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Research Article

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Preliminary assessment of heavy metals as Marine Pollutants in Misurata Port, Mediterranean Sea Libya

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Abstract Heavy metals have long been recognized as one of the most important pollutants in the ecosystem because of their persistence, their ubiquitousness in the environment, and their ready assimilation and bioaccumulation in organisms, determining a potential risk to human health by consuming contaminated food. A coastal survey off the west part of the Libyan coastline which has no river inputs was initiated to measure the existing level and distribution of selected heavy metals (Cadmium (Cd), Lead (Pb), Zinc (Zn), Copper (Cu), and Chromium (Cr)) in surface areas of Misurata Port, Misurata, Mediterranean Sea, Libya. Five sampling sites were selected along Misurata fishing harbor for the study for a period of six months from September 2016 to February 2017. The results showed that the mean concentrations of the heavy metals in the present study were found in the order of Z n > Cd > Pb > Cu, where the presence of chromium metal was not noticeable. The concentrations of all the heavy metals except Cd in the marine water samples in the present study found lower than those reported by WHO. Based on the above results, it was concluded that the seawater of Misurata Port is moderately polluted by heavy metals. The concentrations of the metals studied were compared with the values published by EPA, WHO, TSE and Australian authorities. The average concentration of Cadmium (0.0103-0.236 mg/L) metal was found to be higher than the limit values of all the above standards. The average concentrations of lead (0.000-0.061 mg/L), Zinc (1.001-1.926 mg/L), and Copper (0.000-0.166 mg/L) were recorded a little higher than that of the values of EPA and Australian.

Keywords Heavy Metals, Environmental quality, Seawater, Misrata Port, Libya

Introduction

Water is a valuable natural resource for the survival of human beings. Surface and ground water are very distinct sources of water. Humans have used water systems for numerous purposes such as for drinking, irrigation, fisheries, industrial processes, transportation and domestic waste disposal. With such a high dependence on water, increasing of urbanization, agricultural and industrial practices caused adverse effects on both surface and ground water, thus rapidly decreasing the water quality [1]. This quality refers to the physical, chemical and biological characteristics of water. The term "water quality" is intimately related to water pollution. Water pollution is emerging as a threat to all humanity [2]. The problem of environmental pollution has been generally due to the ever-increasing industrialization, urbanization, high density of population and the unplanned introduction of plant, which often proves to be hazardous to human health [3]. A wide range of human activities in agroindustry, livestock, tourism, and other activities also disposes waste. Without proper treatment, these materials are normally associated with the cause of health problems and environmental pollution [4]. Water pollution is one of the major environmental concerns faced by the world today. Increasing developmental activities has led to a rise in pollution [5]. Marine pollution is a global environmental problem; human activities in the coastal area and marine water contribute to the discharge of various kinds of pollutants such as heavy metals into the marine ecosystems [6, 7]. Determinations of heavy metal concentrations in aquatic organisms are usually preferred than their measurements in seawater and sediment. The concentration of metals in water is very low and shows wide fluctuations. Metal concentrations in the sediment can be changed by the oxidation–reduction potential, organic content, pH, and the grain size composition [8]. On the other hand, sea grass and macro algae can be used as bio-monitors to give information on concentrations of heavy metal or changes in metal availabilities in the surrounding environment, besides their abundance in various environmental systems [9-12]. In general, algae are widely distributed in the aquatic environment and are sedentary, easy to collect, identify, and the bioaccumulation of trace metals occur in high degrees; satisfying all the fundamental requirements for bio-indicators. Heavy Metals are natural constituents of the marine water environments, most of these metals are present in seawater in trace concentration whereas excessive concentration can affect marine biota and pose risk to consumers of sea food [13]. Heavy metals are considered a major anthropogenic contaminant in costal and marine environments worldwide [14]. They pose a serious threat to human health, living organisms and natural ecosystems because of their toxicity, persistence and bioaccumulation characteristics [15]. Unlike hydrocarbons, heavy metals do not undergo biodegradation process, which favor their persistence in the environment, as well as their bioaccumulation and potential damage to organisms [11]. Many heavy metal ions are known to be toxic or carcinogenic to humans [16]. Which is may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture and manufacturing, pharmaceutical, industrial, or residential settings [17]. The toxicity of it arises from their tendency to bind proteins or other molecules and preventing them from functioning in their metabolic role [18]. Even in small amounts metals can cause considerable damage to organisms [19]. This can contribute to the degradation of marine ecosystems by reducing spices diversity abundance, and through the accumulation of metals in living organisms and food chains [20]. The present study considers an attempt to evaluate the levels of heavy metals contamination in Misurata port area and to assess the human impacts on this area. Also, it compares the levels of pollution in the studied area with neighboring and worldwide coastal environments.

