.9	275.0	0.92	2947	0.068	0.394	3.250	12.700	42.110	0.123	0.560	12.000	0.450	0.737	6.000
	SD	0.8	0.2	0.3	3.9	0.12	251	0.010	0.068	0.495	2.065	8.368	0.021	0.124	2.789	0.069	0.114	1.033
Northern	Mean	20.1	40.3	6.3	277.1	1.18	1344	0.048	0.219	0.996	2.090	6.281	0.066	0.306	7.775	0.288	0.268	2.414
Samples	Min	19.8	39.9	5.8	270.0	0.85	918	0.035	0.068	0.700	1.100	2.800	0.018	0.200	3.200	0.120	0.246	1.100
(50-85)	Max	20.3	40.9	6.8	284.0	1.55	1714	0.069	0.392	1.450	2.900	8.400	0.110	0.420	12.000	0.430	0.296	3.800
	SD	0.1	0.3	0.3	4.0	0.19	200	0.010	0.072	0.189	0.475	1.398	0.025	0.065	2.044	0.072	0.014	0.714
All	Mean	21.0	41.4	6.3	271.8	0.82	1916	0.030	0.236	0.957	6.183	15.255	0.063	0.259	6.499	0.202	0.295	3.323
Samples	Min	19.8	39.9	5.8	260.0	0.46	918	0.005	0.068	0.470	1.100	2.800	0.018	0.100	0.380	0.020	0.176	1.100
(1-85)	Max	23.2	42.7	6.9	284.0	1.55	2947	0.069	0.394	3.250	12.700	42.110	0.123	0.560	12.000	0.450	0.737	6.000
	SD	1.0	1.0	0.3	6.0	0.35	544	0.018	0.071	0.395	3.871	10.035	0.023	0.111	2.719	0.102	0.089	1.199

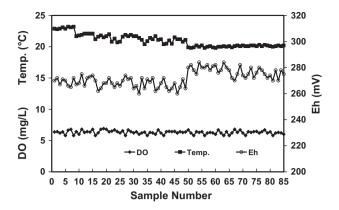


Fig. 2. Temperature, DO and Eh for surface seawater samples collected from the Saudi GoA coast. The sampling points are shown on the map on Fig. 1.

about 30.78 g/m²/year in Aqaba city at the northeasternmost edge of the GoA (Yusuf, 2007) making it one of the highest dust deposition rate areas on Earth (Chase et al., 2006).

The spatial distribution of Zn in surface seawater showed a decreasing pattern northwards (Fig. 4), with slight variations are apparent between sites 50 and 85. The highest level of Zn was observed in the vicinity of the Strait of Tiran, with similar pattern was observed for offshore surface seawater (Shriadah et al., 2004). However, our data are larger than the average oceanic concentration of $0.4~\mu g/L$ (Broecker and Peng, 1982), and than those reported for the Mediterranean surface seawater of $0.17~\mu g/L$ (Tankere and Statham, 1996).

While the eastern coast of the Saudi GoA is currently less populated with minimal human interference, the high concentrations of some metals in seawater are indicative of anthropogenic sources. However, natural sources and processes were also investigated and remain a potential source.

Sediment and rock samples across the coastal area were collected and analyzed for Zn and the average values are tabulated in Tables 2 and 3. The average Zn concentrations in sediment samples were relatively similar in the southern (7.73 μ g/g) and northern samples (7.02 μ g/g) (Table 2). Although the basement rocks (covering the majority of the northern coast) were found high in Zn (38.8 μ g/g; Table 3) compared to the sedimentary rocks in the southern GoA (16.4 μ g/g; Table 3), lower levels of Zn were observed in the northern seawater. This suggests that sediment and rocks are not major sources of Zn to seawater.

The GoA region receives negligible river discharge and atmospheric wet deposition (Ganor and Foner, 1996), therefore, atmospheric aerosol dry deposition is the main external source of trace elements to this marine ecosystem (Chase et al., 2011). Atmospheric fluxes of certain trace metals (e.g.: Cd, Pb, Cu and Zn) to the ocean could exceed those of riverine sources (Guerzoni et al., 1999; Kocak et al., 2005).

The uppermost part of the study area is semi-surrounded (from the east) by mountain ridges of up to 1131 m high, which restrict aeolian fluxes of trace metals to the northern GoA. However, the southern half is characterized by an open area of semi-flat terrain with an elevation ranging between 30 m (below sea level) and 500 m. This suggests that the southern portion is more susceptible

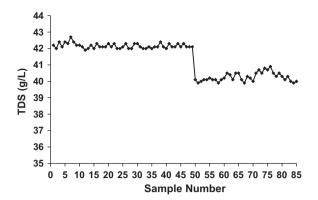


Fig. 3. TDS for surface seawater samples collected from the Saudi GoA coast.

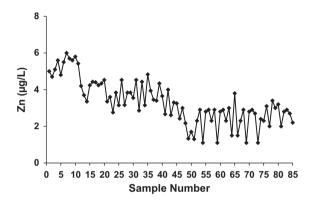


Fig. 4. Zn concentrations in surface seawater samples collected from the Saudi GoA coast.

to dust borne trace metals including Zn. Al is a major component of continental materials and an excellent tracer of atmospheric inputs to the ocean. The elevated Al concentration in sediment samples, particularly in southern GoA (Table 2), suggests the relatively strong impact of mineral dust in this region, and subsequent higher Zn contents in seawater, compared to the northern half. Atmospheric dry flux of Zn to the uppermost northwestern GoA (Eilat city) was estimated to be about 1.68 mg/m²/year (Chen et al., 2008).

