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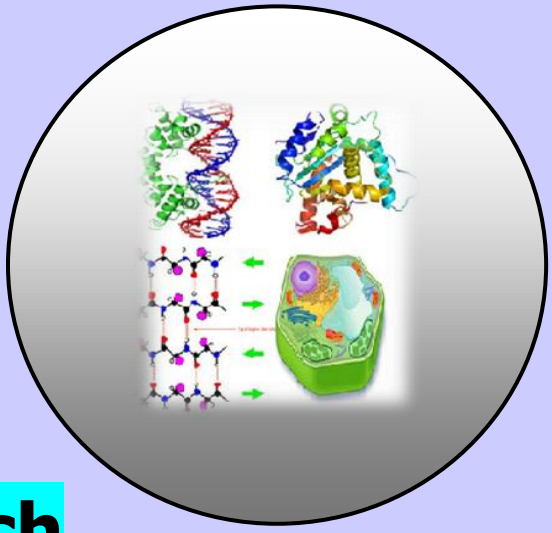

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Comparative Study on Concentration of Heavy Metals in Sediments and Fish, Jazan Area, Saudi Arabia

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ABSTRACT

Jazan region is the third fast growing area in Saudi Arabia. This study was carried out to assess the concentrations of various heavy metals in Jazan area specially Jazan and Beesh cities. Sediment geochemistry of the Jazan region coast was studied. The results showed that Jazan city sediments have the higher concentrations of most of heavy metals than Beesh city mainly from anthropogenic sources. However, a distinguishing anthropogenic heavy metal signature is obviously observable close to wastewater outlets, especially enhanced Zn and Hg at Jazan city. They may be derived from sources like sewage. Ni and Cr showed relatively high concentrations resulted by weathering. On the other hand, agricultural waste and flash flood coming from valleys bring organic matter to the coastal areas. Flash flood flow may cause anthropogenic enhancement of heavy metals in the shore sediments.

Key words: Heavy metals, Anthropogenic, Weathering and Jazan Region.

INTRODUCTION

Many Substances are released to the environment by human activities, some of which can affect human, plant and animals. Reducing pollution to normal level is a critical challenge, which in recent years (Dimov et al. 2004). The heavy metal contamination in sediments of aquatic system, from natural or anthropogenic origin, represents one of the most important coastal environment problems (Ridgway and Shimmield 2002). Heavy metal concentrations in coastal environment have been rapidly increasing due to human activities. Coastal environments are subjected to metal contamination throughout various inputs such as natural, industrial, and urban sources. Metals released into coastal environments rapidly sink to the bottom and accumulate in sediments (Cukrov et al. 2011; Ra et al. 2011). The main sources of the anthropogenic metal load in the sea sediments may be terrestrial or from mining and industrial developments (Sundaray et al. 2011).

The Saudi Arabia coastline extends for about 1840 km (79 %) of the Red Sea eastern coast. Many industrial activities were conducted in Saudi Arabia in the last few years (Badr et al. 2009; Pan et al. 2011). The Saudi coastal environments have been affected by extensive exploitation and metal load. The original sources of coastal pollution are oil pipeline leaks and domestic sewage from coastal cities (Al-Thukair et al. 2007). Globally, oils, tyres and plastic materials were effect on concentrations of heavy metals elements (e.g. East China Sea, Lin et al. 2002; Hong Kong, Li et al. 2001; Europe, Austria, Mueller et al. 1983; Spain, Cobelo-Garcia and Prego 2004; India, Balachandran et al 2005; Callender 2003).

