

Distribution and Partitioning of Heavy Metals in Subtidal Sediments of the Arabian Gulf Coast of Saudi Arabia

Ali S. Basaham

*Faculty of Marine Science, King Abdulaziz University
P.O. Box 80207, Jeddah 21589, Saudi Arabia
abasaham@kau.edu.sa*

Received: 3/3/2009

Accepted: 3/5/2009

Abstract. The surficial sediments of the Arabian Gulf coast of Saudi Arabia are a mixture consisting mainly of calcareous material mostly of marine origin and land-derived terrigenous component with high OC (average $2.1\% \pm 0.6$).

Chemical composition and the partitioning of Fe, Mn, Cu, Zn, Ni, Cr, V and Ba in operationally defined as non-residual (*i.e.* 1M HCl leachable) and residual fractions were determined in the $<63 \mu\text{m}$ fraction of the subtidal sediments. Concentrations of metals varied widely, with no evidence for total and non-residual concentrations enrichment above the background levels in the Gulf sediments.

Partitioning results showed that Fe, Cr and Ba are mainly associated with the residual component, where about 80% of their concentrations are held immobile in this fraction. For Mn, Cu, Zn, Ni and V approximately between 35 and 55 % of their concentrations are associated with the mobile non-residual fraction. Fe-Mn oxyhydroxide appears to be the main host phase for the non-residual fraction of these metals. On the other hand, carbonate materials dilute and mask the role of the major host of these metals in the sediments.

Keywords: Heavy metals; Partitioning; Speciation; Subtidal sediments; Arabian Gulf.

Introduction

The Arabian Gulf, known as Persian Gulf, the Gulf or ROPME (Regional Organization for Protection of Marine Environment) Sea Area (RSA) is a marginal sea of the Indian Ocean (Price and Robinson, 1993) (Fig.1). It is a shallow, semi-enclosed sea with very high evaporation rates and poor flushing characteristics (Sheppard, 1993). Major and trace metals are among other constituents entering the Gulf from both natural weathering processes and anthropogenic or human activities. Oil is documented as the most significant and chronic pollution problem in the Gulf environment (Price and Robinson, 1993). Many industrial complexes and municipal plants discharging wastewaters may also contribute to the pollution burdens in the Gulf environment (ROPME 2003). Because of poor flushing influence, pollution inputs undergo more limited dilution and slower dispersion in the Gulf than would occur in open marine system (de Mora *et al.*, 2004). Metals, particularly trace metals, are particle reactive elements (Stumm and Morgan, 1996). They are toxic, persistent non-degradable chemicals and can be recycled both within the sedimentary component and back to the interstitial and overlying water column; and subsequently become available or free to enter in different biogeochemical cycles. The mobility, biological availability and toxicity of trace metals generally depend on their chemical forms (Forstner and Wittmann, 1983). Sediments can play a pivotal role in regulation of metals concentrations in aquatic environments. Metals in sediments have been introduced in solution and as part of, or in association with, solid inorganic and organic particulate matter.

Partition of the total metal concentrations into non-residual and residual fractions or phases is used in sedimentary geochemistry to provide information regarding the binding sites of metals as well as their source and pathways by which they have been transported to the aquatic environment. The non-residual also known as non-lithogenous or non-detrital fraction is considered to be mobile or environmentally reactive fraction in respect of geological and chemical processes. It represents metals that are brought as dissolved or colloidal material, and adsorbed to or precipitated within sediments among different host phases *viz.*, loosely and exchangeable, carbonate, reducible (iron and manganese) and oxidizable (organic-sulphide). In contrast, the residual also called lithogenous or detrital fraction is usually considered to be immobile or

environmentally unreactive. It presents metals that are transported in solid form. The residual metals are unlikely to be released into solution through dissolution and remain fixed in sediments within matrix of silicates and other detrital minerals (*e.g.* Agemian and Chau, 1976; Chester and Voutsinou, 1981; Loring 1984; Abaychi and Douabul, 1986; Loring and Rantala, 1988; and Jain, 2004). Therefore, sediments have been widely used as indicators to uncover the history of various influences on marine systems. The distribution of metals in different geochemical phases of sediments have been used for different purposes in geochemical and environmental studies, *e.g.* to trace diagenetic reactions (El Ghobary and Latouche, 1982), mineral deposits (Land *et al.*, 2002), palaeoenvironment (Rutten and De Lange, 2003) and pollution assessment (Chester and Voutsinou, 1981).

The Gulf sediments consist principally of carbonate largely intrabasinal in origin and terrigenous materials of pre-existing rocks (Al-Ghadban *et al.*, 1994; Basaham and El-Sayed, 1998 and Maeda *et al.*, 1998). The setting of Saudi Arabia in the Arabian Peninsula with hot arid desert climate, no river runoff and no significant rainfall most of the year, influences the sedimentation process. In the absence of uncontrolled and/or unaltered natural effluents, atmospheric input plays a crucial role in the transport of terrigenous particulate matter largely from the adjacent desert hinterland (Abdul Azis *et al.*, 2000) with associated, adsorbed or coprecipitated, chemical constituents. Also oil spills and industrial and municipal wastewaters discharging to the shallow Saudi coastal area may constitute a source of metals to the area (ROPME, 2003).