Elevated levels of Zn were reported in the Jordanian GoA seawater (at northeastern edge close to the Saudi border) ranging between 5.71 and 11.55 μ g/L (MSS, 1999). These high levels of Zn (originated mainly from the nearby industrial complex) remain a potential source of contamination to coastal water of Saudi GoA.

In addition, water flowing from Red Sea and originating from the Gulf of Suez is a potential source of Zn. Gulf of Suez, located at the western extension of the Red Sea, is shallower than the GoA, which allows for good water exchange with the Red Sea (Hoepner and Lattemann, 2002). Suez city is highly populated with intense human and industrial activities. Discharge of industrial effluents (desalinization plants), chemicals, and mineral dust from fertilizer and cement factories at Suez City, are potential contributors to the land-based sources of pollution affecting coastal waters in the Gulf of Suez and the northern Red Sea (Gerges, 2002).

Table 2 The average levels of trace metals in sediment samples $(\mu g/g)$ collected from the northern and southern GoA.

Location	Al	As	В	Cd	Co	Cr	Cu	Fe	Hg	Mn	Mo	Pb	Se	Zn
Southern GoA	1506	15.1	8.29	0.07	0.77	3.67	10.77	1437	2.37	3.93	0.6	3.72	0.69	7.73
Northern GoA	1044	12.2	7.49	0.06	0.51	7.97	7.57	1172	2.36	3.61	0.7	6.75	0.45	7.02

Table 3 The average levels of trace metals in rock samples ($\mu g/g$) collected from the study area.

Location	Al	As	В	Cd	Со	Cr	Cu	Fe	Hg	Mn	Mo	Pb	Se	Zn
Southern GoA	907	8.6	15	0.11	0.85	4.29	3.8	1483	0.52	105	0.33	2.8	0.88	16.4
Northern GoA	4022	4.7	12	0.52	3.19	7.11	4.3	4997	0.39	264	0.19	21	0.92	38.8

Cu levels in seawater samples exhibited elevated values in the southern half of the GoA, with apparent decreases toward the north (Fig. 5). In the southern GoA, Cu values varied from 4.5 to 12.7 μ g/L, whereas they ranged between 1.1 and 2.9 μ g/L in the northern part (Table 1). These values are greater than the mean ocean level of 0.12 (Broecker and Peng, 1982). Cu concentrations in surface water of the North Atlantic Ocean ranged between 0.07 and 0.1 μ g/L (Yeats and Cambell, 1983; Kennish, 1994), whereas the average Cu in surface waters of the Mediterranean Sea was 0.2 μ g/L (Laumond et al., 1984; Boyle et al., 1985).

It is likely that mixing and dilution of leached Cu with water flowing from the Red Sea, particularly in the winter (the sampling season), is contributing to the lower levels found at the southern end of the GoA, with impacts limited to the Strait of Tiran area.

Relatively similar concentrations of Cu were detected in samples collected from the basement rock in the north (4.3 $\mu g/g)$ compared to the southern part (3.8 $\mu g/g)$ of sedimentary origin (Table 3). Cu content in sediments of the southern GoA showed higher average levels (10.77 $\mu g/g)$ (Table 2) relative to the northern sediments (7.57 $\mu g/g)$. The use of fertilizers, especially following excessive irrigation or during flash floods, is a potential source, where inhabitants in this area rely on agricultural activities for their livelihoods. Excessive flood irrigation, a commonly practice in the adjacent coastal agricultural lands, has also the effect of mobilizing Cu from sediments and rocks or accelerating the natural leaching of Cu from geologic formations.

Cu flux from dry deposition to Eilat city (at the northwesternmost of GoA) was estimated to be $0.38 \ mg/m^2/year$ (Chen et al., 2008) which was attributed to anthropogenic sources, and remains a potentially important source of Cu to seawater in the southern coast.

These Cu contents in seawater reported here are larger than that reported by Shriadah et al. (2004) for the offshore surface seawater of 0.11 μ g/L. This is in part attributed to increased human activities in the GoA region. In addition, as aridity and potentially dust fluxes are expected to increase in the future (Tegen et al., 2004; Woodward et al., 2005), dust-dominated systems may become more common in the GoA. Higher Cu concentration of 5.1 μ g/L was reported in the coastal water next to Al-Ghardaqa city (in the northern Red Sea) (Saad and Kandeel, 1988). The Cu concentrations in seawater of the Jordanian GoA ranging between 0.74

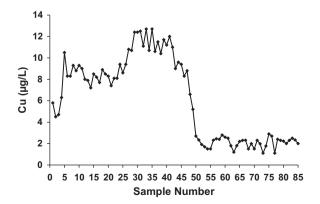


Fig. 5. Cu concentrations in surface seawater samples collected from the Saudi GoA coast.

and 2.28 μ g/L (MSS, 1999), are relatively similar to those measured in this study for the northern GoA.

Similarly, Fe showed substantial spatial variability in surface water concentrations, where higher concentrations were observed in the southern water samples compared to that of the north (Fig. 6). Fe concentration increased steadily northwards up to site 49 (peaking at site 47) before decreasing abruptly but with more uniform values. Fe levels in seawater varied from 11.2 to 42.1 μ g/L in the southern half and from 2.8 to 8.4 μ g/L (Table 1) in the northern half. Lower average value has been reported by Shriadah et al. (2004) for offshore surface seawater of the GoA (1.58 μ g/L).

