Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.20781

83 (2017) 272–276
July

Assessment of soil pollution by toxic metals and petrochemical compounds in western Libya

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Received 7 December 2016; Accepted 1 April 2017

ABSTRACT

The current study aims to assess soil contamination by toxic metals including titanium (Ti), beryllium (Be), tungsten (W), phosphorus (P) and vanadium (V) as well as other heavy metals. The soil samples were collected from Abu-Kammash in Libya which were exposed to petrochemical wastewater generated from the General Company of Chemical Industries (GCCI). The presence of hazardous materials was determined using inductively coupled plasma (ICP-Mass) spectrometry and gas chromatography–mass spectrometry (GC-MS). The results revealed that the soil samples obtained from 100 m of west and east Abu-Kammash were polluted with Ti (39 *vs.* 175 μg kg^{-1}), Be (219 *vs.* 421 μg kg^{-1}), W (0.015 *vs.* 0.041 μg kg^{-1}) and V (18.5 *vs.* 21.3 μg kg^{-1}). The concentration of heavy metal ions ranged from 18.5 μg kg^{-1} of vanadium (V) to 1120 μg kg^{-1} of zinc (Zn). Among the petrochemical compounds determined in this study, tentriacontane (C31H64), 3-methyl-2oxopropylfuran ($C_8H_{10}O_2$) and tertrapentacontane ($C_{54}H_{108}Br_2$) were the most frequently detected elements in the soil samples. The presence of these toxic elements in the environment could pose adverse effects on human health since they might be accumulated in plant tissue and later transmitted to humans via the food chain.

Keywords: Toxic elements; Soil; Petrochemical compounds; Abu-Kammash; GC-MS; ICP-mass

1. Introduction

The disposal of industrial wastes into the environment represents the main source of soil contamination by several toxic elements and compounds [1]. The petrochemical industry produces heavily contaminated wastewater which leads to the contamination of the environment [2,3]. The adverse effects of these hazardous materials on human health and the environment have been documented as well. On the other hand, heavy metals refer to a group of transition elements which play an important role as trace elements in sophisticated biochemical reactions [4,5]. However, some heavy metals ions have toxic effects on organisms. Examples of toxic metal ions include Hg, Cd, and Ag that form strong toxic complexes which make them too dangerous for any physiological function [6]. Heavy metals can be accumulated in plant tissues which can then be transmitted to humans via the food chain. This is a worrying fact. Akrivos et al. [7] indicated that zinc (Zn^{2+}), copper (Cu^{2+}), nickel (Ni^{2+}) and chromium (Cr^{3+}) affects plant growth and crop yields and are known to be cumulative toxins whereas lead (Pb^{2+}), cadmium (Cd^{2+}) and mercury (Hg^{2+}) are toxic to animals or human digestion of plants. These metals might even function as mutagens causing cancer [8].

On the other hand, petrochemical compounds in the environment pose serious risks to human health. These compounds have high toxicity and possess mutagenic as

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Presented at the First International Symposium on Materials, Electrochemistry and Environment (CIMEE 2016), 22–24 September 2016, Tripoli, Lebanon

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well as carcinogenetic properties. They may cause health problems to humans via the consumption of contaminated food. The main concern of these compounds lies in their ability to resist natural degradation and thus they are able to remain in the environment for long periods of time [9,10]. The information on soil contamination by heavy metals in the region investigated here has been unavailable since 40 years ago when the General Company of Chemical Industries (GCCI) was established. Therefore, the present work is the first study aimed at exploring the level of contamination by toxic substances found in the soil samples collected from the Abu-Kammash zone adjacent to the petrochemical wastes generated by GCCI. The toxic substances investigated in this work included titanium (Ti), barium (Ba), tungsten (W), phosphorus (P) and vanadium (V) as well as other heavy metals and hydrocarbon compounds.

2. Materials and methods

2.1. Study area

Abu-Kammash is an industrial area located on the westside of the capital city (Tripoli) (200 km) (Fig. 1). The General Company of Chemical Industries (GCCI) is the main company located at the Abu-Kammashzone. GCCI was established in the 1970s and consists of three units that produce 104,000 tonnes of Ethylene di-chloride, 60,000 tonnes of poly vinyl chloride (PVC), 50,000 tonnes of caustic soda and 45,000 tonnes of chlorine annually. In addition, the company also produces sodium carbonate, sodium hypochlorite and HCl. GCCI has four dumping sites. Two of them are located on the westside of the Abu-Kammash zone while another two are located on the east. The adjacent areas of GCCI at Abu-Kammash are cultivated with olive trees. The

Fig. 1. Google map of the study area.