Previous studies carried out on the sediments of the Saudi Gulf coast focused on the determination of the total metal content in the bulk sediments (Sadiq and Zaidi, 1985; Al-Arfaj and Alam, 1993 and Basaham and Al-Lihaibi, 1993). These studies are generally confounded by the highly variable grain size composition; in this context comparison of the absolute values is generally misleading. This study presents data on the concentrations and the chemical forms of Fe, Mn, Cu, Zn, Ni, V, Cr, and Ba in the mud size fraction of surficial sediments collected from, ecologically sensitive, subtidal areas heavily impacted by the Arabian Gulf 1991 war-related oil spill. It provides information into the sources, transport processes and help identify geochemical processes controlling metal concentrations in the mud fraction of sediment in the Saudi coast and also could be useful in the assessment of sediment quality in the area

because the significance of mud fraction in the distribution of metals as well as contaminants.

Materials and Methods

Nineteen samples of surface sediments collected from the nearshore area of the Saudi Arabian coast of the Gulf during the 1992 R/V *Mt. Mitchell* Cruise (Leg II, 16 March-6 April), were analyzed in this study. Sediments were collected from the subtidal zone of three oil impacted shallow areas (Ras Tanaqib, Al-Masallamiyah and Dawhat Al-Dafi) and kept frozen for further analysis (Fig. 1). In order to minimize interference that may result from grain size variability, only the mud size fraction ($<63\ \mu\text{m}$) was considered in this study. Besides neutralizing the grain size effect, this approach largely reduces the dilution by chemically inert carbonate grains that primarily exist in substantial proportion in the coarse fraction of the Gulf sediments (Basaham and El-Sayed, 1998 and Maeda *et al.*, 1998). The mud fraction was separated by wet sieving through $63\ \mu\text{m}$ sieve using nanopure water, oven dried at 40°C to constant weight, ground in agate mortar and used for geochemical analysis.

Metal contents in the mud fraction of sediments were determined using two stage chemical extraction technique to differentiate between two operationally defined host fractions: (1) Non-residual fraction, *i.e.* the portion of metal incorporated into sediments from solution and (2) residual fraction, *i.e.* the metal bound within silicates and other detrital minerals lattice (Agemian and Chau, 1976; and Chester and Voutsinou, 1981).

The non-residual fraction of metals were extracted by treating 1 g of each representative sample with 20 ml of 1M HCl, and agitation in a mechanical shaker for 4 h at room temperature. This technique is supposed to remove both inorganic and organic loosely bound metals in coastal and estuarine sediments without or with little effect on lithogenous silicate material (Agemian and Chau, 1976; and Chester and Voutsinou, 1981). For the determination of the residual fraction of metals, the 1M HCl solid insoluble residue were recovered, placed in capped Teflon cups and completely digested with concentrated HNO_3/HF acids at 120°C (Basaham and El-Sayed, 1998). Reagent blanks were determined using the same analytical protocol. The final extracts were

analyzed for Fe, Mn, Cu, Zn, Ni, V, Cr, and Ba by atomic absorption spectrophotometry (Varian SpectraAAS 250 plus).

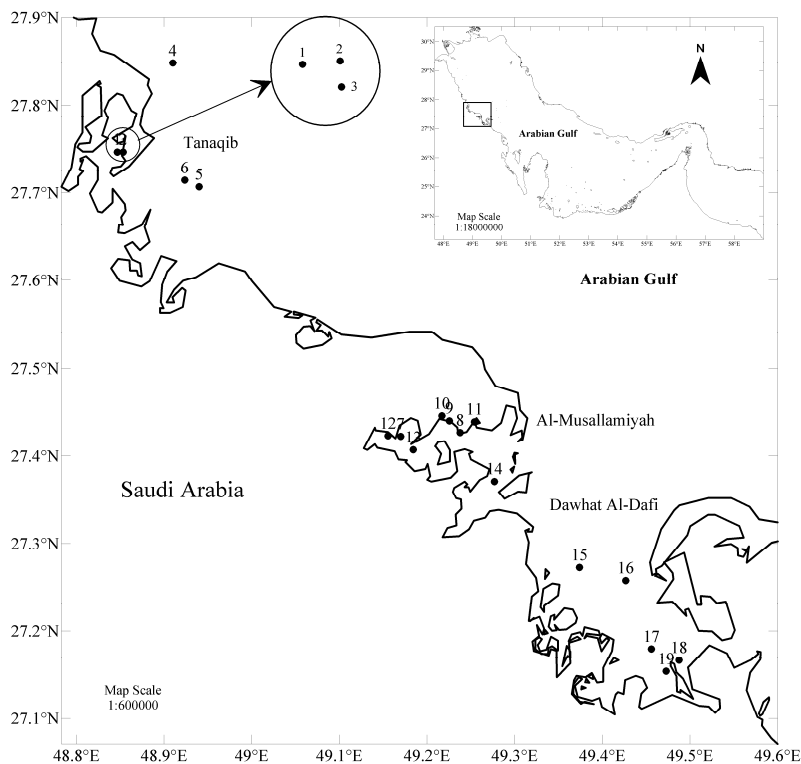


Fig. 1. Map showing the study area and sampling stations in the Saudi Gulf coastal area.