Broecker and Peng (1982) reported a mean oceanic concentration of Fe of about $0.04 \,\mu g/L$, whereas Landing and Bruland (1987) reported surface concentrations of dissolved Fe in the Pacific Ocean in the range of $0.042-0.07 \,\mu g/L$ that decreased offshore. In Mediterranean, Fe concentrations ranged from 0.056 to $0.336 \,\mu g/L$ (Saager et al., 1993).

Because of the proximity of the sample sites (up to 49) to Feoxide-rich sandstone of Sharik Formation, it is presumed that they received water rich in Fe and contributed to the higher Fe values. While Fe content was higher in northern basement rocks (4997 $\mu g/g$), they are resistant to weathering and are probably minor sources of Fe in seawater in the northern GoA. It is possible that water propagating northwards from the Red Sea is mixed with water in the southern GoA and decreased Fe levels in seawater near the Strait of Tiran.

However, higher Fe content was found in sediments collected from the southern coast (1437 $\mu g/g)$ compared to 1172 $\mu g/g$ in the northern sediment. These results suggest that Fe release from sediment probably accounts for a portion of Fe in seawater, with larger impacts in the southern GoA.

Fe-borne dust conveyed to the Gulf from the surrounding deserts is another potential source of elevated Fe levels. The atmospheric deposition rate of Fe to the ocean surface varies over three orders of magnitude, from minimum values in the remote Pacific and Southern Ocean to maximum values near desert source regions (Duce and Tindale, 1991; Fung et al., 2000). Chen et al. (2008) estimated the Fe dry deposition flux to the northwestern GoA (Eilat city) to be about 216 mg/m²/year. These large quantities of crustally derived Fe were higher than those reported for the

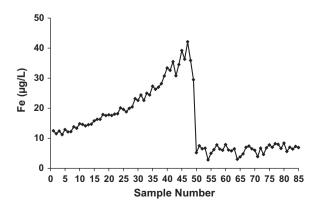


Fig. 6. Fe concentration in seawater samples collected from the Saudi GoA coast.

neighboring Mediterranean area. A surface water enrichment of Fe occurs during the stratified summer (Chase et al., 2006), where mixing of water column in winter results in lower Fe concentrations.

Boron is a common element in marine water with a typical concentration of $4.5 \, \text{mg/L}$ (Moss, 1981) which may vary depending on the location and seasonal effects. Patterns of B levels during the study period showed a relatively similar trend to Cu. Higher concentrations were observed in the southern portion ranging between 1.9 and 2.9 mg/L (Fig. 7), whereas the northern seawater samples showed lower B concentrations (between 0.9 and 1.7 mg/L) (Table 1).

B content in rock and sediment samples also showed higher mean values in southern coast (8.29 μ g/g and 15 μ g/g, respectively) compared to the northern half (8.29 μ g/g and 12 μ g/g, respectively) (Table 3). This suggests that the elevated B values may be related to seawater interaction with sediments, shale and evaporites cropped out in southern area. B dissolution is accelerated by wave activity, especially during winter storm events. The strong tidal currents and relatively shallow reefs at the southern edge near the Strait of Tiran (Murray et al., 1984) create turbulence that accelerates B dissolution into the surface waters, which are then carried into the GoA.

Elevated Se levels were observed next to the Strait of Tiran (up to site 18) followed by a slight decrease in concentration and remained largely unchanged (Fig. 8). Se concentrations showed relatively larger variations in the southern seawater ranging between about 0.18 and 0.74 μ g/L, compared to about 0.25 and 0.30 μ g/L in the northern GoA (Table 1).

Se is commonly found in marine sedimentary deposits (Al-Taani et al., 2012). The presence of relatively high level of Se across the southern portion is related to leaching of nearest localized shale outcrops observed in the area. Se levels in rock samples showed relatively similar average values (0.88 μ g/g in the north and 0.92 μ g/g in the south). However, higher Se content was found in sediment sampled from the southern part (0.69 μ g/g), whereas a mean value of 0.45 μ g/g was detected in the northern sediment.

In contrast, Mn, As, Pb and Cd exhibited high values in the northern GoA. Mn showed a surface maximum next to the Strait of Tiran and decreased gradually to approach its minimum value at sampling site 49 before the concentration increased and remained relatively high (Fig. 9). Mn content in southern water samples varied from about 0.1 to 0.56 μ g/L (Table 1), whereas the northern values ranged between 0.20 and 0.42 and μ g/L with little variations and no spatial trend (Table 1 and Fig. 9). These values are higher than the average oceanic concentration of 0.01 μ g/L and than the mean value that reported by Shriadah et al. (2004) of

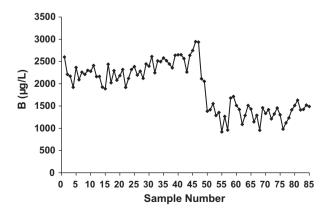


Fig. 7. Boron concentrations in surface seawater samples collected from the Saudi GoA coast.

