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CASE STUDY

Speciation of heavy metals in coastal water of Qeshm Island in the Persian Gulf

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ABSTRACT: Fuel storage tanks are one of the main sources of water pollution as well as loss of crude oil and oil products in refineries. In the process of utilization of these tanks, considerable amounts of hydrocarbons may find their way into the coastal water, which eventually lead to loss of valuable hydrocarbons. Oil type, climatic condition and characteristics of oil tanks are among the main variables in computing evaporative losses. The present study brings out the results of a project that was carried out to investigate the adverse effects of oil terminal on coastal waters of Qeshm Island and aims to elaborate on speciation of metals in coastal waters. For this purpose, 12 stations were sampled. Water chemistry software was used to draw Eh-pH diagrams. Along with the speciation of heavy metals, cluster analysis was carried out by MVSP software. According to the results, HSC diagrams showed that Cu and Cd were present as free ions. Lead, manganese, cobalt, zinc and nickel were respectively present as PbOH, MnOH, ZnOH, CoOH and NiOH in the Persian Gulf. Speciation of Cu and Ni was in the form of Cu_2O and NiO. Vanadium was also present in combination with hydroxide. Since all the studied elements were within the water stability range, they were stable, and there were no environmental risks of contamination and toxicity. The results of cluster analysis did not show any relation between Eh and pH. This clearly showed that Eh-pH was governed by different mechanisms in coastal waters of Qeshm Island. Vanadium and Ni concentration was governed by pH, while Cu and Cd concentration was controlled by Eh.

KEYWORDS: *Entropy; Heat capacity; Multivariate statistical package (MVSP); Oil tank; Water pollution.*

INTRODUCTION

Energy is recognized as one of the main factors of the formation and development of industrial communities (Rota *et al.,* 2001). The importance of oil and petroleum is highlighted at their basic role in human life (Horner *et al.,* 2000). Iran has an important position in this field due to its great capacity of energy resources, especially oil and gas, and also special geopolitical position. During the recent years, oil products have been decreased because of the population growth, increase of the demand for oil products and decrease of crude oil extraction for export purposes (Karbassi *et al.,* 2007a). One way to save oil products and to prevent the evaporation loss or leakage is suitable usage of storage tanks (Chork, 1977). Evaporation or leakage of hydrocarbons and their products from the storage tanks has become a special concern in the recent years (Tepavitcharova *et al.,* 2010). Storage tank of hydrocarbons is an important evaporation and leakage source of volatile organic compounds (VOCs) (Martinez *et al.,* 2009). These tanks are one of the most important industrial facilities that are exposed to risks of toxic substances release, fire and explosion (Rao *et al.,* 2005; Martinez *et al.,*2004). In a study on chemical risk assessment in 2007, the causes of risk in industries, which attributed to three factors of human error, equipment failure and