The weight loss resulting from the 1M HCl dissolution stage included calcium carbonate minerals, aragonite and calcite, and was considered equivalent to the CaCO_3 of the sediment and expressed in % (Al-Ghadban *et al.*, 1994; and Basaham and El Sayed, 1998). Organic carbon content (OC) was determined using wet dichromate-sulphuric acid oxidation method modified from the method described by Le Core (1983). This method is based on the removal of carbonate and chloride ions in powdered sediment sample with phosphoric acid at 110°C , then oxidation of organic matter in the sample with 1N potassium dichromate acidified with concentrated sulphuric acid, followed by titration of the sample mixture with 0.1N ferrous ammonium sulphate solution in the presence of ferroin as an indicator.

Results and Discussion

Carbonate and Organic Carbon

The average concentration of CaCO_3 in the ensemble of the analyzed samples ($n = 19$) from Ras Tanaqib, Al-Masallamiyah and Dawhat Al-Dafi is $56\% \pm 17$; concentrations varied from 17 to 88% (Table 1). Inter-site variability showed that sediments of Ras Tanaqib have the lowest carbonate content (average 45%) compared to 62% at Al-Masallamiyah and 57% at Dawhat Al-Dafi. This variation in CaCO_3 content is probably due to the nature and the extents to which sediment source materials are mixed. Sediment components consist mainly of carbonate mostly of marine biogenic origin and land-derived terrigenous materials. The generally high, but variable CaCO_3 content in the Gulf sediments appears to be behind the low abundance of terrigenous minerals in agreement with previous studies (Al-Ghadban *et al.*, 1994; Basaham and El Sayed, 1998 and Maeda *et al.*, 1998).

Organic carbon (OC) content varied from 1.1 to 3.2% with an average of $2.1\% \pm 0.6$. The average OC contents are comparable in sediments from Ras Tanaqib and Al-Masallamiyah; however sediments from Dawhat Al-Dafi showed slightly lower OC concentrations (Table 1). The intertidal and subtidal habitats of Ras Tanaqib, Al-Masallamiyah and Dawhat Al-Dafi were affected by the 1991 war-related Kuwait oil spill (Price and Robinson, 1993; and Jones *et al.*, 1998). Oil pollution may increase OC input to the sediments. The OC input into the Arabian Gulf region belongs to several sources of different nature. The most important of which is the organic matter of petroleum origin and that resulting from the natural biological activity, especially benthic communities; in the nearshore area other sources such as the disposal of municipal and industrial wastewater should also be considered (Al-Ghadban *et al.*, 1994). Hartmann *et al.* (1971) pointed out that OC in the Gulf sediments generally lies in the range from 0.5 to 1%, or at the most 2%. However, Al-Ghadban *et al.* (1994) showed that organic carbon (TOC) content in the Gulf sediments vary between 0.46 and 2.8%, and exceeding the Gulf natural background level (average $0.7\% \pm 0.3$). The OC concentration in about 43% of the studied samples lies within the range of natural background given by Hartmann *et al.* (1971). The rest of the samples appear therefore slightly enriched in OC with respect to the

same background level. OC concentration is generally dependent on sediment grain size distribution (Poppe and Commeau, 1992). It is generally adsorbed onto and hence correlates well with the fine mud fraction due to its relatively high surface area (Buckley and Winters, 1992; and El Sayed *et al.*, 2002). The war-related oil residue remains partly valid as a probable source for the excess (>2%) OC trapped in the subtidal sediments throughout the Saudi Arabia coastal environment. However, the balance between accumulation and degradation rate of the organic matter is probably the key factors which control the concentration of OC in the Gulf sediments.

Total Metals Concentration in Sediments

Total metal concentrations (*i.e.* the summation of the concentrations of operationally defined non-residual and residual fractions) of Fe, Mn, Cu, Zn, Ni, V, Cr, and Ba varied widely (Table 1). The average total metal concentration of Mn, Ni, Cr, V and Ba in the subtidal sediments showed a north-south gradual decreasing trend from Ras Tanaqib, to Al-Masallamiyah and Dawhat Al-Dafi (Table 1, Fig.1). Other metals Fe, Cu and Zn showed their lowest average concentration in Al-Masallamiyah sediments. Regardless of textural uniformity of sediments used in this study, wide variations are still observed in the total metal concentrations. The differences in sediment characteristics may affect the concentration of metals. The same observation has been shown in the mud fraction of unpolluted sediments in the inner part of the Gulf (Maeda *et al.*, 1998). These authors attributed the variability in chemical composition to variations in textural composition, and the component composition of the host sediment. The mineral composition of the mud fraction of the Gulf sediment is a mixture mainly of carbonate, aluminosilicate, and ferromagnesian minerals (Maeda *et al.*, 1998).