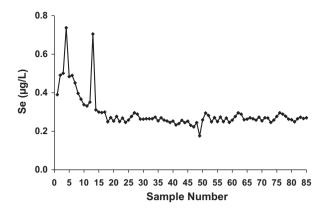


Fig. 8. Spatial distribution of Se in surface seawater samples collected from the Saudi GoA coast

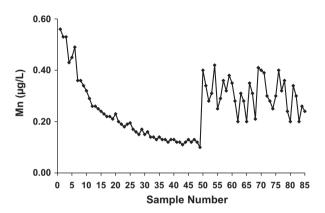


Fig. 9. Concentrations of Mn in surface seawater samples collected from the Saudi GoA coast.

 $0.11 \,\mu g/L$ for offshore seawater. Mn levels in North Atlantic surface waters ranged between around 0.05– $1.5 \,\mu g/L$ and were attributed to terrestrial sources (1982; Millero, 1996) and between 0.11 and 0.19 $\,\mu g/L$ in the neighboring Mediterranean Sea (Saager et al., 1993).

Sediment collected from the southern coast showed relatively similar Mn content (3.93 $\mu g/g$) to that of the north (3.61 $\mu g/g$; Table 2). However, rock samples showed lower levels of Mn in the southern part (105 $\mu g/g$) than the northern GoA (264 $\mu g/g$; Table 3). While rocks remain a source of Mn to seawater, its impact are likely significant in the southern portion where the widely distributed of sedimentary rocks are easily weathered and leached, compared to the northern basement rocks. In particular, the mudstone outcrops commonly occur in the vicinity of the southern coast. The dry deposition fluxes of Mn to the uppermost GoA (Elat city) were 5.28 mg/m²/year and were mainly derived from anthropogenic emissions (Chen et al., 2008).

Mn is likely associated with water discharged from desalination plants (thermal multi-stage flash (MSF) and membrane-based reverse osmosis (RO)) in Eilat, Taba and Haql cities in the northern GoA (Al-Rousan et al., 2007; Batayneh et al., 2013b). Thermal desalination plants can discharge a variety of heavy metals, including Mn, depending on the alloys present in the process line, which may affect water quality (Hoepner, 1999; Lattemann and Hopner, 2008).

Cd concentrations in seawater showed generally low values, though they exhibited similar spatial distribution to that of Mn. Higher Cd levels were observed next to the Strait of Tiran which decreased to sampling site 49 before the content increased (Fig. 10). The average Cd contents in surface seawater were

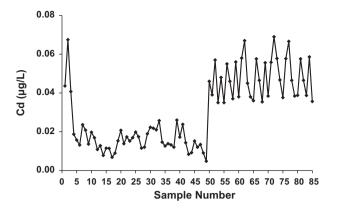


Fig. 10. Concentrations of Cd in surface seawater samples collected from the Saudi GoA coast.

 $0.02~\mu g/L$ and $0.05~\mu g/L$ in the southern and northern GoA, respectively (Table 1).

Higher values of Cd were reported by Shriadah et al. (2004) for the offshore seawaters, with an average value of 0.53 μ g/L for the lower GoA, with no spatial variability across the GoA. The North Atlantic Cd distributions showed a surface concentration below 0.005 μ g/L (Boyle et al., 1976; Millero, 1996), whereas the mean oceanic concentration of Cd is 0.07 μ g/L (Broecker and Peng, 1982).

These values of Cd reflect nearshore values and are primarily attributed to local influences through dissolution and leaching from adjacent geologic materials. These metals remain close to the coastline and are not dispersed offshore due to the winter northwards wind (at the Strait of Tiran). While higher Cd concentrations in rock samples collected from the north were observed (Table 3), Cd content in sediments showed fairly similar average value in both halves (Table 2). The high concentrations of Cd northern GoA are in part associated with discharge of wastewater from the MSF and RO desalination plants found adjacent Haql, Taba and Eilat city. In addition, aeolian dust remains a potential source of Cd, where 0.012 mg/m²/year of Cd was estimated in Eilat city which was primarily related to anthropogenic sources (Chen et al., 2008).

The concentration of industrial activities at the northeastern part of GoA in Jordan (near the Saudi border) including the discharge of cooling water and sewage discharge, phosphate loading are possible sources of Cd, Pb and Co measured in the northern part of the study area (Abu-Hilal et al., 1998; Abu-Hilal and Badran, 1990; Abu-Hilal, 1993).

Arsenic was detected in low concentrations, though they were spatially variable (Fig. 11). As contents in seawater varied from about 0.85 to 1.55 μ g/L in the northern sampling sites, and from 0.46 to 0.92 μ g/L in the southern part (Table 1).

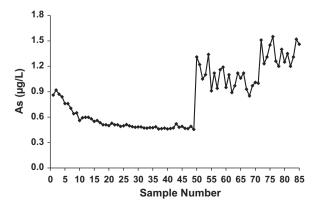


Fig. 11. Arsenic levels in seawater samples collected from the Saudi GoA coast.

High As concentrations have been reported in alluvial deposits (i.e.: Bhattacharya et al., 1997; Acharyya et al., 2000; Gates et al., 2011). Comparison of fluctuations in As concentrations were not consistent with variations in As content in rock and sediment samples, where they showed relatively higher average levels of As in the southern part compared to the northern GoA. The average values of As in sediment and rocks were 15.1 μ g/g and 8.6 μ g/g in the southern GoA, respectively (Table 2). However, in the northern part, the mean contents of As were 12.1 μ g/g in sediment and 4.7 μ g/g in rock samples (Table 3). These data suggest that the seawater in the northern GoA were subjected to other sources, in particular, the water discharged from thermal desalination plants.