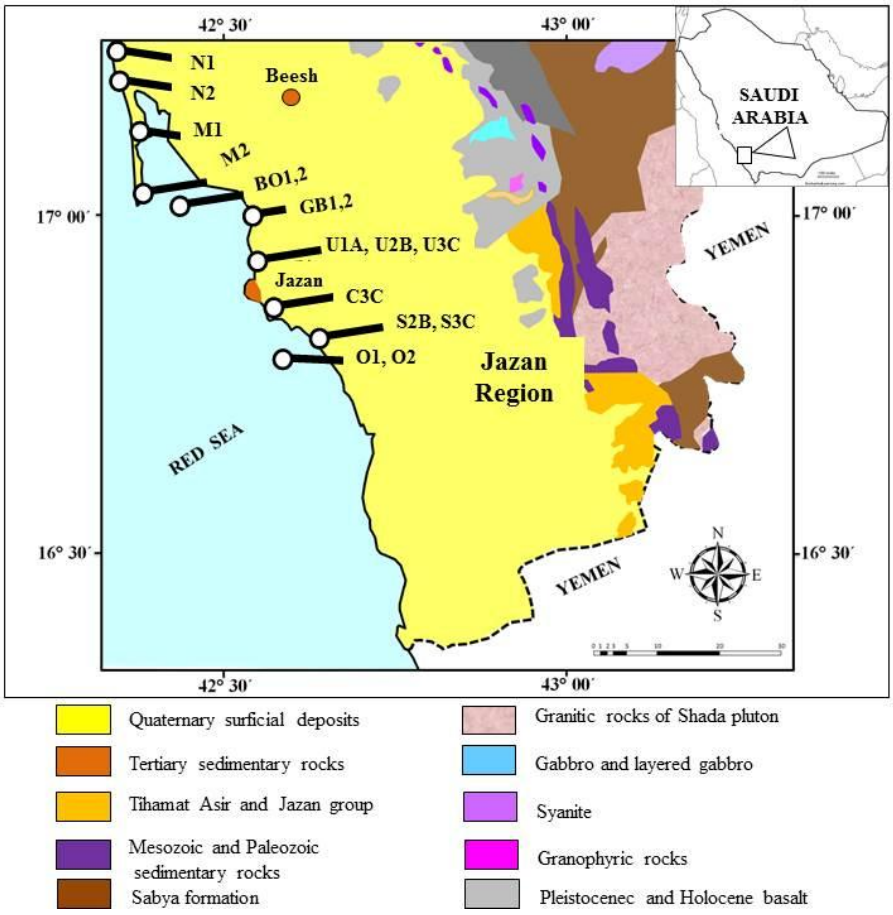

Fig. 1. Study area with location samples.

Jazan and Beesh cities are belonging to the Jazan region. It is characterized as agricultural land with many wadis (Ephemeral River) that discharge into the Red Sea coast. In the last years, Jazan city become the 3rd top fast growing cities in Saudi Arabia due to development and infrastructure activities. Additionally, economic city of Jazan opens on 2020 and many industrial activities (e.g Steel Factory, Portand Aramco Refinery). Several studies have been carried out to investigate the heavy metal contaminations in the sediments of the northern and central Red Sea coast (e.g., Basham 2008; Badr et al. 2009; Pan et al. 2011; Usman et al. 2013; Harb et al. 2015; Youssef and El-Sorogy 2016). Most of the previous studies showed that the surface sediments are highly contaminated.

This study seeks to (1) investigate the analysis of heavy metals and determine their level in the sediments in two cities on Jazan and Beesh and (2) to identify potential sources of contamination. Results of this study will be helpful for developing effective coastal management plan and using integrated coastal management tools to protect coastal areas from the possible contamination, also to establish a scheme of sustainable coastal development in the area. To the best of our knowledge, this is the first work in Jazan area on the assessment of heavy metals.

