Quality of Underground Water and Environment Adjacent to Petrochemical Industry Zone in Libya

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Abstract

The hazardous material resulted from the industrial activities have many of negative effects on the human and environmental health. The wastewater generated from petrochemicals factories have heavily loads of heavy metals, the direct discharge of these wastes into the landfill and water system contribute in the contamination of water resource. In the present study, the level of underground water pollution with heavy metals was evaluated. The underground water samples were collected from the surrounding area of General Company of Chemical Industries (GCCI) at Abu-Kammash, Libya. The concentrations of heavy metals were determined using inductively coupled plasma (ICP-Mass) Spectrometry. The results revealed a detectable concentrations of heavy metals in the water samples but their concentration still within the rage recommended by WHO standards. About 80% of fish exceeded the Food and Agriculture Organization (FAO) standards (1 µg g^{-1}). The maximum concentrations was noted in *Sarpasalpa*and *S. aurata* (3.95 *vs.* 7.86 and 1.05 *vs.* 10.3µg g^{-1} for tissue and liver respectively). Detectable concentrations of Cu^{2+} and Hg^{2+} were determined in the Grape, Figs andOlive leaves obtained from environmentadjacent to petrochemical industry zone. It can be concluded that the heavy metals in the surrounded area of GCCI represent a real hazards for human and environment.

Key words: toxic elements, underground water, Zuwarah, Abu-Kammash, ICP-Mass

Introduction

Heavy metal pollution is a problem associated with the direct discharge of the factories wastewater into the environment [1]. The possibility of heavy metal to contaminate the underground water depend on the properties of soil which received the disposed wastewater. The soil might play an important role for filtration of polluted water. However, the over discharge of the wastewater into the soil contribute significantly in the immigration of metal ions into the underground water [2]. Heavy metal ions is quite different from other chemical pollutants, since it has no subjected for the biodegradation process which take place by the microorganism in the soil [3]. Rather than, it might be accumulated in the plants tissue and transmitted into the human and animals. Again

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once the type of the soil as acidic or alkaline soil might effect on the level of contamination of underground water, in the acidic soil the metal ions become more applicable to immigrate into the wells and underground basin. In the contrast, the alkaline soil might contribute in participating of metal ions and limit their transmission into the lower layer of the soil and then into the underground water.The ability of heavy metals to persist in the water system and the environment for long time represent a real hazards for the peoples in the developing countries, since most of these peoples depend on the well waters as a main source for the drinking water without farther treatment [2]. On the other hand, the consumption of contaminated foods such as fish, vegetables and fruits or the products such as olive oil contaminated with Hg^{2+} might lead to increase the Hg^{2+} concentrations in the body systems [4]. The methylmercury poisoning resulted from consumption of mercury-contaminated fish has reported in different region in the world [5]. The high concentrations of Hg in the cells lead to causes damage of their functions [6].

In the present work, the concentrations of Cu^{2+}, Cd^{2+}, Hg^{2+} in the underground water, Grape, Figs andOlive Leaves, Different fishes species (tissue and liver) was evaluated in order to understand the level of pollution generated from the direct discharge of General Company of Chemical Industries (GCCI) wastewater into the environment and water system.

Materials and Methods

Study area

Abu-Kammash is an industrial area about 200km far from the capital city (Tripoli), while GCCI is company located at Abu-Kammash zone which has established on 1970s. GCCI has four units include poly vinyl chloride (PVC) (60, 000 tons/year), Ethylene di-chloride (with productivity of 104,000 tons/year), caustic soda (50,000 tons/year) and chlorine (45,000 tons/year). Besides, the compant produce sodium carbonate, sodium hypochlorite and HCl. The wastewater geneertaed from GCCI are discharged into the surounded envionmnt and natural water systems [3].

Collection of samples

A total of 62 samples (in triplicate) included, water, plant leaves and fisheswere collected from different locations around GCCI during the period from January to September 2015. Table 1 illustrated the types of samples collected and their sources.