Mo concentrations were highly variable but showed no trends (Fig. 12). It ranged in concentration between 0.4 and $12 \mu g/L$ with an average of 5.6 $\mu g/L$ in the southern GoA, and between 3.2 and $12 \mu g/L$ (averaging 7.8 $\mu g/L$) in the north (Table 1). These average values are relatively lower than the mean oceanic concentrations of $11 \mu g/L$ (Broecker and Peng, 1982) and the average seawater concentrations in the Pacific Ocean (10.5 $\mu g/L$; Collier, 1985; Millero, 1996). Higher Mo concentrations were also reported in the Eastern Mediterranean Sea with an average value of $13.4 \mu g/L$ (Van der Weijden et al., 1990).

Mo in sediment samples showed relatively lower average value in the southern half of the study area compared to the northern half (Table 2). However, rock samples showed higher average level in the south of the GoA (Table 3). Mo is also related to the brine of MSF plants. Hoepner and Lattemann (2002) indicated that Cu is not the only corrosion product discharge from desalination plants in the GoA and Red Sea, but also Ni, Cr, Mo and Fe among others.

Patterns of Cr showed high levels at site 1, which decreased afterwards (to site 15) followed by a gradual increase before approaching its maximum concentration close to sampling site 50 (Fig. 13). Then Cr decreased sharply again before it showed slight variations. Cr levels varied from 0.47 to 3.25 μ g/L in the southern portion, and from 0.7 to 1.45 μ g/L in the northern GoA (Table 1). These results of Cr in seawater of the GoA are higher than the mean oceanic contents of 0.33 μ g/L (Broecker and Peng, 1982) but comparable to those reported in the surface water of Mediterranean Sea of 3.4 μ g/L (Emelyanov and Shimkus, 1986; Furness and Rainbow, 1990).

Both sediment and rock samples showed higher average levels of Cr in the north, with 7.97 μ g/g and 7.11 μ g/g, compared to 3.67 μ g/g and 4.29 μ g/g in the southern part of the study area, respectively (Table 2 and Table 3). In addition to the igneous rocks spread over the middle coast, Sharik Formation, cropped out mainly in the central coast, is probably a primary source of Cr (ilmenite sandstone).

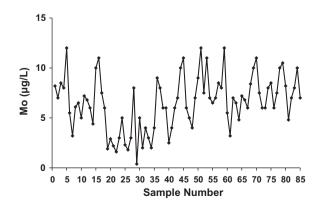


Fig. 12. Mo levels in (a) seawater and (b) rock samples collected from the Saudi GoA coast.

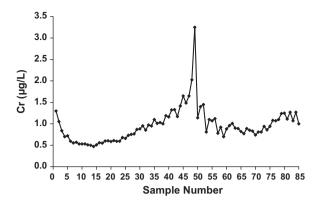


Fig. 13. Cr levels in seawater samples collected from the Saudi GoA coast.

This pattern of Cr suggests that the relative higher Cr levels at the northern and southern ends are probably attributed to discharge of water from desalination plant (Hoepner and Lattemann, 2002), and to water-borne Cr flowing from Red Sea (originating from the Gulf of Suez), respectively. Additional sources, include, cement-producing plants from the Jordanian GoA and dust borne Cr. Cr flux from aerosols to Eilat city was estimated to be 0.96 mg/m²/year (Chen et al., 2008).

Co concentrations in seawater showed little spatial variations (Fig. 14), with average Co values of about $0.25~\mu g/L$ and $0.22~\mu g/L$ in the southern and northern seawater samples, respectively (Table 1). The average Co contents in offshore seawater were $0.15~\mu g/L$ and $0.17~\mu g/L$ in the north Red Sea and southern GoA, respectively (Shriadah et al., 2004). Co exists in seawater at concentrations below $0.005~\mu g/L$ (Danielsson, 1980; Millero, 1996), whereas in the North Atlantic at around $0.004~\mu g/L$ (Kennish, 1994) and in the Mediterranean Sea at concentration of $1~\mu g/L$ (Migon and Nicolas, 1998).

Co in sediment of the southern GoA showed an average value of 0.77 μ g/g, whereas 0.51 μ g/g was found in the northern samples (Table 2). However, the rock samples showed average values of 0.85 μ g/g in the southern half, and 3.19 μ g/g in the northern basement rocks (Table 3). Potential sources of Co in seawater are likely similar to those of Cr. Co content in aerosol dust particles collected from Eilat city was about 0.1 mg/m²/year (Chen et al., 2008).

Low Hg contents were found with a relatively stable pattern across the sampling sites (Fig. 15). The average value of Hg was 0.061 μ g/L in the southern portion, whereas 0.066 μ g/L in the northern part (Table 1).

Similar concentrations of Hg were measured in sediments collected from the southern and northern coastal sediments, with averages of 2.37 μ g/g and 2.36 μ g/g, respectively (Table 2). Rock samples showed higher levels of Hg with average values of 105 μ g/g and 264 μ g/g in the southern and northern samples,

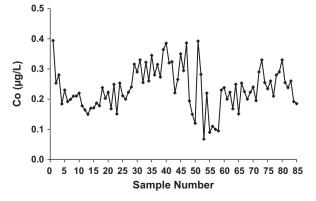


Fig. 14. Co levels in seawater samples collected from the Saudi GoA coast.

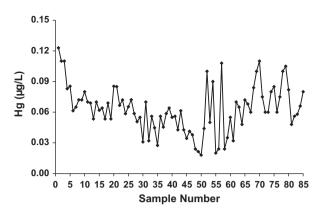


Fig. 15. Spatial distribution of Hg in surface seawater samples collected from the Saudi GoA coast.