Study area and sample locations

The study area, located on the southern western part of Red Sea at longitude 42° 30` E and latitude 17° 00` N, is characterized by arid climate, hot and high humid rate influenced by the Red Sea with the poor yearly precipitations rate. Jazan and Beesh cities have high temperature and humidity over the year. However, there is no big variation during the seasons. The annual mean temperature is 28°C, relative humidity 62%, and annual precipitation 62 mm (Saudi presidency of meteorology and environment, unpublished data). Jazan region coast is composed primarily of muddy and sandy beach; dominated by mangrove swamps (*Avicennia marina*). The tide in Red Sea is semidiurnal type with less 0.5 meter range at study area which is not high affected for the coast of Jazan region. Jazan region is a part of the Arabian-Nubian Shield. It quadrangle includes a small area of proterozoic rocks in the east which are composed of low grade, mainly metasedimentary schist of the Sabya formation and granitic rocks of the Shada pluton. In the center, the Cambrian to lower Tertiary rocks are predominantly sedimentary rocks. They are composed of Wajid sandstone, the sandstone and shale of Khums formation and sandstone, limestone Amran formation, and tuff of Tawilah formation. In the west, a large area of middle tertiary to Quaternary rocks (volcanic and sedimentary rocks of Jazan group and intrusive rocks of the Tihama Asir complex and Miocene to Pleistocene sandstone, shale and evaporates) beneath a persistent veneer of Quaternary surficial deposits (Fig 1).

Sample sedements were collectedfrom two cities of Jazan region Beesh and Jazan (Fig. 1). Jazan samples S2B and S3C were taken directly from the outlet of a wastewaterpipewhich is dominated by mangrove swamps, C1A, C2B and C3C samples were gathered from coral coast which is rockyshore, U1A, U2B and U3C samples were from university coast at the north of Jazan and characterized by sandy beach. O1 and O2 samples were collected from intertidal zone (Muddy area).Beesh city samples were collected from N1, N2, M1 and M2 at sandy shore whereas BG1 and BG2 from muddy shorewhich is common by mangroves. Two samples were taken from intertidal zone BO1 and BO2. In these places, the coastal line are affected by flow rain, flash flood and agricultural activities.

MATERIAL AND METHODS

Analytical work was carried out at Institute of Mineralogy and Economic Geology, RWTH Aachen University, Germany. For the analysis major elements of sediments, samples were dried at 50 °C and ground in an agate mortar prior to determination of weight loss on ignition during heating the sample for 120 min. at 1000 °C. Major elements were analysed on fused discs diluted 1:10 with a Li-tetraborate/Li-metaborate mixture (FX-X65, Fluxana, Kleve, Germany) by energy dispersive x-ray fluorescence (Spectro XLab2000).

The system was equipped with a Pd-tube operated at acceleration voltages between 15 and 40 kV and currents between 6 and 12.0 mA. Enhancement of signals was achieved by application of secondary targets of Co, Ti and Al. Data computation was performed using a fundamental parameter procedure. The precision of major element determination is < 0.9 %. For analysis of trace elements the dried (50 °C) samples were digested with aqua regia (2h at 120 °C). Sample solutions were later diluted with 0.5 N HNO_3. The elements Cr, Ni, Cu and Zn were determined by ICP-OES (PerkinElmer Optima 2000 DV) using the wavelengths 267.718 nm (Cr), 327.399 nm (Cu), 231.605 nm (Ni) and 206.201 nm (Zn). Samples were transferred to the plasma via a cross-flow nebulizer and a Scott spray chamber. A quadrupole ICP-MS system (Perkin Elmer Elan DRCe) with a quartz glass cyclone spray chamber combined with a Meinhard nebulizer was applied for analysis of Pb and As. Elements were detected using the masses 208 for Pb and 91 for As O at dwell times of 50 ms. Arsenic was analysed as oxide after introduction of oxygen to the reaction cell in order to avoid interference with 40Ar35Cl at mass 75.

Mercury was analysed by cold vapour technique with a Perkin Elmer FIMS-100 using 0.2 % NaBH4 as reducing agent and Ar as carrier gas. Precision of determination of trace element concentrations is <10%.

To check for accuracy USGS Geochemical Exploration Reference sample GXR2 soil from Park City, Utah, was analysed after total dissolution with a HF-HNO3-HCl-H3PO4 mixture. The recommended values were reproduced as indicated in brackets: Cu 76 µg/g (109 %), Ni 21 µg/g (78 %), Zn 530 µg/g (83 %), Cr 36 µg/g (101), 690 µg/g (85 %). The deviation from recommended values is ≤ 22 %.

