World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:11, No:5, 2017

Human Health Risk Assessment from Metals Present in a Soil Contaminated by Crude Oil

M. A. Stoian, D. M. Cocarta, A. Badea

Open Science Index, Environmental and Ecological Engineering Vol:11, No:5, 2017 publications.waset.org/10007768.pdf

***Abstract*—**The main sources of soil pollution due to petroleum contaminants are industrial processes involve crude oil. Soil polluted with crude oil is toxic for plants, animals, and humans. Human exposure to the contaminated soil occurs through different exposure pathways: Soil ingestion, diet, inhalation, and dermal contact. The present study research is focused on soil contamination with heavy metals as a consequence of soil pollution with petroleum products. Human exposure pathways considered are: Accidentally ingestion of contaminated soil and dermal contact. The purpose of the paper is to identify the human health risk (carcinogenic risk) from soil contaminated with heavy metals. The human exposure and risk were evaluated for five contaminants of concern of the eleven which were identified in soil. Two soil samples were collected from a bioremediation platform from Muntenia Region of Romania. The soil deposited on the bioremediation platform was contaminated through extraction and oil processing. For the research work, two average soil samples from two different plots were analyzed: The first one was slightly contaminated with petroleum products (Total Petroleum Hydrocarbons (TPH) in soil was 1420 mg/kg$_{d.w.}$), while the second one was highly contaminated (TPH in soil was 24306 mg/kg$_{d.w.}$). In order to evaluate risks posed by heavy metals due soil pollution with petroleum products, five metals known as carcinogenic were investigated: Arsenic (As), Cadmium (Cd), Chromium^{VI} (Cr^{VI}), Nickel (Ni), and Lead (Pb). Results of the chemical analysis performed on samples collected from the contaminated soil evidence soil contamination with heavy metals as following: As in Site 1 = 6.96 mg/kg$_{d.w}$; As in Site 2 = 11.62 mg/kg$_{d.w}$, Cd in Site 1 = 0.9 mg/kg$_{d.w}$; Cd in Site 2 = 1 mg/kg$_{d.w}$; Cr^{VI} was 0.1 mg/kg$_{d.w}$ for both sites; Ni in Site 1 = 37.00 mg/kg$_{d.w}$; Ni in Site 2 = 42.46 mg/kg$_{d.w}$; Pb in Site 1 = 34.67 mg/kg$_{d.w}$; Pb in Site 2 = 120.44 mg/kg$_{d.w}$. The concentrations for these metals exceed the normal values established in the Romanian regulation, but are smaller than the alert level for a less sensitive use of soil (industrial). Although, the concentrations do not exceed the thresholds, the next step was to assess the human health risk posed by soil contamination with these heavy metals. Results for risk were compared with the acceptable one (10^{-6}, according to World Human Organization). As, expected, the highest risk was identified for the soil with a higher degree of contamination: Individual Risk (IR) was 1.11×10^{-5} compared with 8.61×10^{-6}.

***Keywords*—**Carcinogenic risk, heavy metals, human health risk assessment, soil pollution.

I. Introduction

CRUDE oil and petroleum products have harmful effect on environment. According data provided by the European Environment Agency in 2015, at the European level, there are two categories sources of soil pollution: oil industry (14.1 %) and accidental oil spills (2.1 %) [1]. Soil polluted with crude oil and others petroleum products affect all the elements involved in natural life cycle – atmosphere, waters, and biosphere [2]. The chemical compounds which characterize this type of pollution are TPH and metals [3]. According to United States Environmental Protection Agency (U.S. EPA), the individual contaminants of TPH and metals are known as contaminants of concern (COCs). The TPH group contains volatile and semivolatile organic compounds (VOCs, SVOCs), like BTEX (benzene, toluene, ethylbenzene, xylene) and PAHs. COCs from metals category are: As, Cd, Chromium (Total Chromium and Hexavalent Chromium – Cr^{VI}), Pb, Ni, and Zinc (Zn) [4]. Among the contaminants listed above, there are compounds from soil polluted with crude oil or petroleum products that could negatively affect human health. There are different methods for assessing the risks associated with these hazards [5]. According to U.S. EPA, human health risk assessment implies the following steps: Hazard identification, dose-response assessment, exposure assessment and risk characterization [6]. Human health risk assessment presumes that a scenario is established, concentrations of chemicals in the contaminated soil are identified and specific equations for each exposure pathway are used [7]. Metals from contaminated soil can affect human health through accidentally ingestion of soil, diet, inhalation and dermal contact. Metals generally are not volatile chemicals and they are transported by water and by air through dust [8]. The dust is settled on grass, crops, vegetable or fruit and thus the human diet is contaminated. Moreover, the contaminated dust can reach on skin and people are exposed to heavy metals by dermal contact [9].