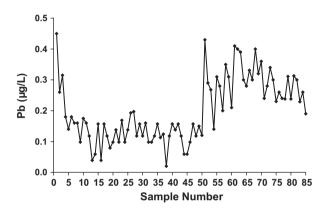


Fig. 16. Pb concentrations in surface seawater samples collected from the Saudi GoA coast.

respectively (Table 3). These results indicate the importance of geologic materials as a source of Hg to seawater. No results have been published for the relative contribution of Hg from dry deposition.

The lead distribution showed relatively low values with slight variations (Fig. 16). The average Pb values were about $0.14~\mu g/L$ and $0.29~\mu g/L$ in the southern and northern parts, respectively (Table 1). These concentrations are considerably higher than the average Pb concentration in oceans of $0.001~\mu g/L$ (Broecker and Peng, 1982). Pb occurs in North Atlantic open ocean waters at concentrations from 0.001 to $0.036~\mu g/L$, and was significantly influenced by anthropogenic activities (Furness and Rainbow, 1990). Schaule and Patterson (1981) reported Pb concentrations in the North Pacific oceanic surface water to be $0.01-0.01~5~\mu g/L$, with the concentrations increasing from the coast to the open ocean waters. In the Mediterranean Sea, the average Pb concentration was $0.05~\mu g/L$ (Laumond et al., 1984; Migon and Nicolas, 1998).

While these high Pb values are indicative of anthropogenic origin, natural materials were also found high in Pb. Rock and sediment samples exhibited higher average values in the northern GoA compared to the south (Tables 2 and 3). The average Pb contents in sediments were 3.72 μ g/g and 6.75 μ g/g in the southern and northern GoA, respectively (Table 2). Pb content in rock samples were found with mean values of 2.8 μ g/g in the southern samples and 21 μ g/g in the northern GoA (Table 3).

The uppermost part of the GoA received high Pb flux of 0.8 mg/m²/year from dry deposition (Chen et al., 2008) which was mainly attributed to emission of fuel burning. Shriadah et al. (2004) have reported similar values for offshore seawater in the southern GoA and northern Red Sea. The high values reported for the northern Red Sea remain a potential source of contamination to the

southern GoA. The coastal water of the Jordanian GoA were found high in Pb ranging between 0.73 and 1.43 µg/L (MSS, 1999).

Acknowledgments

This work has been funded by the National Plan for Science, Technology and Innovation (NPST) program, King Saud University, Saudi Arabia (Project No. 11-WAT1731-02). Thanks is due to the staff at General Directorate of Water in Al-Bad' City (Ministry of Water & Electricity, Saudi Arabia) for their assistance and invaluable information during the fieldwork.