Fe is a geochemical conservative metal that was used to correct for variations related to non-homogeneity in granulometric and mineralogy of the bulk sediment on trace metals concentrations (*e.g.* Tam and Yao, 1998; and Munoz-Barbosa *et al.*, 2004). Fe largely resides in lithogenous aluminosilicates and other detrital minerals and its concentration has been shown to be correlated with trace metals in the Gulf sediments (Basaham and El-Sayed, 1998 and Maeda *et al.*, 1998). The concentrations of Mn, Cu, Zn, Ni, Cr, V and Ba were normalized to

Fe to identify sites of enrichment and depletion and to determine a reference baseline (*i.e.* natural) concentration in the study area. The regression plots showed that Ni, Cr, V and Ba have significant positive correlations with Fe. All the samples are within the 95% confidence level, which represents the natural variability of metals concentrations in mud fraction; r-values ranged between 0.75-0.90 (Fig.2). For the other metals some samples showed a relative enrichment being out and above the 95 % confidence level (for Mn sample19, Cu sample 18 and Zn samples 3&18). The outliers were removed, and the remaining data points were used to regenerate a new regression to obtain the baseline concentrations; r-values ranged between 0.64-0.78 (Fig. 2). It can be concluded that these metals compose a single pool and belong to a unique origin.

Sediment Quality and Extent of Metal Enrichment

The possible enrichment of metals in the mud fraction of the sediments was evaluated in terms of both total concentration and the concentration of the non-residual (1M HCl leachable) fraction that reflects the water quality and is usually used as a proxy indicator of metal enrichment or pollution in sediment (Chester and Voutsinou, 1981). The averages of total metal concentrations (Table 1) are compiled with those reported for texturally equivalent unpolluted surface sediments from the Gulf region (Abaychi and Douabul, 1986; Al-Abdali *et al.*, 1996 and Maeda *et al.*, 1998) for comparative purpose.

It appears from the results of this study that Mn, Cu, Zn, Ni, Cr and V are generally lower, while Fe is within the natural baseline concentrations (Table 1). Comparison for Ba is not possible due to absence of data. There is, therefore, no indication of metal enrichment from natural geogenic and anthropogenic sources in the subtidal sediments and the concentrations are comparable to those of the baseline values of the Gulf sediments. This agrees with the earlier reports indicating that the 1991 Gulf oil pollution and the human activities had a minimal contribution to the absolute total concentrations of the metals in sediments (Fowler *et al.*, 1993; Basaham and Al-Lihaibi, 1993; Al-Abdali *et al.*, 1996; Basaham and El-Sayed, 1998 and Maeda *et al.*, 1998).

Table 1. The average and range of total metal concentrations in the mud fraction of the Arabian Gulf.

Area in the Gulf	CaCO ₃	OC %	Fe mg/g	Mn	Cu	Zn	Ni µg/g	Cr	V	Ba	Reference
Ras Tanaqib	45 (22-60)	2.2 (1.3-3.2)	10.8 (8.3-10.3)	187 (162-218)	19.0 (18.4-21.2)	32.5 (26.8-38.4)	57.1 (40.8-68.8)	83.7 (52-98)	45.7 (36-56.4)	131.6 (62.4-186)	This study
Al-Masallamiyah	62 (57-64)	2.1 (1.1-2.8)	5.6 (8.8-10.5)	169 (145-195)	12.7 (10.4-15.6)	23.6 (20-27.2)	49.5 (42-56.8)	67.8 (46.4-82.8)	36.2 (27.2-40.8)	72 (58-84.8)	This study
Dawhat Al-Dafi	57 (17-88)	1.8 (1.3-2.8)	7.1 (6.3-9.5)	159 (136-209)	15.2 (10-25.2)	27.9 (16.8-45.2)	41.2 (29.2-52.8)	43.9 (37.6-80)	33.1 (30-42.4)	41.8 (28-60)	This study
Average subtidal (western part)	56	2.1	9.40	171	15.4	25.3	50.7	69.2	39.1	84.1	This study
Average Northwest (coastal part)			5.87	1158	25	33	456	88	166		Abaychi and Douabul, 1986
Average Offshore (Inner part)			6.30	354	18	42			47		Maeda <i>et al.</i> , 1998
Natural background levels†			10.0 - 20.0	300 - 600	15 - 30	30 - 60	70 - 80		20 - 30		Al-Abdali <i>et al.</i> , 1996

† estimated upper limits for the Gulf marine environment

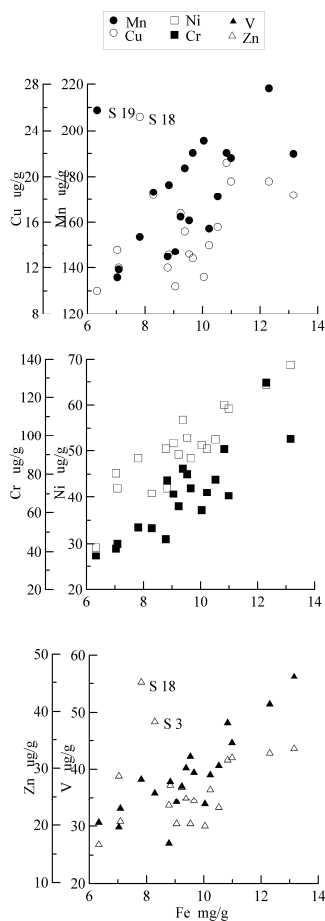


Fig. 2. Relationship between total metals concentrations.