The most important pathway of exposure associated to soil contaminated with metals is ingestion of vegetable grown in polluted areas [10]. Risks to humans associated to exposure to metals are classified as carcinogenic or non-carcinogenic. According to Twelfth Edition of Report of Carcinogens, As, Cd, Cr^{VI}, Ni, and Pb are human carcinogens [11]. Furthermore, metals affect also the neurological, gastrointestinal, cardiovascular, immunological, epidermal systems and others [12].

II. Material and Methods

A. Soil Sampling and Chemical Analyses

The investigated soil was accidentally contaminated with crude oil. After of being excavated from two different plots, the contaminated soil was deposited on a concrete platform in order to prevent accidental leaks of chemicals into soil.

M. A. Stoian and D. M. Cocarta are with the University Politehnica of Bucharest, Faculty of Power Engineering, Department of Power Engineering and Use, Splaiul Independentei 313, Bucharest, Romania (e-mail: stoian_mihaela20@ yahoo.com, dmcocarta@gmail.com).

A. Badea is with Academy of Romanian Scientists, Bucharest, Romania (e-mail: adrian.badea@energ.pub.ro).

Successively, representative samples were collected for soil characterization. The soil samples were transported to the laboratory for chemical analysis. The chemical analyses were performed according to national and international Standard Methods in force (Table I).

TABLE I
STANDARD METHODS USE FOR CHEMICAL ANALYSES

Contaminant	Standard Methods
Arsenic (As)	ISO 20280:2007
Cadmium (Cd)	SR ISO 11047:1999
Total Chromium (Cr)	SR ISO 11047:1999
Hexavalent Chromium (Cr^{VI})	EPA 7196A:1192
Copper (Cu)	SR ISO 11047:1999
Iron (Fe)	SR ISO 11047:1999
Manganese (Mn)	SR ISO 11047:1999
Mercury (Hg)	ISO 16772:2004
Nickel (Ni)	SR ISO 11047:1999
Lead (Pb)	SR ISO 11047:1999
Zinc (Zn)	SR ISO 11047:1999

The obtained results revealed a less contaminated soil (Site 1) and intense contaminated soil (Site 2). The chemical concentrations of metals identified in soil polluted with crude oil are presented in Table II.

TABLE II
MEASURED CHEMICAL CONCENTRATIONS

Contaminant	Soil sample no 1 (mg/kg$_{d.w.}$)	Soil sample 2 (mg/kg$_{d.w.}$)
As	6.96	11.62
Cd	0.08	1.00
Cr	72.08	116.31
CrVI	0.10	0.10
Cu	35.30	64.91
Fe	3.88	4.289
Mn	921.35	921.38
Hg	0.793	0.497
Ni	37.00	42.46
Pb	34.67	120.44
Zn	108.32	320.60

An important aspect in case of soil contaminated with crude oil is the level of concentration of TPHs in soil. In this regard, in the framework of the present study, we analyzed the relation between measured chemical concentrations of metals and Total Petroleum Hydrocarbons (TPHs). Concerning the level of contamination with TPHs in soil, the chemical analysis revealed that Soil sample no 1 is characterized by a level of contamination equal with 1420 mg/kg$_{d.w}$, while in case of Soil sample no 2 the contamination with TPHs is 24306 mg/kg$_{d.w.}$ (Fig. 1). Heavy metals concentrations into soil for both analyzed soil samples are presented in Fig. 2. In both figures, the concentration of each chemical is higher for Soil sample no 2 than for Soil sample no 1. Additionally, it can be noticed that the high level of TPHs in contaminated soil with crude oil involves the increasing of metals concentrations.

B. Legislative Aspects

For the assessment of soil contamination degree, the identified concentrations of pollutants in soil are compared with the acceptable thresholds of each country. In Romania, the limit levels are specified in Ministerial Order (M.O.) 756/1997 [13]. The national regulation established three different thresholds: normal, alert threshold and intervention threshold. Alert and intervention thresholds depend on the type of land use: agricultural and industrial. The present study considered the industrial use as the excavated soil was from an industrial area. Accordingly, the human exposure to the contaminated soils occurs through accidentally soil ingestion and dermal contact. In Table III are presented the national thresholds for each chemical identified in investigated soil.