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other factors (natural and intentional acts of terrorism), were enumerated and evaluated (Yacine *et al.,* 2002; Sivakumar, 2016). From the past, the aquatics have been exposed to toxic heavy metals (Karbassi *et al.,* 2007b). Industrialized world has laid a significant load of toxic heavy metals on the community and environment (Ucekaj *et al.,* 2004). Oil pollution is one of the most common types of environmental pollution (Gawalko *et al.,* 2001). Gasoline is a combination of 240 separate hydrocarbons most of which have varying degrees of toxicity to organisms and plants (Campbell *et al.,* 2000). There is always possibility for leakage of oil products to the environment due to leakage from tanks or pipes or spill of products during loading and fueling (Mizuike, 2013; Pazouki and Hasanidarabadi, 2017). In general, consumption of oil products in Iran is in such a condition that a vital need to save the products and prevent the losses is felt (Karbassi *et al.,* 2006). Similar studies on hydrocarbon release during fuel storage and transfer at gas stations have been carried out in many parts of the world. Such studies bring out various aspects of storage tanks. These aspects can be amount of evaporation, structural conditions of storage tanks, health and environmental effects and, even in more recent years, safety of storage tanks. Some of these studies have clearly brought out the adverse environmental health effects of evaporative hydrocarbons (Akland *et al.,* 1993; Hilpert *et al.,* 2015; Wallace *et al,* 1989), while others have attempted to bring out the right methods of measurements as well as chemical mass balances (Periago *et al.,* 1997, Levitin *et al.,* 2016; Watson *et al.,* 2003). It has been shown that spill frequencies can have direct effect on the mounts of vapor (Morgester *et al.,* 1992). Most of the studies imply that the amount of evaporation is less than 1% of the total storage capacity (Abdelmajeed *et al.,* 2009). For instance, Abdelmajeed *et al.,* (2009) showed that internal floating roof storage tanks in Khartoum would have an evaporation loss of about 0.5%. More recently, various types of software namely AERMOD and ALOHA are used to model the dispersion of VOCs under normal and accidental scenarios (Karbassi *et al.,* 2007). The results of such studies indicate that wind direction plays an important role in the dispersion of VOCs, while the danger zone mostly falls within the first 10-meter diameter of incident (Howari, 2015; Ashrafi *et al.,* 2012; Kumar *et al.,* 1993). This study investigates the emissions to water environment from oil products tanks which are automatically constructed in all structures required for loading of products onto oil tanker vessels, ships and trucks and in terminals fueled by special tankers. Given the above and location of the study area in Qeshm Island as well as the sensitive ecosystem of Suza city, where rare species of turtle are living in, modeling of various types of pollution, especially water pollution, has been considered as necessities of project construction in this study. The aim of the present study, which has been performed in 2015, is to bring out the speciation of metals in coastal waters of Qeshm Island in Iran.

MATERIALS AND METHODS

Comprehensive information is needed to estimate the amount of leakage of oil products from storage depots and oil transfer pipelines to the link spans. A visit was paid to the oil storage tanks of Ofogh-e Qeshm project in order to collect the required information and learn more about the tanks. To investigate the metal speciation, concentration of the elements in the Persian Gulf within the range of direct impact of the project was measured in 12 sampling stations (Fig. 1). Water samples were collected by Nansen bottles and transferred into 1L per acid cleaned bottles. Eh-pH was measured in-situ by portable Eh-pH meter. Water samples were passed through filters and they were concentrated over 50 times at 70 ^{o}C. Metal measurement was carried out by inductively coupled plasma (ICP). HSC software (enthalpy-entropy and heat capacity) was also used to bring out speciation of trace elements in the study area. Eh-pH diagram was obtained by entering the necessary data into the HSC software. These data included temperature, atmospheric pressure concentration of metals and Eh-pH values.

RESULTS AND DISCUSSION

Oil products depot project with all necessary structures is implemented to automatically load products into tanker vessels, ships and trucks. These tanks are one of the most important industrial facilities that are exposed to risks of toxic substances release, fire and explosion (Rao *et al.,* 2005). The terminal is also fueled by special tanks. A total of 25 tanks with a volume of about 324,000 cubic meters are used in this project. A variety of hydrocarbon materials including fuels such as gasoline, gasoil, heavy oil, kerosene and other oil products will be stored in these tanks.