References

- Abu-Hilal, A., 1993. Observations on heavy metal geochemical association in marine sediments of the Jordan Gulf of Aqaba. Mar. Pollut. Bull. 26, 85–90.
- Abu-Hilal, A., Al-Najjar, T., 2004. Litter pollution on the Jordanian shores of the Gulf of Aqaba (Red Sea). Marine Environ. Res. 58, 39–63.
- Abu-Hilal, A., Badran, M., 1990. Effect of pollution source on metal concentration in sediment cores from the Gulf of Aqaba. Mar. Pollut. Bull. 21, 190–197.
- Abu-Hilal, A., Badran, M., de Vaugelas, J., 1998. Distribution of trace elements in Callichirus laurae burrows and nearby sediments in the Gulf of Aqaba, Jordan (Red Sea). Marine Environ. Res. 25, 233–248.
- Acharyya, S.K., Lahiri, S., Raymahashay, B.C., Bhowmik, A., 2000. Arsenic toxicity of groundwater of the Bengal basin in India and Bangladesh: the role of Quaternary stratigraphy and Holocene sea-level fluctuation. Environ. Geol. 39, 1127–1137.
- Al-Rousan, S.A., Al-Shloul, R.N., Al-Horani, F.A., Abu-Hilal, A.H., 2007. Heavy metal contents in growth bands of Porites corals: record of anthropogenic and human developments from the Jordanian Gulf of Aqaba. Mar. Pollut. Bull. 54, 1912–1922.
- Al-Taani, A.A., Batayneh, A., El-Radaideh, N., Al-Momani, I., Rawabdeh, A., 2012. Monitoring of selenium concentrations in major springs of Yarmouk Basin, north Jordan. World Appl. Sci. J. 18, 704–714.
- Al-Taani, A.A., Batayneh, A., Mogren, S., Nazzal, Y., Ghrefat, H., Zaman, H., Elawadi, E., 2013. Groundwater quality of coastal aquifer systems in the eastern coast of the Gulf of Aqaba, Saudi Arabia. J. Appl. Sci. Agric. 8, 768–778.
- Al-Trabulsy, H.A.M., Khater, A.E.M., Habbani, F.I., 2013. Heavy elements concentrations, physiochemical characteristics and natural radionuclides levels along the Saudi coastline of the Gulf of Aqaba. Arabian J. Chem. 6, 183–
- Badran, M.I., 2001. Dissolved oxygen, chlorophyll a and nutrients: seasonal cycles in waters of the Gulf Aqaba, Red Sea. Aquatic Ecosystem & Health Manage. 4, 139–150.
- Batayneh, A., Ghrefat, H., Zaman, H., Mogren, S., Zumlot, T., Elawadi, E., Laboun, A., Qaisy, S., 2012. Assessment of the physicochemical parameters and heavy metals toxicity: application to groundwater quality in unconsolidated shallow aquifer system. Res. J. Environ. Toxicol. 6, 169–183.
- Batayneh, A., Zaman, H., Zumlot, T., Ghrefat, H., Mogren, S., Nazzal, Y., Elawadi, E., Qaisy S., Bahkaly, I., Al-Taani, A., 2013a. Hydrochemical facies and ionic ratios of the coastal groundwater aquifer of Saudi Gulf of Aqaba: implication for seawater intrusion. J. Coastal Res. (in press).
- Batayneh, A., Elawadi, E., Zaman, H., Al-Taani, A.A., Nazzal, Y., Ghrefat, H., 2013b. Environmental assessment of the Gulf of Aqaba coastal surface waters; Saudi Arabia. J. Coastal Res. 30, 283–290.
- Batayneh, A., Ghrefat, H., Zumlot, T., Elawadi, E., Mogren, S., Zaman, Z., Al-Taani A.A., Nazzal, Y., Elwaheidi, M., 2013c. Assessing of Metals and Metalloids in Surface Sediments along the Gulf of Aqaba Coast, Northwestern Saudi Arabia. J. Coastal Res. http://dx.doi.org/10.2112/JCOASTRES-D-13-00143.1.
- Bhattacharya, P., Chatterjee, D., Jacks, G., 1997. Occurrence of arsenic-contaminated groundwater in alluvial aquifers from the Delta Plain, Eastern India: options for a safe drinking water supply. Water Resour. Dev. 13, 79–92.
- Boyle, E.A., Sclater, F., Edmond, J.M., 1976. On the marine geochemistry of cadmium. Nature 263, 42–44.
- Boyle, E.A., Chapnick, S.D., Bai, X.X., Spivack, A., 1985. Trace metal enrichments in the Mediterranean Sea. Earth Planet. Sci. Lett. 7, 405–419. Broecker, W.S., Peng, T.H., 1982. Tracers in the Sea, Lamont-Doherty Geological
- Observatory. Columbia University, Palisades, New York, USA.
- Chase, Z., Paytan, A., Johnson, K.S., Street, J., Chen, Y., 2006. Input and cycling of iron in the Gulf of Aqaba, Red Sea. Global Biogeochem. Cycles 20, GB3017.
- Chase, Z., Paytan, A., Beck, A., Biller, D., Bruland, K., Measures, C., Sañudo-Wihelmey, S., 2011. Evaluating the impact of atmospheric deposition on dissolved tracemetals in the Gulf of Aqaba, Red Sea. Mar. Chem. 126, 256–268.
- Chen, Y., Paytan, A., Chase, Z., Measures, C., Beck, A.J., Sañudo-Wilhelmy, S.A., Post, A.F., 2008. Sources and fluxes of atmospheric trace elements to the Gulf of Aqaba, Red Sea. J. Geophys. Res. 113, D05306.
- Clark, M., 1986. Explanatory notes to the geologic map of the Al Bad' Quadrangle, sheet 28A, Kingdom of Saudi Arabia. Saudi Arabian Deputy Ministry for Mineral Resources. Geoscience Map Series GM-81A, C, scale 1:250,000, p. 46.
- Collier, R.W., 1985. Molybdenum in northeast Pacific Ocean. Limnol. Oceanogr. 30, 1351–1357.

- Danielsson, L.G., 1980. Cadmium, Cobalt, Copper, Iron, Lead, Nickel, and Zinc in Indian Ocean Water. Mar. Chem. 8, 199–215.
- Duce, R.A., Tindale, N.W., 1991. Atmospheric transport of iron and its deposition in the ocean. Limnol. Oceanogr. 36, 1715–1726.
- Emelyanov, E.M., Shimkus, K.M., 1986. Geochemistry and Sedimentology of the Mediterranean Sea. D. Reidel Publishing Company, Boston, USA.
- Fung, I.Y., Meyn, S.K., Tegen, I., Doney, S.C., John, J.C., Bishop, J.K.B., 2000. Iron supply and demand in the upper ocean. Global Biogeochem. Cycles 14, 281–295.
- Furness, R.W., Rainbow, P.S., 1990. Heavy Metals in the Marine Environment. CRC Press Inc., Boca Raton, Florida, USA.
- Ganor, E., Foner, H.A., 1996. The mineralogical and chemical properties and the behavior of Aeolian Saharan dust over Israel. In: Guerzone, S., Chester, R. (Eds.), The Impact of Desert Dust Across the Mediterranean. Kluwer Academic Press, pp. 163–172.
- Gates, J.B., Nicot, J.P., Scanlon, B.R., Reedy, R.C., 2011. Arsenic enrichment in unconfined sections of the southern Gulf Coast aquifer system, Texas. Appl. Geochem. 26, 421–431.
- Genin, A., Lazar, B., Brenner, S., 1995. Vertical mixing and coral death in the Red Sea following the eruption of Mount Pinatubo. Nature 377, 507–510.
- Gerges, M.A., 2002. The Red Sea and Gulf of Aden Action Plan–Facing the challenges of an ocean gateway. Ocean Coast. Manage. 45, 885–903.
- Guerzoni, S., Chester, R., Dulac, F., Herut, B., Loye-Pilot, M.D., Measures, C., Migon, C., Molinaroli, E., Moulin, C., Rossini, P., Saydam, C., Soudine, A., Ziveri, P., 1999. The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea. Prog. Oceanogr. 44, 147–190.
- Hoepner, T., 1999. A procedure for environmental impact assessment (EIA) for seawater desalination plants. Desalination 124, 1–12.
- Hoepner, T., Lattemann, S., 2002. Chemical impacts from seawater desalination plants a case study of the northern Red Sea. Desalination 152, 133–140.
- Hulings, N.C., 1979. Currents in the Jordan Gulf of Aqaba. Dirasat 6, 21–31.
- Hulings, N.C., Kirkman, H., 1982. Further observations and data on seagrasses along the Jordanian and Saudi Arabian coasts of the Gulf of Aqaba. Tethys 10, 218–220.
- Kennish, M.J., 1994. Practical Handbook of Marine Science, second ed. CRC Press Inc., London, England.
- Klinker, J., Reiss, Z., Kropach, C., Levanon, I., Harpaz, H., Halicz, E., Assaf, G., 1976.