Materials and methods

Study area

Misurata Port is located on the far western edge of the gulf of Sirt (Khalij Surt) (32˚ 00 N', 18˚ 00 E'), an extensive gulf is entered between Qasr Ahmed (Misurata Marina) and Benghazi, several important oil terminals are situated on the shores of the Gulf [17, 18]. Misurata Port established in 1978 with total area of 300ha and in 2006 it belonged to Misurata Free Zone (MFZ), the coordinates of the port of Misurata located between longitude E 15˚13′ 0.00″ east and latitude N 32˚ 22′ 0.00″ north, 12 Km from Misrata city. Misurata Port has a variety of pavements of various purposes and specialties, with a total length of about 5 Km, they have diffferent depths ranging from 2.5 to 12 M. (Figure 1).

Figure 1: Misurata Port (Source, Google earth)

Sampling and analytical methods

The samples were collected using polyethylene bottles, which was pre-washed with HNO_3 and distilled water. Before sampling, the bottles were rinsed at least for three times with water from the sampling location. The bottles were immersed to about 30 cm below the water surface level from the five different sites monthly, were collected a total of 30 samples in triplicate from Misrata Port, as shown on the map (Figure 2).

Figure 2: Fishing docks and sampling location (Source, google earth)

All samples transferred to the laboratory for analysis [19], metals in seawater samples were extracted by using liquid oxidizing agents (Five ml of 37% HCl, and Two ml of 63% HNO_3) added to 100 ml of each water sample placed in 250 ml beaker, heating at 90 to 95^0C, until the volume reach to about 15-20 ml, then cool the beaker, the solutions were filtered through Whattman number 40 filter paper [19], the concentrate was transferred to a 100 ml volumetric flask and diluted to mark with distilled water, and measurement was made with (Atomic Absorption Spectrometer VARIN).

Statistical Analysis

The heavy metals data were entered as Microsoft Excel sheets uploaded to statistical Package for Social software (SPSS V21) and analyzed using the values recorded.

Result and Discussion

The Mediterranean region, home to around 480million people living across three continents: Africa, Asia and Europe, has been undergoing intensive demographic, social, cultural, economic and environmental changes in the last decades. Since 1950s, the countries bordering the Mediterranean Sea have experienced a drastic increase in population, especially in the southern and eastern rim where further growth is still expected [21]. Most of this urbanisation takes place in the coastal zone where people live in increasingly overcrowded coastal strips, exacerbating the pressures on the environment, such as through waste and wastewater generation. Such land-based sources of pollution constitute a major threat to the health of coastal and marine ecosystems [22]. Many toxic or potentially toxic heavy metals are released into the oceans, especially into the coastal zones. Iron, copper, zinc, cobalt, manganese, chromium, molybdenum, vanadium, nickel, zinc and selenium are known to be essential for living organisms, but even these essential metals become toxic if present in excessive quantities. Apart from waste discharge, the oceans receive heavy metals (together with other materials) through the atmosphere, land run-off and rivers [24]. Natural processes such as degassing, weathering and erosion mobilize these metals. Heavy metals mobilized by man enter into the natural biogeochemical cycles at rates comparable to or even exceeding the natural rates. The prediction of the rate and the pathway of a heavy metal mobilized by man is further complicated by the observation that the pathways and rates of mobilization depend on the physico-chemical state of the element [25]. Often, however, anthropogenic mobilization produces physico-chemical forms which are different from the natural ones. As a consequence, an artificially mobilized heavy metal can appear in a component of the marine system in which it was not anticipated and cause unexpected damage to marine biota and create hazards for human health [26]. Owing to the difficulties in determining heavy metals in sea-water (low concentration, contamination of the sample, etc.) relatively few measurements have been made in the Mediterranean Sea. Heavy metals are considered to be among the highest serious pollutants of water ecosystems, because of their high possibility to enter and being accumulated in nourishment chain [27 -30].