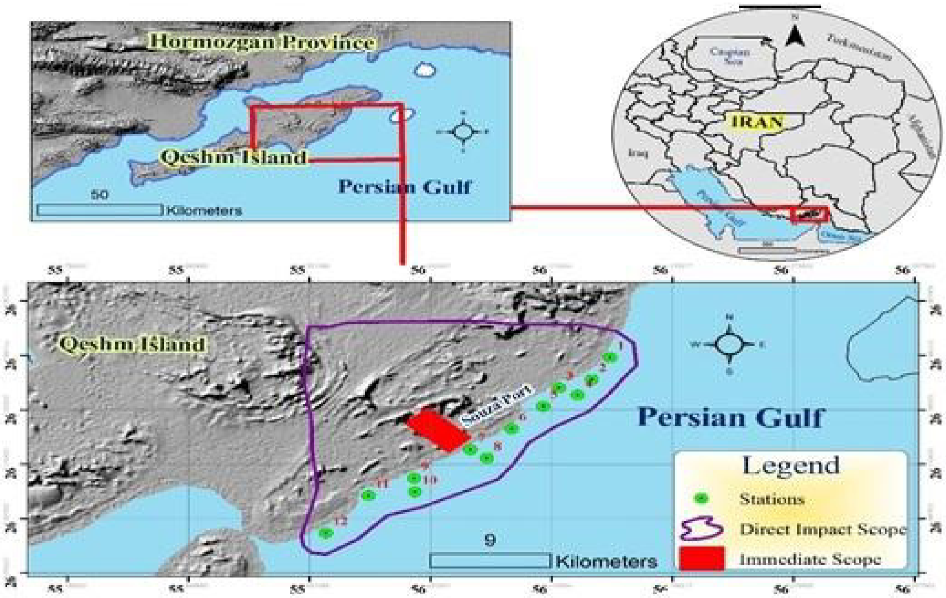

Fig. 1: The study area and water sampling stations

Table 1: Physicochemical specifications and concentrations of the elements in the Persian Gulf within the area opposite to Ofogh Project (Data are expressed in µg/L)

Station	Temperature (ºC)	Eh(Mv)	pH	Cu	Cd	Co	Mn	Ni	Pb	V	Zn
1	23.1	-67	7.9	25	15	19	74	43	20	49	30
2	23.2	-68	8.1	32	9	19	77	52	19	62	32
3	23.1	-67	8.1	29	12	21	70	51	12	60	28
4	23.1	-67	8	44	11	14	63	42	14	54	28
5	23.3	-63	8	39	17	13	89	49	17	57	28
6	23.4	-70	8.1	32	13	12	82	49	19	57	31
7	23.2	-68	7.9	35	12	12	80	47	17	58	30
8	23.2	-63	7.9	29	16	12	86	47	17	54	32
9	23.1	-67	8	22	12	14	80	47	20	54	30
10	23.2	-75	8.1	24	14	17	71	48	19	56	28
11	23.3	-69	8	27	11	19	75	48	14	56	29
12	23.1	-69	8	22	10	17	77	46	17	54	30
Minimum	23.1	-70	7.9	22	9	12	63	42	12	49	28
Maximum	23.4	-63	8.1	44	17	21	89	52	20	62	32
Mean	23.1	-67.75	8	30	12.6	15.7	77	47.4	15.4	55.9	29.9

Evaporation or leakage of hydrocarbons and their products from the storage tanks has become a special concern in recent years (Tepavitcharova *et al.,* 2010). Such tanks with the mentioned volume at a distance less than 2 km from the Persian Gulf as well as the extension of oil pipelines along the seabed can cause potential water pollution in case of leakage from the tanks and oil pipelines in oil platforms and this issue shows the necessity for modeling the speciation of elements in the Persian Gulf. In order to model the metal contents in the Persian Gulf, concentrations of the trace elements in the Persian Gulf within the range of direct impact of the project were determined in 12 stations. The results of sampling are provided in Table 1.