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Table 1 Types of samples collected and heavy metals analysed in the study

No.	Sample types	No. samples	Source	Heavy metals analysed
1	Water	20	underground water	Cu^{2+}, Cd^{2+}, Hg^{2+}
2	Grape, Figs andOlive Leaves	4 for each	Surrounding area	Hg^{2+}, Cu^{2+}
3	Different fishes species (tissue and liver)	30	Marine water	Hg^{2+}

Plastic bottles (1 L) were used for the collection of water samples, 2.4 mL of a 15 % solution of ethylene di-amine-tetra acetic acid (EDTA) tetra-sodium salt (R & M Marketing, Essex, UK), was added as a chelating agent to sample. Grape, figs andolive leaves (about 100 g for each)were collected into paper bags. Fishes samples were collected using local fishermen from the sea batch closed to GCCI. All the samples were transported inside ice box to the laboratory and kept in deep freezer at -4°C until analysis.

Determination of heavy metals

The experimental analyses of heavy metals were conducted at International Centre of Environmental technologies in Tunisia. Fish samples preparation and analysis were carried out according to Bernhard [7]. Liver, muscle, gill, heart, air sac and stomach-intestine were removed before the analysis [8]. Fish samples were homogenized in a blender. Grape, figs and olive leaves were cut out into small pieces (5 mm in diameter) and then homogenized in a blender. A weight of 10 gram of homogenate for each of fish as well as grape, figs and olive leaves were digested as described above. The heavy metals were extracted from the water samples by the nitric acid digestion method [9]. The concentrations of heavy metals in the digested samples were determined by using inductively coupled plasma (ICP-Mass) Spectrometry, the samples were sent to CITET in Tunisia for this purpose.

Results and Discussion

The current study aimed to assessment the toxic metals in the environment adjacent to petrochemical industry zone in Libya. Three types of samples were collected included underground water, plants and fish. The concentrations of heavy metals in these samples were carried out to evaluate the level of pollution in the environment adjacent to petrochemical industry zone in comparison to the international standards. The concentrations of these metals in the underground water samples (Table 2) and plants leaves (Table 3) were low. Cu^{2+} in the water samples ranged from 0.007 to 0.01 mg L^{-1}, while the Hg^{2+} concentrations was less than 0.002

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mg L^{-1}. In the plants leaves, the concentrations of Cu^{2+}were less than 5 mg kg^{-1} dry wt. in Grape, Figs andOlive leaves. Moreover, concentrations of Hg^{2+} differed among the type of plant, the highest concentration was recorded in olives leaves (ranged from 0.078 to 1.72 mg kg^{-1} dry wt.) followed by figs leaves (ranged from 0.568 to 0.766 mg kg^{-1} dry wt.).

Table 2 Heavy metal concentrations in groundwater samples collected from wells adjacent to petrochemical industry zone in Libya (n=20)

Heavy metals	**Metal concentrations (mg L^{-1})**			**Standards (mg L^{-1})**
	Min	**Max**	**Mean**	
Cu^{2+}	0.007	0.01	0.009	0.01
Cd^{2+}	0.003	0.003	0.003	0.003
Hg^{2+}	<0.0002	<0.0002	<0.0002	0.006

Table 3 concentrations of Cu^{2+} and Hg^{2+} in Grape, Figs andOlive leaves collected from environment adjacent to petrochemical industry zone in Libya (n=4 sample for each)

Heavy metal	**Concentrations (µg kg^{-1} dry wt.)**								
	Grape Leave			**Figs Leave**			**Olive Leave**		
	Min	**Max**	**Mean**	**Min**	**Max**	**Mean**	**Min**	**Max**	**Mean**
Cu^{2+}	<5	<5	<5	<5	<5	<5	<5	<5	<5
Hg^{2+}	<0.001	0.70	0.351	0.568	0.766	0.667	0.078	1.72	0.899