 Observation on the circulation pattern in the Gulf of Aqaba, Red Sea. Israel J. Earth Sci. 25, 85–103.
- Kocak, M., Kubilay, N., Herut, B., Nimmo, M., 2005. Dry atmospheric fluxes of trace metals (Al, Fe, Mn, Pb, Cd, Zn, Cu) over the Levantine Basin: a refined assessment. Atmos. Environ. 39, 7330–7341.
- Landing, W.M., Bruland, K.W., 1987. The contrasting biogeochemistry of iron and manganese in the Pacific Ocean. Geochim. Cosmochim. Acta 51, 29–43.
- Laumond, F., Copin-Montegut, G., Courau, P., Nicolas, E., 1984. Cadmium, Copper and Lead in the Western Mediterranean Sea. Mar. Chem. 15, 251–261.
- Lattemann, S., Hopner, T., 2008. Environmental impact and impact assessment of seawater desalination. Desalination 220, 1–15.
- Manasrah, R., Badran, M., Lass, H.U., Fennel, W., 2004. Circulation and winter deepwater formation in the northern Red Sea. Oceanologia 46, 5–23.
- Migon, C., Nicolas, E., 1998. The trace metal recycling component in the Northwestern Mediterranean. Mar. Pollut. Bull. 36, 273–277.
- Millero, F.J., 1996. Chemical oceanography. In: Marine Science Series, 2nd ed. CRC Press Inc., New York, USA.
- Moss, S.A., 1981. Ambient water quality guidelines for boron. In: Water Quality Standards-British Columbia 2. Boron Environmental aspects, Prepared pursuant to Section 2(e) of the Environment Management Act, British Columbia Water Protection Branch.
- MSS (Marine Science Station), 1999. Environmental Appraisal of the Jordanian coast of the Gulf of Aqaba, unpublished report. Aqaba, Jordan. pp. 88.
- Murray, S.P., Hecht, A., Babcock, A., 1984. On the mean flow in the Tiran Strait in winter. J. Mar. Res. 42, 265–287.
- Paldor, N., Anati, D.A., 1979. Seasonal variation of temperature and salinity in the Gulf of Elat (Aqaba). Deep Sea Res. 26, 661–672.
- Saad, M.A.H., Kandeel, M.M., 1988. Distribution of copper, iron and manganese in the coastal Red Sea Waters in front of Al-Ghardaqa'. Proc. Indian Nat. Sci. Acad. 54, 642–652.
- Saager, P.M., Schijf, J., deBaar, H.J.W., 1993. Trace metal distributions in seawater and anoxic brines in the eastern Mediterranean Sea. Geochim. Cosmochim. Acta 57, 1419-1432
- Schaule, B.K., Patterson, C.C., 1981. Lead concentrations in the northeast Pacific: evidence for global anthropogenic perturbations. Earth Planet. Sci. Lett. 54, 97–116.
- Shriadah, M.A., Okbah, M.A., El-Deek, M.S., 2004. Trace metals in the water columns of the Red Sea and the Gulf of Aqaba, Egypt. Water, Air, Soil Pollut. 153, 115–124.
- Tankere, S.P.C., Statham, P.J., 1996. Distribution of dissolved Cd, Cu, Ni, and fn in the Adriatic Sea. Mar. Pollut. Bull. 32, 623–630.
- Tegen, I., Werner, M., Harrison, S.P., Kohfeld, K.E., 2004. Relative importance of climate and land use in determining present and future global soil dust emission. Geophys. Res. Lett. 31 (5).
- Van der Weijden, C.H., Middleburg, J.J., de Lange, G.L., van der Sloot, H.A., Hoede, D., Woittiez, J.R.W., 1990. Profiles of the redox-sensitive trace elements As, Sb, VI Mo, and U in the Tyro and Bannock Basins (eastern Mediterranean). Mar. Chem. 31, 171–186.
- Woodward, S., Roberts, D.L., Betts, R.A., 2005. A simulation of the effect of climate change-induced desertification on mineral dust aerosol. Geophys. Res. Lett. 32 (18).
- Yeats, P.A., Cambell, J.A., 1983. Nickel, copper, cadmium and zinc in the northwest Atlantic Ocean. Mar. Chem. 12, 43–56.
- Yusuf, N., 2007. Dust activity over the Jordanian Red Sea coast. ABHATH AL-YARMOUK: Basic Sci. Eng. 16, 211–227.