Table 1 shows the results of total concentration of heavy metals in each 12 stations. As Table 1 indicates, mean concentration of elements in water follows the pattern: Mn>V>Ni>Cu>Zn>Co. Zinc concentration varies between 28 to 32 µg/L with a mean value of 29.9 µg/L. The concentration of Pb varies between 12 µg/L in stations 3 to 20 µg/L in stations 1 and 9. Ni concentration ranges from 42 µg/L in stations 4 to

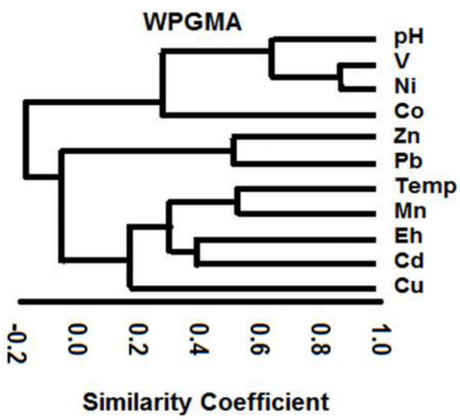

Fig. 2: Cluster analysis of elements in the Persian Gulf water

52 µg/L in station 2. Mn concentration varies from 63 µg/L in station 4 to 89 µg/L in station 5. Cobalt concentration is 12 µg/L in station 6 and 21 µg/L in stations 3. Cadmium concentration varies from 9 µg/L in stations 3 to 17 µg/L in station 5. Copper concentration ranges from 22 to 44 µg/L in various stations with a mean value of 30 µg/L. The aquatics environment of the Persian Gulf has been subjected to various degrees of toxic metals (Karbassi *et al.,* 2007). It is noticeable that mean temperature of water in the selected stations in the Persian Gulf is 23.1 ºC. The mean values for Eh-pH range from -67.75 to +8. Subsequently, multivariate statistical package (MVSP) software was used to determine the relationship amongst various parameters. Results of cluster analysis for various parameters in coastal waters of the Persian Gulf are shown in Fig. 2.

Quality of coastal water is undoubtedly impacted by the geology of Qeshm island as well as that of the Persian Gulf and finally by the human activities. Industrialized world has laid a significant load of toxic heavy metals on the community and environment (Ucekaj *et al.,* 2004). According to the cluster analysis, nickel and vanadium have the same source in the coastal water of Qeshm and are under control of pH. Since pH controls the concentrations of these elements, it may be concluded that presently there are not any oil pollutions in coastal water of Qeshm. Though oil pollution is one of the most common types of environmental pollution, its presence was not detected in the present study (Gawalko *et al.,* 2001). pH itself is controlled by geology. Various geologies in Qeshm island cause such extensive changes in coastal sediments (such as presence of limestone, salt domes and igneous rocks). Apart from the above three parameters, other elements and physicochemical parameters do not show any specific trend. Imbalance between the parameters may be due to anthropogenic activities. In this study, water desalination plants in Laft Village in Qeshm Island have been used. However, it may be stated that zinc and lead have similar behaviors, whereas temperature plays an effective role in controlling the concentration of manganese in the studied water. Other parameters such as Eh (mV), cadmium and copper do not show a meaningful trend. In addition to anthropogenic activities, the natural factors are also effective in water behavior and chemistry because in some parts of Qeshm Island there are accumulated materials and sediments and in some other parts, erosion is largely ruling (Karbassi and Pazoki, 2015). Furthermore, the cluster analysis shows that there are no meaningful relationships between Eh-pH in coastal water of Qeshm Island. The known Eh-Eh of the water cam be very effective in chemistry of elements and their future patterns, because solubility of elements in aquatic environments is a function of pH and Eh (Karbassi and Heidari, 2015). Reduced environments are the most dangerous places from environmental point of view because they lead to mobility of most elements and they also contribute to expansion of contaminated area while oxidation environments constitute the least dangerous places (Campbell *et al.,* 2000). Thus lack of correlation between the two parameters implies that Eh-pH does not simultaneously act in coastal water of Qeshm. As Eh value is close to zero (slightly negative), chemical forms of heavy metals are expected to be changed in coastal water of Qeshm in near future. Eh-pH diagrams were drawn and speciation of elements was carried out using HSC model. Eh-pH diagrams show the status of speciation of heavy elements within various ranges of Eh-pH. In HSC software, Eh-pH diagrams are drawn for X-H-O system. X symbolizes an element such as Cu or Mn. This model is the most important system to chemically explain the elements in aquatic environments. Eh-pH diagrams show the thermodynamic stability of all types of element species in solution phase of water. This stability is achieved in relation with performance of Eh-pH as well as electrochemical potential of water. Stability ranges are usually shown