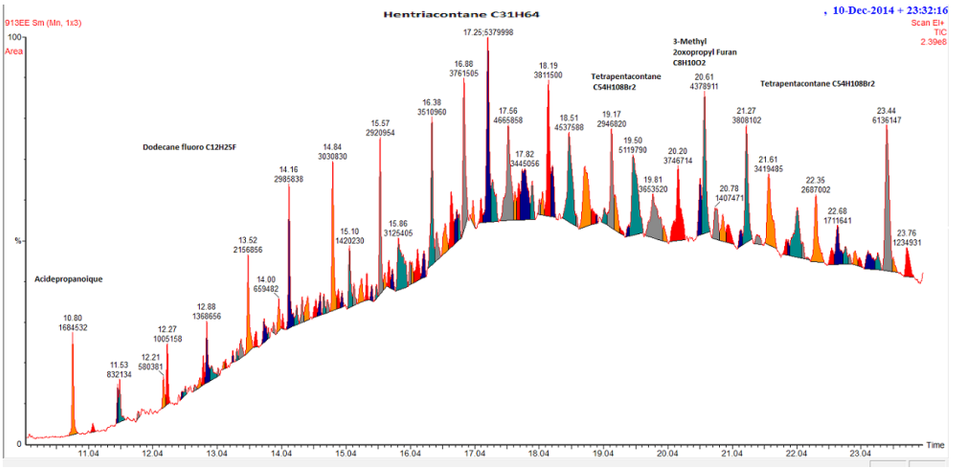

Fig. 2. Petrochemical compounds in soil around General Company of Chemical Industries (GCCI) at Abu-Kammash in Libya.

olives are commonly used by the people and represent a main part of the daily diet in the region.

2.2. Collection and analysis of soil samples

Seven surface soil samples (1 kg) were collected from the west and east of the Abu-Kammash zone with diameter areas measuring 100 m and 500 m, respectively. The control samples were collected from Zuwarah city (20 km away from the Abu-Kammash zone).

The toxic metal concentration for titanium (Ti), barium (Ba), tungsten (W), phosphorus (P) and vanadium (V) as well as zinc (Zn), nickel (Ni), chromium (Cr) and cobalt (Co) were determined from the soil samples using inductively coupled plasma (ICP-Mass) spectrometry according to APHA [11] and Moor et al. [12] (Table 1).

In order to determine the presence of hydrocarbon compounds, the soil samples collected from 100 m east of GCCI were sent to the International Centre of Environmental Technologies in Tunisia. The samples were selected for the analysis of hydrocarbon compounds because they exhibited a higher content of toxic metals than those collected from the westside of the Abu-Kammash zone.

Table 1
Qualitative analysis of heavy metals using ICP

Toxic metal	Wave length (nm)	Black Sample (ppb)	Looking Sample (ppb)
Al	396.153	2.5310^3	5.30×10^3
Co	228.616	2.67	37.9
Cr	267.716	14.4	24.3
Zn	206.200	37.7	1.12×10^3
Ni	231.604	8.41	16.2
V	290.880	8.61	15.3
Ti	334.940	77.1	157
Ba	233.527	23.3	392
P	213.617	No standard	No standard
W	207.912	No standard	No standard

Aluminium (Al); Cobalt (Co); Chromium (Cr); Zinc (Zn); Nickel (Ni); Vanadium (V); Titanium (Ti); Barium (Ba); Phosphorus (P); Tungsten (W).

3. Results and discussion

The presence of toxic metals in the environment represents a real hazard towards human health. This is because they have high potential to cause several diseases. It has been established that the presence of heavy metals in the environment, even in low concentrations, is able to cause a multitude of diseases, respiratory problems and several kinds of cancer [4,5]. In the present study, the concentrations of heavy metals in soil samples collected from the Abu-Kammash zone were determined to understand the role of the factory in the contamination of the environment and also to estimate the levels of these metals in the surrounding soil. The results are illustrated in Table 2.

It can be noted that the concentrations of heavy metals of the soil located at the west and east (100 m) side of GCCI were high. The highest concentrations of toxic metals were recorded for Al in soil samples collected from the east side of GCCI (8300 ppb) followed by Zn in samples collected from both east and west regions of GCCI (1120 ppb). The presence of heavy metals which includes Co, Cr and Ni were detected in the soil samples. Co concentrations ranged from 2.67 to 41 ppb while Cr concentrations ranged from 8.3 to 43.3 ppb. ICP-Mass Spectrometry was very accurate in detecting the presence of toxic metals in soil samples which included V, Ti, Be and W even at very low concentrations. These metals ranged from less than detection limits (0.0001 ppb) to detectable concentrations. Concentrations of V ions ranged from 0.001 to 21.3 ppb. Be metal was available at high concentrations in comparison to Ti and W. The maximum concentrations of Be was 421 ppb while the maximum concentration was 175 ppb for Ti. The concentrations of W and P were quite low as the highest concentrations were 0.064 and 0.041 ppb respectively. This study is the first study which investigated the presence of toxic metals in soil located near GCCI. However, a previous study conducted