Concentrations of Cadmium (mg/l)

The concentration values of Cd in seawater were ranging between 0.0103 to 0.236. The highest concentration of Cd, 0.236 mg/l was observed in October 2016 at site 1, whereas the minimum value of Cd concentration 0.0103 mg/l was noted in January 2017 at site 3. The result was found to be higher than the permissible limits (Figure 3).

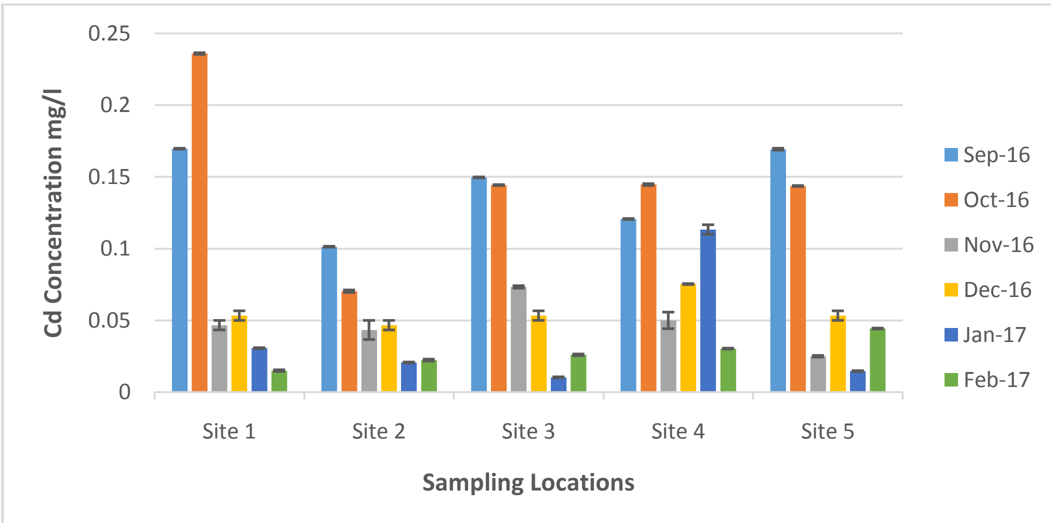

Figure 3: Variations of Cd conc. for the marine aquatic samples

Concentrations of Lead (mg/l)

The concentration of Lead in seawater surface is ranged from 0.000 to 0.061 mg/l. The highest value 0.061 mg/l concentration of Pb in the collected samples was observed in November 2016 at site 2 and the value 0.000 was at sites 4 & 5 in October 2016. The values show us slightly higher than of the values of EPA and Australian guidelines (Figure 4).