On the other hand, concentrations of metals in the non-residual fraction were compared to the concentrations determined by Abaychi and Douabul (1986) in the mud fraction of sediments from the northwestern part of the Gulf (Table 2). Composition of pre 1991 oil spill non-lithogenous fraction reported for unpolluted sediments (Abaychi and Douabul, 1986) provides an overview about metals that are generally introduced by river runoff in this arid region, and subsequently removed from the water through adsorption onto suspended particulate matter and precipitated within authigenic and biogenic phases settled in sediments. It appears from the concentrations of metals in the non-residual fraction (Table 2) that, excepting Zn, there is no evidence of metal anomalies had affected the average metals concentrations in the study area. The lower

concentrations in the study area are most probably the result of higher carbonate content. Fluvial sediment dominates in the northwestern part of the Gulf. This appears in accordance with the statement that the fluvial run-off is the principal transport pathway that supplies dissolved and particulate material derived from the continental crust to the oceans when compared to the atmospheric transport (Chester, 2000). The average non-residual Zn is $10\mu\text{g g}^{-1}$ in subtidal sediments of the present study, which receive no river input, compared to $3\mu\text{g g}^{-1}$ in northwestern part of the Gulf. It is difficult to relate precisely this discrepancy to natural processes or to local anthropogenic activities. The possible pathways that influence non-residual metal fraction in coastal sediments include dissolution of mineral particles of the source rocks and sediments, ions released during diagenetic processes and/ or discharge into dissolved form from anthropogenic sources (Loring, 1984).

Metal Partitioning

Range and averages of metal concentrations in each of the operationally defined non-residual and residual fractions in the subtidal areas of Ras Tanaqib, Al-Masallamiyah and Dawhat Al-Dafi area are shown in Table 3. The overall average partitioning of the metals between the non-residual and residual fractions is presented in Table 2 and the percentage distribution is illustrated graphically in Fig. 3. Metals show differences in partitioning trends that would induce differences in mobility or reactivity.

The average residual Fe, Mn, Cu, Zn, Ni, Cr, V and Ba concentrations show gradual decrease from north to south in the order of Ras Tanaqib, Al-asallamiyah and Dawhat Al-Dafi (Table 3). The decrease in residual metal is indicative of geographic changes in the supply of terrigenous components in the area that is influenced by desert atmospheric input and high CaCO_3 sedimentation.

The partitioning data indicate that Fe, Cr and Ba have a common feature; they have intense detrital or terrigenous character with $\geq 80\%$ of their average total concentration constantly contributed from the residual fraction in the three areas (Table 3). The overall distribution trends (Table 2 and Fig. 3) means that Fe, Cr and Ba are largely chemically inert in the Saudi Gulf coastal sediments. They are principally transported and deposited within the terrestrially derived detrital minerals. On the other hand, the fractionation patterns for Zn, V and Ni

have similar distribution in the three areas (Table 3) with overall averages of 59 to 66% are locked in the residual fraction (Table 2 and Fig. 3). Mn and Cu show variable proportions and in most cases < 50% of their average concentration are held in the residual fraction in the three areas (Table 3). However, the overall distribution of these metals in residual fraction (Table 2 and Fig. 3) suggests the decreasing importance of terrigenous signal in the study area compared to that for Fe, Cr and Ba. Concentrations of metals in the residual fraction are largely controlled by the minerals compositions and grain size variations of the sediments. In nearshore area, terrigenous materials incorporate a wide variety of minerals of different chemical composition. The terrigenous components in the Saudi Gulf coastal area are presumably determined notably by the deposition of wind-blown materials. The overall average concentrations of residual metals in sediments of this study (Table 2) are remarkably lower for Ni, V, Mn, Cu and Zn whereas Fe is higher and Cr is approximately equal, relative to the sediments of the northwestern part of the Gulf influenced largely by river input (Abaychi and Douabul, 1986). This amplifies the differences in terrigenous distribution on the regional scale. Therefore, it is most likely that under normal oxic conditions the local and regional variations in metals concentrations in residual fraction is mirroring the changes in the strength of land-derived contribution and/or variations in the mineralogical composition as well as grain size composition within the mud fraction of the sediments.

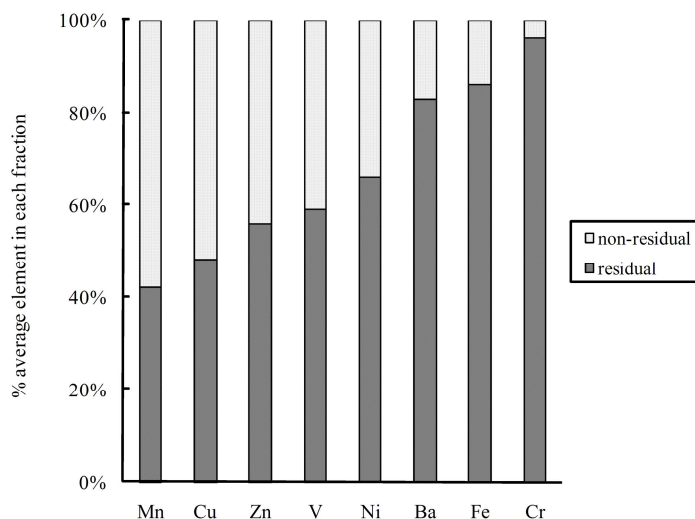


Fig. 3. Partitioning of elements between the residual and non-residual fractions.