Table 2
Concentrations of toxic metals in soil samples collected from Abu-Kammash zone

Toxic metal	Concentrations of metals in soil samples (ppb)				
	West of GCCI		East of GCCI		
	<100 m	500 m	<100 m	500 m	Control sample
Al	945 ± 0.34	140 ± 5.18	8300 ± 34.21	253 ± 8.12	100
Co	41 ± 0.61	6.23 ± 2.11	37.9 ± 4.02	2.67 ± 0.91	0.13
Cr	37.45 ± 2.34	8.3 ± 2.55	43.3 ± 3.33	14.4 ± 1.24	2.14
Zn	1120 ± 16.89	83.5 ± 22.11	1120 ± 20.42	37.7 ± 3.34	5.17
Ni	27.96 ± 2.14	1.41 ± 0.21	32.2 ± 5.17	8.41 ± 3.21	1.12
V	18.5 ± 3.61	0.001 ± 0.00	21.3 ± 3.33	8.61 ± 1.02	2.33
Ti	93 ± 6.19	0.001 ± 0.00	175 ± 4.27	77.1 ± 4.14	0.0001
Ba	219 ± 22.71	<0.0001	421 ± 8.81	23.3 ± 7.34	0.000
P	0.064 ± 0.01	<0.0001	0.0187 ± 0.001	<0.0001	0.000
W	0.015 ± 0.00	<0.0001	0.041 ± 0.001	<0.0001	0.000

by Banana et al. [15] revealed the presence of high concentrations of Hg in soil and plant samples which were also collected from the GCCI zone. The effects of heavy metals on human health have been reported extensively. Many of these metals have the ability to cause diseases due to their potential to react with the sulfhydral group (–SH) and bind protein molecules by forming bridges between the groups. The cellular metabolism is disrupted and the microorganism dies due to the deactivation of enzymes [13,14]. Studies confirmed that heavy metals might have a direct influence on human health by impairing mental and neurological function, influencing neurotransmitter production and utilisation and altering numerous metabolic body processes. The presence of heavy metals in the human system might lead to induced impairment and dysfunction of the cardiovascular system, detoxification of endocrine pathways and energy production pathways and enzymes. It could also damage the gastrointestinal system, immune system, nervous (central and peripheral) systems, reproductive system and even the urinary system [15,16]. Alinovi et al. [17] investigated the toxicity of cobalt (CoNPs) and titanium oxide nanoparticles (TiNPs) on two primary endothelial cell lines derived from the human aorta (HAECs) and the human umbilical vein (HUVECs) by comparing oxidative stress, cell viability, the release of chemokines during NP exposure and the expression of adhesion molecules. Both NPs increased adhesion molecule (ICAM-1, VCAM-1, E-selectin) *m*RNA and protein levels and the release of monocyte chemoattractant protein-1 (MCP-1) and interleukin 8 (IL-8). The exposure towards Becan lead to the development of acute, necrotizing, hemorrhagic, exudative pneumonitis and intra-alveolar fibrosis. It has been reported that tungsten concentrations are strongly associated with an increase in the prevalence of stroke [18].

The list of petrochemical compounds determined in this study is presented in Table 3. Among several petrochemical compounds detected in the soil, Hentriacontane ($C_{31}H_{64}$) was the most prevalent followed by 3-méthyl-2oxopropylfuran ($C_8H_{10}O_2$) and Tertrapentacontane ($C_{54}H_{108}Br_2$) (Fig. 1). These compounds have adverse effects on human health since they exhibit carcinogenic and mutagenic properties [19]. It has been reported that the soil contaminated with petroleum compounds should be excluded from crops and subjected to reclamation processes [20]. However, the area investigated in this study is surrounded by olive trees. These findings imply that the people who consume the olive oil produced in this particular area may be subjected to the risk of cancer.

Table 3
Hydrocarbon compounds analysed by GC/MS

Compound	Chemical Formula	Retention time
Dodecane Fluoride	$C_{12}H_{25}F$	11.50–14.7
Hentriacontane	$C_{31}H_{64}$	14.84–18.20
Tertrapentacontane	$C_{54}H_{108}Br_2$	18.51–20.2
3-methyl-2oxopropylfuran	$C_8H_{10}O_2$	20.6
Tertrapentacontane	$C_{54}H_{108}Br_2$	20.3–23.44
Pentadecane	$C_{15}H_{32}$	

4. Conclusion

The adjacent area of GCCI at Abu-Kammash, Libya is contaminated with several toxic elements and petrochemical compounds. The concentrations of toxic metals were low but the concern lies in their accumulation in plants which may possibly be transmitted to humans via the food chain. Therefore, the soil should be not be used for agriculture until it is properly treated in order to ensure human health.

Acknowledgments

The authors would like to thank the Environmental Research Centre in Zwara for allowing them to use the laboratories and for providing support during the research period.

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