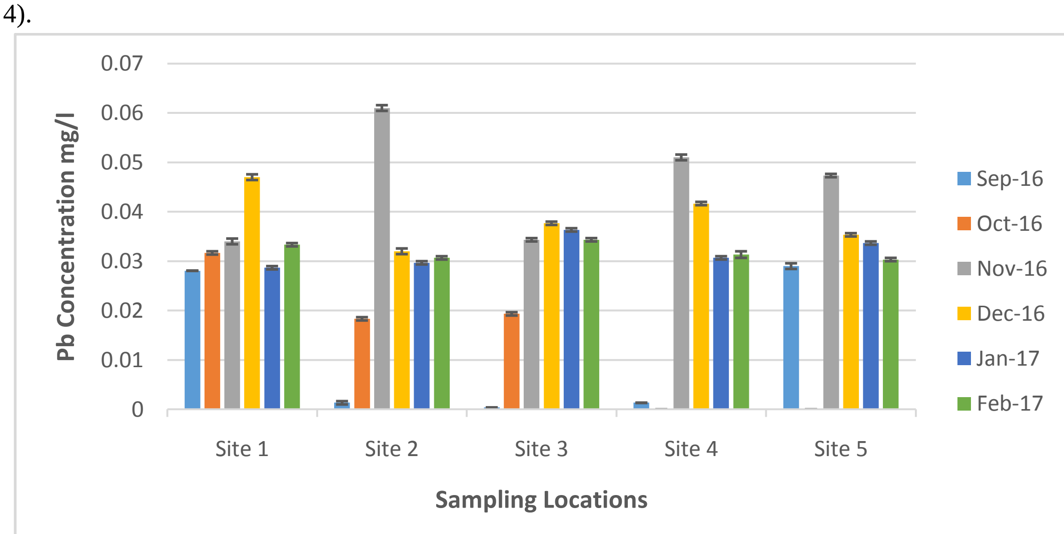

Figure 4: Variations of Pb conc. for the marine aquatic samples

Concentrations of Zinc (mg/l)

The analyzed concentrations of Zinc in marine aquatic samples were ranging between 1.001 & 1.926 mg/l. The highest concentration of Zinc 1.926 mg/l in seawater was observed in January 2017 at site 5 and the lower concentration of Zinc 1.001 mg/l was noted for the month of November 2016 at site 5. The average concentration of Zinc was found a little higher than that of the values of EPA and Australian guideline (Figure 5).

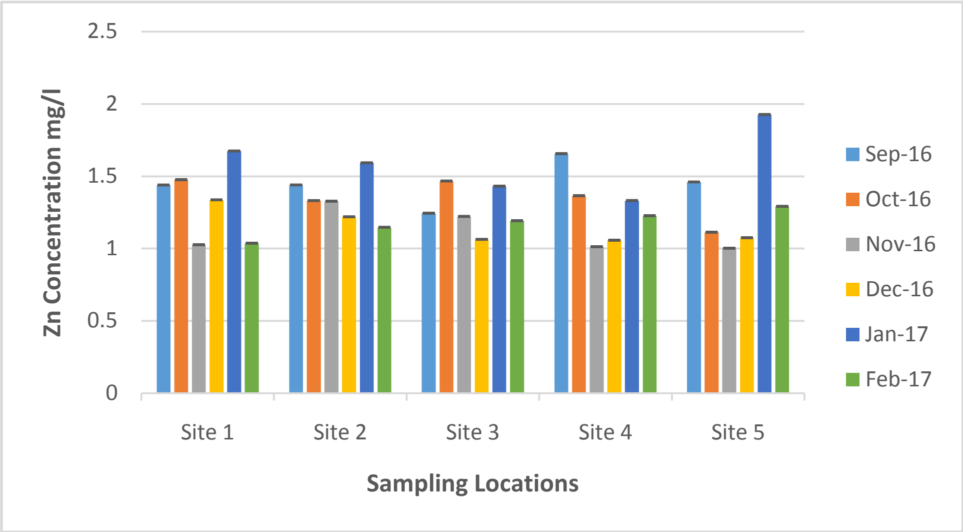

Figure 5: Variations of Zn conc. for the Marine Aquatic Samples

Concentrations of Copper (mg/l)

The concentration values of Cu in marine aquatic samples collected near the Misrata Port at five different sites were ranging between 0.000 to 0.166 mg/l. The highest concentration of Cu, 0.166 mg/l was noted for the month of February 2017 at site 3. However, there were no traces of Cu were found at many sites in all the months except in January and February 2017. The average concentration of Copper concentration was slightly higher than the values recorded by EPA and Australian guidelines (Figure 6).