Table 2. The average and range of metal concentration in the non-residual and residual fractions in the mud fraction of the Arabian Gulf sediments ($\mu\text{g/g}$), for Fe (mg/g).

Area in the Gulf	Fraction	Fe	Mn	Cu	Zn	Ni	Cr	V	Ba	Reference
Subtidal (western part)	Non-residual	1.33	96	7	10	17	3	16	14	This study
% contribution		(0.39-2.10)	(66-169)	(2.8-16.0)	(4.8-30.8)	(12.4-21.2)	(1.2-4.8)	(11.2-23.2)	(4.4-36.4)	
Northwest (coastal part)		14	56	47	38	34	4	41	17	Abaychi and Douabul, 1986
% contribution		1.82	755	7	3	91	6	22		
		(0.85-2.44)	(590-1090)	(4.4-12.4)	(2.0-6.4)	(66-119)	(5.2-15.2)	(16-26)		
		31	65	28	10	20	7	13		
Subtidal (western part)	Residual	8.09	75	8	16	33	66	23	70	This study
% contribution		(5.08-11.57)	(40-109)	(4.8-10.8)	(8.8-22.4)	(16-52.4)	(35.2-125.2)	(11.2-38.4)	(19.2-162)	
Northwest (coastal part)		86	44	53	62	66	96	59	83	Abaychi and Douabul, 1986
% contribution		4.04	403	18	30	365	82	144		
		69	35	72	90	80	93	87		

Examination of the results (Table 2 and Fig. 3) permits the arrangement of the metals according to their relative decrease in non-terrigenous (*i.e.* non-residual) character in the order of $Mn > Cu > Zn > V > Ni > Ba > Fe > Cr$. Two groups of metals could be characterized on the basis of their geochemical mobility/reactivity. The first group includes Fe, Cr and Ba which are low mobile elements. Their dominant association in the unreactive residual fraction leads to low storage in the reactive non-residual fraction that varies between 4 and 17% (Table 2, Fig. 3). This may indicate that diagenetic mobilization of these metals may not be a common process in the surficial subtidal sediments. The non-residual concentrations of the low mobile elements Fe, Cr and Ba follow the trend of the residual fraction, decreasing in the three areas in the order of Ras Tanaqib, Al-Masallamiyah and Dawhat Al-Dafi (Table 3). The second group includes Mn, Cu, Zn, Ni and V which are, relatively, strongly mobile. They are partly incorporated from solution and trapped in sediment components at the oxic surface layer. Their availability in the reactive non-residual fraction varies between 32 to 67 % in the three areas (Table 3); with overall averages contribution ranging from about 35 to 55 % (Table 2 and Fig. 3). Thus, unlike Fe, Cr and Ba, the distribution of Mn, Cu, Zn, Ni and V is really not regulated by the primary minerals lattice structure of deposited sediments. They generally have their lowest concentrations in Al-Masallamiyah area (Table 3) that shows the highest carbonate content (average $CaCO_3 = 62\%$). In contrast, higher concentrations of non-residual Mn, Cu, Zn, Ni and V are found in sediments from Ras Tanaqib and Dawhat Al-Dafi characterized by relatively lower $CaCO_3$ (Table 1). The observed trend highlights the dilution effect of carbonate materials on other non-carbonate components of the sediments.

The minor role of carbonate fraction as metals carrier is reflected by the negative correlations between the non-residual Fe, Mn, Cu, Zn, Ni, Cr, V and Ba with $CaCO_3$ (Table 4). This conclusion agrees with the previous studies in the Gulf sediments which stated that carbonate materials, due to their small specific surface area, act as diluents and masks metals input from other sedimentary components (Basaham and El-Sayed, 1998 and Maeda *et al.*, 1998).

Table 3. The average and range of metal partitioning in the non-residual and residual fractions in the mud fraction of the Saudi Gulf sediments ($\mu\text{g/g}$), for Fe (mg/g).