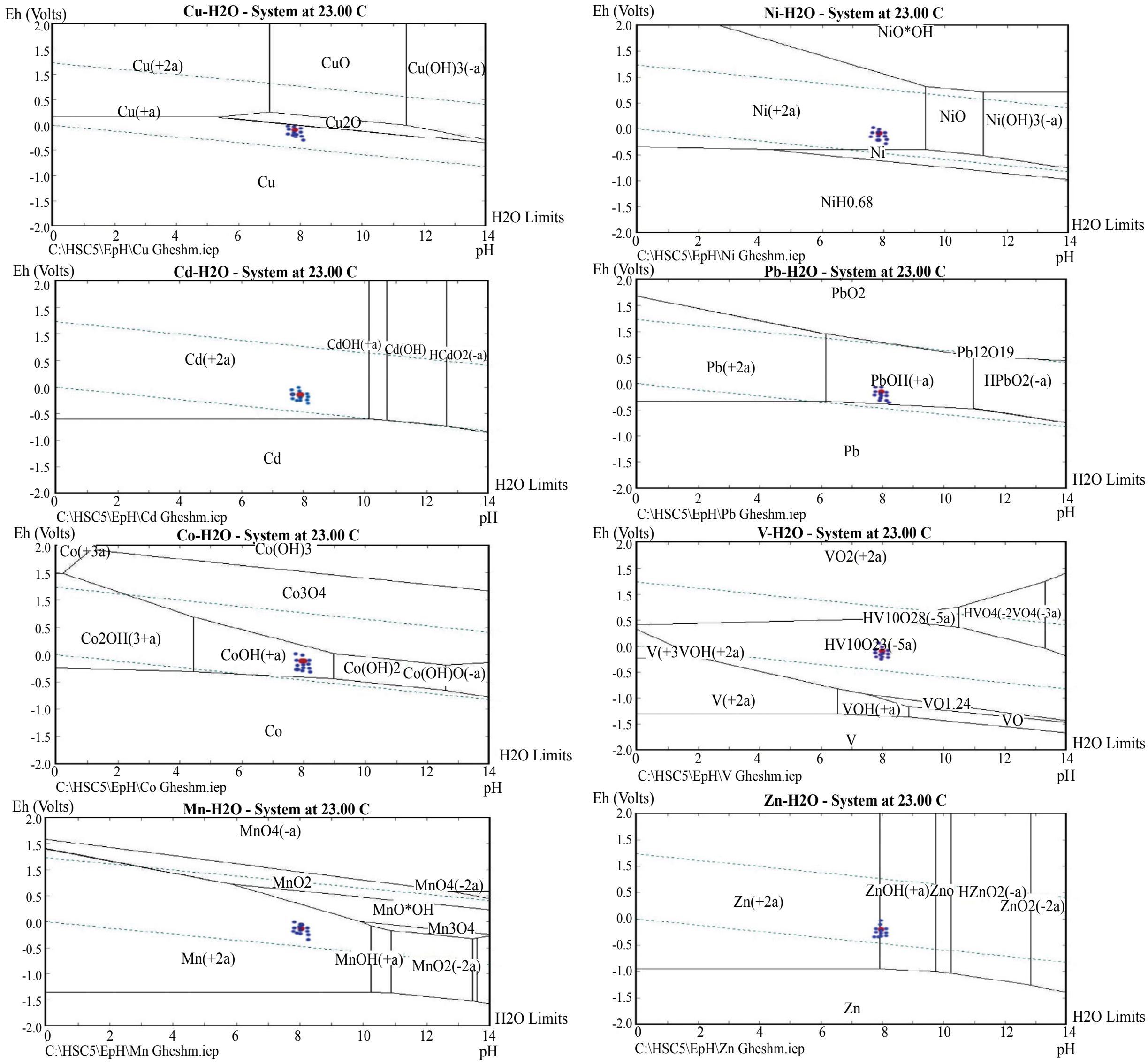

Fig. 3: Speciation of heavy metals (Cu, Cd, Co, Mn, Ni, Pb, V and Zn) in coastal waters of Qeshm Island