These findings are in agree with previous study, which revealed high concentrations of Hg^{2+} in the sediments and marine plants samples which were also collected from Farwa island [3]. Some of heavy metals in the soil are necessary for plant growth because they acts as a trace elements and cofactors for several enzymes. For instance, Cu^{2+} is an important metal for many biological functions, but at 0.1 to 1.0 mg L^{-1} is become more toxic to a number of plants [10]. In contrast, some of metals such as Hg^{2+} and Pb^{2+} are toxic elements, and has no usefulness for biological function in the plants [3,11,12]. Akrivos et al. [13] indicated that Zn^{2+}, Cu^{2+}, Ni^{2+} and Cr^{3+} effects on plant growth and crop yields and are known to be cumulative toxins, while Pb^{2+}, cadmium Cd^{2+} and Hg^{2+} are toxic to the animal or human digest of the plants and might be mutagen causing cancer [14].

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Hence, the presence of these metal with concentrations recorded here represent areal hazards for human and environment.

In order to confirm the hazards of heavy metals on the aquatic organisms the concentrations of Hg^{2+} in liver and tissue of different types of fish (Table 4).

Table 4 Hg^{2+} concentrations in fish tissue and liver specimens collected from water body adjacent to petrochemical industry zone in Libya (n=30), FAO standards limits (1 μg g^{-1})

Fish species		Mean concentration of Hg^{2+} (μg g^{-1})		
		Min	Max	Mean
Mullussurmuletus	Tissue	0.1	1.6	0.85
	Liver	2.4	5.3	3.85
Amphilophuscitrinellus	Tissue	0.8	1.7	1.25
	Liver	0.2	2.6	1.4
Serranusscriba	Tissue	0.3	2.2	1.25
	Liver	0.2	1.9	1.05
Sarpasalpa	Tissue	2.2	5.7	3.95
	Liver	5.3	10.43	7.87
Sparusaurata	Tissue	0.3	1.8	1.05
	Liver	3.3	17.3	10.3
Lithognathusmormyrus	Tissue	0.11	1.8	0.96
	Liver	1.1	2.7	1.90
Diplodusanunularis	Tissue	1.2	1.8	1.5
	Liver	0.8	3.8	2.3
Oedalechiluslabeo	Tissue	1.9	3.2	2.55
	Liver	1.04	2.3	1.67
Dicentrarchus labrax	Tissue	0.1	0.32	0.21
	Liver	0.01	0.2	0.11
Pagruspagrus	Tissue	0.01	0.2	0.11
	Liver	0.01	0.09	0.05

The results revealed presence high concentrations of Hg in the liver and tissue. Hg^{2+} concentrations in liver were more than the tissue among seven fish types tested in the study. The maximum concentrations was noted in *Sarpasalpa*and *S. aurata* (3.95 *vs.* 7.86 and 1.05 *vs.* 10.3μg g^{-1} for tissue and liver respectively). These concentrations are more than that reported in the previous work [3] which might be related to the source of these fishes where were obtained from very close water to the GCCI region which is the main downstream of the

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wastewater generated from the factory. Among 10 types of fish examined here, eight types (80%) contains Hg more than the standards limits recommended by Food and Drug Administration (FDA) and FAO-WHO(1 µg g^{-1-}) [15,16] as well as United States Environmental Protection Agency (USEPA) (0.3 µg g^{-1}) [17]. These findings indicate to the presence a risk for human who consuming these fishes. It has reported that the fish is one of the main source of Hg^{2+} for human, because the Hg^{2+} are accumulated in tissue and livers of fish and then transmitted into the human via consuming the fish [11,12].

Conclusions

It can be concluded that the heavily contamination of fish samples reflect the high level of Hg^{2+} pollution in the environment adjacent to petrochemical industry zone in Libya. Therefore, the surrounding area need to be treated to minimize the health risk hazardsassociatedwith the direct discharge of industrial wastewaterin order to prevent the negative effects on the human and environment associated with mercury contamination.

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