RESULTS AND DISCUSSION

Hg and Zn show extreme highest enrichment in S2B and S3C in Jazan city Table (1). Concentrations of Hg range from 307.8 to 374.3 whereas Zn 93.57 to 176.1. This may be due to anthropogenic enrichment from the wastewater treatment plant in Jazan city. Indicating that these sediments are contaminated by wastewater. Many infrastructure projects are in progress along the coast of Jazan region such as wastewater treatment plant, port and industrial zone and the wastes are dumped into the sea either treated or partially treated. The coastal areas in Jazan region is the target for intensive dredging and reclamation; many upcoming major housing, tourism, and industrial projects.

High concentration of Zn in the cities often related to vehicle tyres (Li et al. 2001). The south city of Jazan is dominated by Mangroves with a narrow tidal rage, which is significant in accumulation of heavy metals in area. Guitouni et al. (2016) found that mangroves (*Avicennia marina*) absorb large amounts of heavy metals in the Arabian Gulf from their environment and cleaning the marine environment from pollutant. Mangroves absorb heavy metals through their roots, or even through their stems and leaves; and accumulate them in their tissues (Ramos et al., 2006). In Muddy shore samples S2B and S3C, the concentrations of Cu, Ni, Cr and Pb are varied between (34.78, 15.73, 10.11 and 25.97), respectively. O1 and O2 samples which were taken at intertidal zone show low concentrations on Hg, Zn, Cu, Ni, Pb and relative high concentration of Cr which may result from weathering. The sample C3C, was taken within intensive swimming beach but characterized by less polluted area and show very low concentrations of heavy metals Pb, Cu, Zn and Hg varied between (3.03, 0.52, 9.36 and 3.78), respectively Table (1).

Cr shows high enrichment in U1A compared to U2B and U3C. This site characterized by less population and pollution which considered being from geoganic sources. In Jazan city, there is no heavy industrial source of metals. However, high concentrations of Zn and Hg were shown. The anthropogenic sources at a sampling site, such as sewage discharge or agricultural runoff were observed and may have an impact on the heavy metal concentration independent of the mineralogical composition. In addition, intensive land filling was observed in study area. Dredging and reclamation processes are typically associated with elevated levels of heavy metals (Guerra et al. 2009; Hedge et al. 2009).
The coast of Beesh city is sandy shore with Mangrove forest at the southern part of the city. The beach is characterized as low disturbance. The concentrations of Hg range from 5.394 to 9.982. The concentrations of as were shown higher than Jazan city varied between 19.666 - 29.333. The concentrations of Pb range from 4.472 to 8.371. Concentrations of Cu range from 3.71to 18.74. The highest Zn concentration 39.56 is measured in sample BG1. Concentrations of Cd are very low in both cities with values less than 1 except sample N1 (1.17). The concentrations of Cr range from 16.78 to 33.79 with the highest value in sample BG2 which characterized by Mangrove trees and muddy shore. The concentrations of Ni have approximately double value of Pb range from 8.48 to 17.59 Table (1). In Beesh city the high concentrations were found in mangrove forest rather than sandy shore. The samples at intertidal zone BO1 and BO2 were shown low concentrations of heavy metals compared to the samples BG1 and BG2 at Mangroves area Table (1).

Table 1. The comparison samples between Heavy Metals in the cities of Jazan and Beesh.