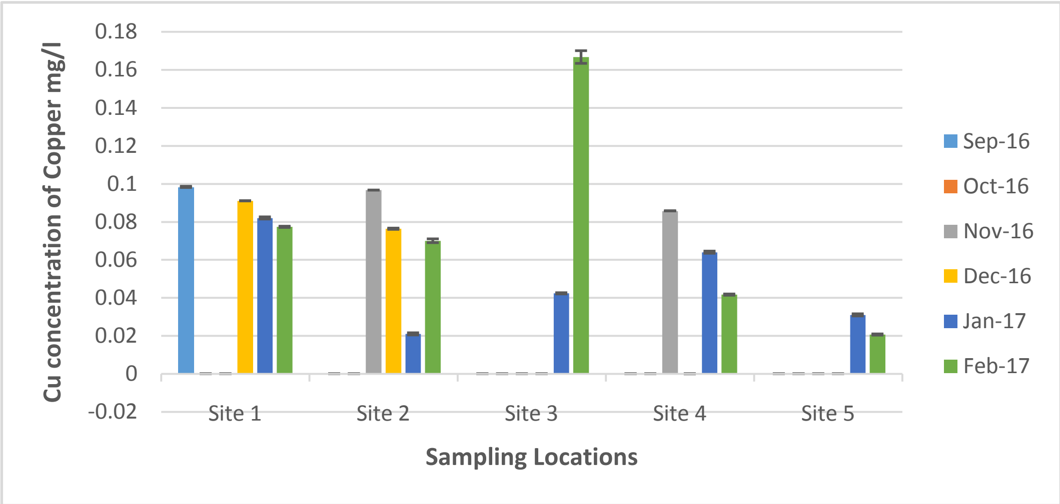

Figure 6: Variations of Cu conc. for the marine aquatic samples

Concentrations of Chromium (mg/L)

In the present study, Cr was less than the detection limit of the detection limit of the instrument, in any of the five sites during study of six months from September 2016 to February 2017.

Table 1: Limits of Heavy metal concentration as per the EPA, WHO, TSE, Australian and the recorded values in marine aquatic samples collected near Misurata Port area

Metal	**EPA (µg/l)**	**WHO (mg/l)**	**TSE (mg/l)**	**Australian (µg/l)**	**Present Study (mg/l)**
Cadmium (Cd)	71	0.01	0.01	5.5	0.0103-0.236
Lead (Pb)	2	0.050l	0.050l	4.4	0.000-0.061
Zinc (Zn)	1180	30-100	-	15	1.001-1.926
Copper (Cu)	45	10-100	- 1		0.000-0.166
Chromium (Cr)	-	-	-	-	N.D.

All marine aquatic sample concentrations of this study are in mg/l

-, data not available

N.D. not detected.

Conclusions

The data obtained would be useful as guidelines for the environmental researchers for their studies to identify future anthropogenic impacts at the study area with respect to the studied metals**.** The average concentrations of the metals in the present study were found in the order of Zn > Cd > Pb > Cu. Where the presence of Chromium metal was not noticed at all. The concentrations of the metals studied were compared with the values published by EPA, WHO, TSE and Australian authorities. The average concentration of Cadmium (0.0103-0.236 mg/l) metal was found to be higher than any of the values of the above authorities. The average concentrations of Lead (0.000-0.061 mg/l), Zinc (1.001-1.926 mg/l), and Copper (0.000-0.166 mg/l) were recorded a little higher than that of the values of EPA and Australian. As the concentrations of all the heavy metals except Cadmium (Cd) in the present study were found to be lower than those reported by WHO, it was inferred that the sea waters in the study areas of Misurata Port were moderately polluted with heavy metals.

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