Area in the Gulf	Fraction	Fe	Mn	Cu	Zn	Ni	Cr	V	Ba
Ras Tanaqib	Non-residual	1.40 (0.39 - 2.10)	103 (95 - 113)	10 (7.6 - 13.6)	15 (10.8 - 25.6)	18 (15.6 - 20)	4 (2.4 - 4.8)	18 (13.2 - 23.2)	23 (15.2 - 36.4)
Average % contribution		14	57	53	45	32	5	40	20
Al-Masallamiyah		1.38	95	5	8	16	3	14	11
Average % contribution		(0.95 - 2.07)	(66 - 122)	(2.8 - 6.8)	(4.8 - 13.6)	(12.4 - 18)	(1.2 - 4)	(11.2 - 16)	(5.6 - 13.2)
Dawhat Al-Dafi		1.22	108	9	15	18	3	17	8
Average % contribution		(1.10 - 1.29)	(81 - 169)	(5.2 - 16)	(8 - 30.8)	(13.2 - 21.2)	(2.4 - 3.2)	(16.8 - 18.8)	(4.4 - 11.2)
		17	67	56	46	41	7	50	21
Ras Tanaqib	Residual	9.39 (6.18 - 11.57)	84 (60 - 109)	9 (4.8 - 10.8)	18 (12.8 - 22.4)	39 (23.6 - 52.4)	80 (47.2 - 125.2)	28 (15.2 - 38.4)	109 (37.2 - 162)
Average % contribution		86	53	47	55	68	95	60	80
Al-Masallamiyah		8.2	74	7	15	33	65	22	61
Average % contribution		(7.57 - 9.49)	(58 - 88)	(6.4 - 8.8)	(13.6 - 17.2)	(29.6 - 39.2)	(42.4 - 74.4)	(11.2 - 26.4)	(46.4 - 71.6)
Dawhat Al-Dafi		86	45	57	65	67	96	59	84
Average % contribution		(5.08 - 8.54)	(40 - 78)	(4.8 - 9.2)	(8.8 - 16.4)	(16 - 34.4)	(35.2 - 77.2)	(13.2 - 26.4)	(19.2 - 50)
		83	36	47	54	59	94	50	80

However, it is worthy indicating that in the Gulf shallow environment the penetration of oxygen-rich seawater to the bottom floor insures the prevalence of oxic conditions in the surface sediments (Seibold and Berger, 1982). Clay minerals, Fe-Mn oxides/hydroxides and organic matter, are the most important metal host phases under oxidizing conditions (Turner *et al.*, 2004). On a carbonate-free basis, the dilution effect of carbonate materials is neutralized and the importance the association of the elements with the redox sensitive Mn, Fe is clearly evidenced (Table 4). The concentration of Mn (average 56%) relative to Fe (average 14%) in non-residual fraction (Fig. 3) reinforces the redox effect in sediments. In fact, diagenetic reactions, which take place during organic matter mineralization, are of prime importance in precipitation or dissolution of Fe and Mn compounds at sediment-water interface and within sediment column (Basaham, 1998 and Chester, 2000). In oxic environment Mn and Fe are intimately governed by the formation of mixed oxides and hydroxides. Under suboxic low reducing non-sulphadic conditions near the surface, oxides and hydroxides of Mn are reduced faster than Fe. Tidal cycles and to a lesser extent biological processes play important role in changing continually the redox conditions of the superficial sediments (El Ghobary and Latouche, 1982).

Table 4. Correlation matrix of the constituents in the non-residual fraction of the Saudi Gulf sediments.

Metal	raw data				carbonate-free basis		
	CaCO ₃	OC	Fe	Mn	OC	Fe	Mn
Cu	-0.61	0.11	0.15	0.04	-0.02	0.80	0.72
Zn	-0.54	0.01	0.25	0.06	-0.22	0.75	0.63
Ni	-0.35	0.48	0.11	-0.32	-0.25	0.91	0.88
Cr	-0.15	0.30	0.47	0.07	-0.23	0.91	0.86
V	-0.19	0.01	0.41	0.20	-0.35	0.91	0.93
Ba	-0.38	0.33	0.21	0.03	-0.14	0.85	0.65

The negative correlation of OC with all examined metals (Table 4) suggests that OC does not have important role in the binding of these metals under oxic conditions at the sediment surface. On the other hand, the strong positive relationships between non-residual Fe and Mn with the Cu, Zn, Ni, Cr, V and Ba (Table 4 and Fig. 4) implies that these metals are mainly incorporated in or adsorbed on the same mineral particles. The redox conditions certainly control the chemical composition of surficial sediments and promote precipitation of Fe and Mn oxides and hydroxides that have a scavenging effect and act to coprecipitate or adsorb a variety of dissolved heavy metals. Therefore, non-residual Cu, Zn, Ni, Cr, V and Ba are most likely to be influenced by the strong association with Fe-Mn oxides/ hydroxides phase in the oxidizing zone of surface sediments.