Jazan samples								
	Cd	**As**	**Cu**	**Ni**	**Pb**	**Cr**	**Zn**	**Hg**
S2B	0.17	11.93	34.78	15.73	10.11	25.97	93.57	374.3
S3C	1.27	5.97	32.17	17.56	14.5	29.39	176.1	307.8
C3C	0.27	11.70	0.52	3.82	3.03	9.28	9.36	3.78
U1A	0.17	14.77	15.62	14.78	5.16	54.06	22.75	12.54
U2B	0.23	6.63	4.50	7.50	3.20	14.00	10.87	3.22
U3C	0.23	9.87	5.52	8.688	4.222	16.56	13.08	5.365
O1	0.17	13.60	14.93	19.25	7.09	32.09	26.29	7.70
O2	0.13	14.40	7.76	15.11	5.38	24.67	19.87	8.08
Beesh samples								
	Cd	**As**	**Cu**	**Ni**	**Pb**	**Cr**	**Zn**	**Hg**
N1	1.17	19.67	3.71	8.48	4.76	17.22	18.03	6.01
N2	0.07	22.43	4.08	8.52	4.47	16.78	17.83	9.80
M1	0.13	24.87	11.68	15.57	7.73	32.62	34.38	9.43
M2	0.13	22.73	11.96	15.89	7.93	33.43	33.94	7.66
BG1	0.10	27.07	14.58	17.53	8.37	33.04	39.56	7.51
BG2	0.07	25.60	18.74	17.59	8.37	33.79	33.29	10.20
BO1	0.27	29.33	6.84	9.31	5.28	19.03	22.56	5.39
BO2	0.17	21.97	10.47	9.60	5.70	21.48	17.26	9.98

The other pollution sources could be agricultural waste and weathering as well as flash flood runoff. Flash floods could be one of contamination sources that are generated by heavy rain in Jazan region from the wadis (valleys) e.g. Jazan and Beesh which contain eroded sediments from the surrounding rocks. Most of wadis at Jazan region debouching into the Red Sea coast pass densely populated and agriculturally areas, their sediments certainly act as a first important sink to anthropogenic input of heavy metals. These wadis are characterized by significant sediment discharge, which is mainly due to the high seasonality in rainfall at hot and humid conditions. Cr and Ni were shown varied between two cities which are resulted from weathering. However, Zn, Hg, Pb, Cd and Cu concentrations are probably derived from human activities. Generally, the highest concentrations in both cities were dominated at Mangroves area (muddy shores) due to accumulation of these elements. However, low concentrations in the sandy shore with low sedimentation which is characterized by less disturbances of human activities.

Table (2) shows the Spearman rank correlation coefficient (rs) matrix for concentration data of the sediment samples. Cu, Pb, Hg and Zn strongly correlated to each other (rs = 0.72–0.90). This indicates that these metals were emitted from the same source. Relatively weak correlation between Cr, Ni and Hg were observed. The correlations coefficients are shown in Table 2 indicate no correlation of Cd, Sn, and As with Cu, Ni, Pb, Cr, Zn and Hg. The correlation between Cd and As is significant at level 0.05, whereas presence Cd is negatively correlated with all analyzed metals.

Table 2. The correlation coefficients of heavy metals.

	Cd	As	Cu	Ni	Pb	Cr	Zn	Hg
Cd	1							
As	-0.336	1						
Cu	0.201	-0.051	1					
Ni	-0.063	0.284	0.759	1				
Pb	0.368	0.090	0.909	0.794	1			
Cr	-0.155	0.304	0.589	0.826	0.541	1		
Zn	0.563	-0.237	0.845	0.517	0.903	0.296	1	
Hg	0.384	-0.360	0.837	0.337	0.720	0.129	0.868	1

CONCLUSIONS

The high concentrations of Zn and Hg in samples S2B and S3C, taken in Mangrove area may be derived from sewage outlet which characteristic as anthropogenic sources. Cr and Ni are resulting from weathering and erosion process probably flash flood. It is clear that Jazan city sediments have the highest concentrations of most of heavy metals. On the other hand, Beesh city sediments have the lowest concentration heavy metals due to low population and less human activities. The main sources of contaminations in the study areas are natural by weathering and anthropogenic activities such as sewage. Jazan city is more anthropogenic affected due to diffusion from sewage plant, landfill and reclamation whereas Beesh city is disturbed mainly by flash floods resulting from wadi Beesh which is classify as the largest valley in the southern part of Saudi Arabia.

Mangrove plants in Jazan region is useful to absorb the contaminants and cleaning of the marine environment, so it should be protected from human activities e.g. destruction due to urbanization, sewage discharge and camel grazing. The area that represent the third fast growing city in Saudi Arabia need more attention in monitoring and investigation of heavy metals to establish effective coastal zone management plan. This is important terms of marine environmental conservation, fisheries, eco-tourism, and coastal area protection.

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