Table 2: Summary of speciation status of heavy elements within various ranges of Eh-pH in the Persian Gulf

	Element	Element species			
		Free ion	Hydroxide	Solid phase	Oxide
Water	Mn	✓			✓
	Cu	✓			✓
	Ni	✓	✓		✓
	Pb	✓	✓		✓
	Zn	✓	✓		
	Co		✓		
	V		✓		
	Cd	✓			

between two dotted lines of diagrams, and out of this range, the considered element is not stable and may be toxic to the aquatic environment. Diagrams of HSC model show that Cu and Cd may appear as free ions. Lead, manganese, cobalt, zinc and nickel are present in the Persian Gulf as PbOH, MnOH, ZnOH, CoOH and NiOH respectively. The speciation of Cu and Ni is in the form of Cu_2O and NiO respectively and vanadium is present in combination with hydrogen (Fig 3).

Since the studied heavy metals in all 12 sampling stations are located between the two lines of stability range and they are stable, there is no risk of pollution and toxicity in the environment at the present time. In this study, the results of speciation of the studied elements using HSCp software are shown in Table 2.

Although solid phase and free ion show the highest types of speciation, this trend may not be seen for manganese which is present as a free ion. The reason may be due to strong mobile tendency of manganese in aquatic environment.

CONCLUSION

The results of Eh-pH diagrams by HSE model showed that all the studied elements in all sampling stations are located between two lines of water stability range. Thus they are stable at present time, and there are no risks of pollution and toxicity in the environment. Due to the industrial activities, the Eh-pH values can be changed and eventually alter the speciation of metals. The present study provides the environmental base data before the initiation of oil terminal in Qeshm Island. However, it is recommended to continue the annual monitoring of key parameters several years after oil terminal operation. It is recommended to monitor V, Eh and pH on seasonal basis. It is vital to develop an online monitoring system to measure the Eh-pH values. This simple monitoring can efficiently provide useful information about any changes in status of an aquatic environment.

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CONFLICT OF INTEREST

The authors state that there is no conflict of interests concerning the publication of this manuscript.

ABBREVIATIONS

AERMOD	American Meteorological Society/ Environmental Protection Agency Regulatory Model
ALOHA	Areal Locations of Hazardous Atmospheres
Co	Cobalt
CoOH	Cobalt hydroxide
Cd	Cadmium
Cluster	It is a method that aims to bring out relations among parameters
Cu	Copper
Dendrogram	A tree diagram, especially one showing taxonomic relationships
Eh	Redox potential
Eh-pH	Diagrams that illustrate the fields of stability of chemical species
ICP	Inductively coupled plasma
HSC	Enthalpy-entropy and heat capacity
L	Liter
µg/L	Microgram per liter
Mn	Manganese
$Mn(OH)_2$	Manganese hydroxide
Monitoring	Processes and activities that characterize and monitor the quality of the environment
Mv	Millivolts
MVSP	Multivariate statistical package
Ni	Nickel
NiO	Nickel oxide
NiOH	Nickel hydroxide
°C	Celsius degree
Pb	Lead
PbOH	Lead hydroxide
pH	Alkalinity and acidity
Speciation	Refers to the distribution of an element amongst chemical species in a system
V	Vanadium
VOH	Vanadium hydroxide
VOC	Volatile organic carbon
Zn	Zinc
$Zn(OH)_2$	Zinc hydroxide

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