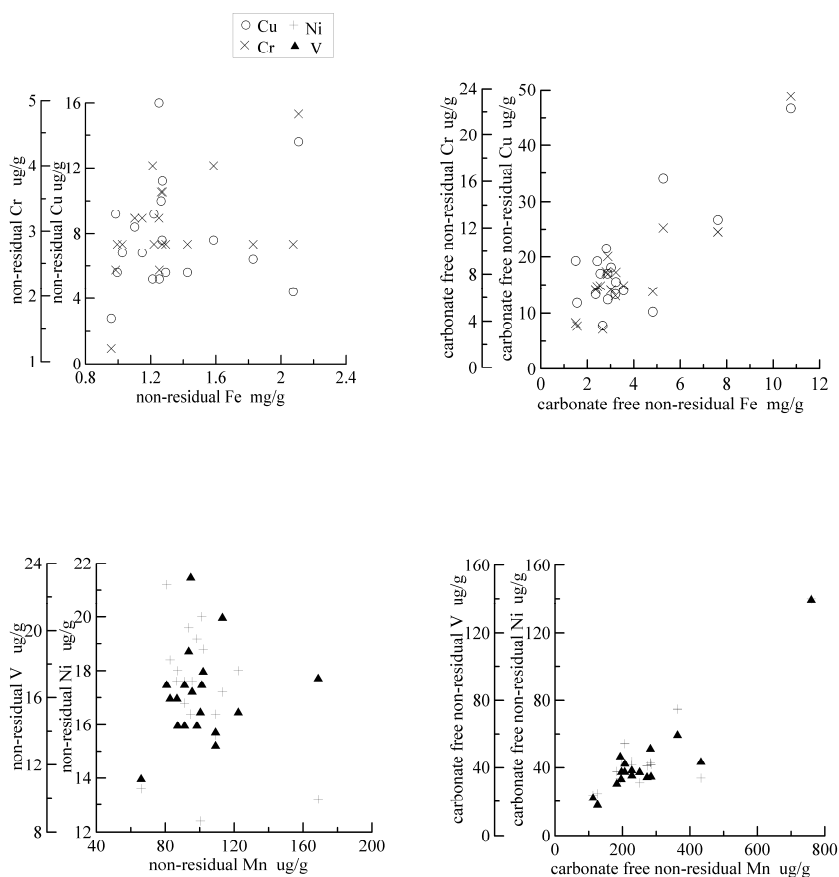


Fig. 4. Selected relationships between metals in the non-residual fraction.

Conclusions

The mud fraction of surficial sediments collected from the subtidal areas of Ras Tanaqib, Al-Masallamiyah and Dawhat Al-Dafi are characterized by a mixture of carbonate largely intrabasinal in origin and terrigenous materials of pre-existing rocks. It will be worth mentioning that this is the area which was heavily affected by the 1991 war related Kuwait oil spill.

The results obtained indicate that CaCO_3 content in sediments are generally controlled by the mixing of carbonate and terrigenous components. The high CaCO_3 content is a result of low abundance of terrigenous minerals. The OC concentrations vary (1 to 3.2%) in sediments and in the majority (57%) of the samples exceeds the natural background level defined for the Gulf sediments (0.5 to 1 % or at most 2%).

Total metal concentrations of Fe, Mn, Cu, Zn, Ni, V, Cr and Ba in sediments showed a wide range of variations probably due to differences in texture, and composition of the host sediment. The concentrations of metals in general indicate a common source and represent the natural variability in the mud fraction.

The distribution of metals in non-residual and residual fractions showed differences in partitioning signatures that induce changes due to mobility. Fe, Cr and Ba are mainly terrigenous in character with approximately 80% of their concentrations in sediments are fixed in inert positions within the residual fraction. The elements Mn, Cu, Zn, Ni and V have between ~ 35 and 55 % of their average concentrations supplied from solution and removed into the mobile non-residual fraction. Fe-Mn oxyhydroxides form seem to be the main carrier phase for the non-residual fraction of these metals, whereas, carbonate materials dilute and mask the role of the major host of these metals in the oxic sediments. The data suggest that total and non-residual concentration of Fe, Mn, Cu, Ni, V, Cr, and Ba in subtidal sediments remain comparable with the natural baseline levels in the Gulf sediments.

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توزيع وتقسيم العناصر الثقيلة في رواسب منطقة أدنى المد لساحل الخليج العربي، المملكة العربية السعودية

علي سعيد بسحم

كلية علوم البحار - جامعة الملك عبدالعزيز،

جدة - المملكة العربية السعودية

abasaham@kau.edu.sa

المستخلص. تتكون الرواسب السطحية لساحل الخليج العربي للمملكة العربية السعودية من خليط تكثر فيه المكونات الكلزية ذات الأصل البحري والفتاتية القارية المنقولة، وقد وجد أن هذه الرواسب تحتوي على نسبة عالية من الكربون العضوي (المتوسط 2.1 ± 0.6).

تمت دراسة التركيب الكيميائي وتقسيم عناصر الحديد، والمنجنيز، والنحاس، والزنك، والنيكل، والكروم، والفناديوم، والباريوم في أجزاء معرفة عملياً بالجزء الذائب في ١ عياري حمض الهيدروكلوريك، والجزء المتبقي لحبيبات الرواسب الأقل من ٦٣ ميكرون في منطقة أدنى المد. بينت النتائج وجود اختلاف واسع في تراكيز العناصر، ولكن من دون تواجد زيادة في التركيز الكلي وفي تركيز الجزء الذائب لتلك العناصر فوق المستويات القياسية المرجعية لرواسب الخليج.

أوضحت نتائج تقسيم العناصر بين الجزء الذائب والجزء المتبقي من الرواسب، أن حوالي ٨٠٪ من تركيز الحديد، والكروم، والباريوم توجد مستقرة في الجزء المتبقي، في حين أن ما بين ٣٥

الى ٥٥٪ تقريباً من تركيز المنجنيز، والنحاس، والزنك، والنيكل، والفناديوم يعتبر نشطاً ومتحركاً بيئياً، ويكون محمولاً بصحبة الجزء الذائب. ويبدو أن أكاسيد وهيدروكسيدات الحديد والمنجنيز هي الحاضن الرئيسي للعناصر المصاحبة للجزء الذائب من الرواسب. بينما تعمل مواد الكربونات على تخفيف تراكيز العناصر، وعلى إخفاء دور الحاضن الرئيسي لها في الجزء الذائب من الرواسب.