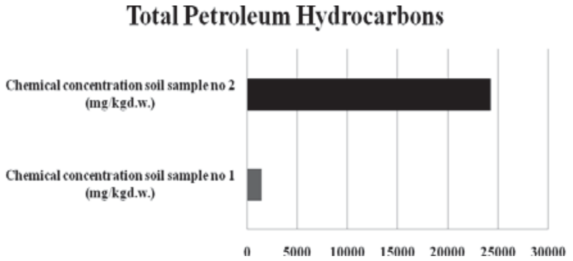

Fig. 1 TPHs concentration in soil

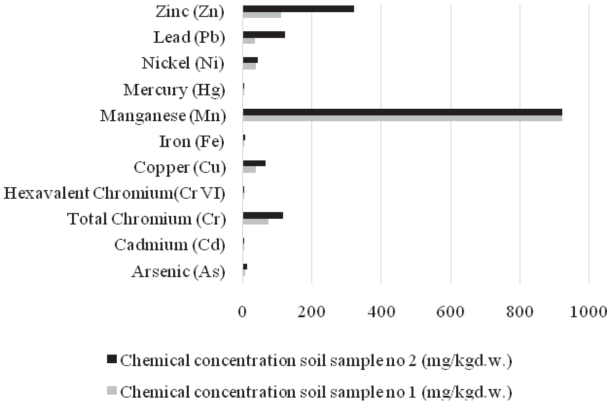

Fig. 2 Heavy metals concentrations in soil

TABLE III
THRESHOLD VALUES ACCORDING TO M.O. 756/1997

Contaminant	Normal value (mg/kg $_{d.w.}$)	Alert thresholds (mg/kg $_{d.w.}$)	Intervention thresholds (mg/kg $_{d.w.}$)
As	5	25	50
Cd	1	5	10
Cr	30	300	600
Cr^{VI}	1	10	20
Cu	20	250	500
Fe	-*	-*	-*
Mn	900	2000	4000
Hg	0.1	4	10
Ni	20	200	500
Pb	20	250	1000
Zn	100	700	1500

*Not Available Data

The identified concentration levels for each metal exceed the Normal Value established in M.O. 756/1997 for both soil samples (Fig. 3).

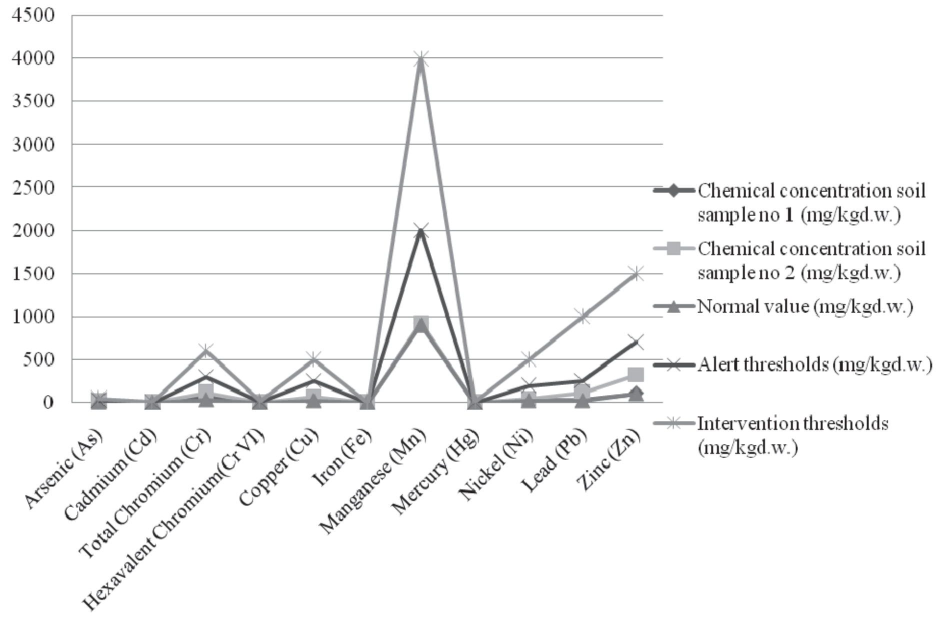

Fig. 3 Measured chemical concentrations (Site 1, Site 2) and the regulated values (M.O. 756/1997)

The exceeding of regulated values conducted to the necessity for the development of the human health risk assessment from the contaminated soils.

C. Human Health Risk Assessment

Human health risk assessment aims to identify and evaluate the possible effects on people health in case of their exposure to contaminants [6]. In the framework of the present study was considered the industrial use of soil, and the two pathways of exposure to metals: soil ingestion and dermal contact. The risk was assessed for the adult's exposure. The parameters that allowed to assess risk are presented in Table IV.

TABLE IV
COMMON PARAMETERS OF THE EXPOSURE SCENARIO

Parameters	Unit	Adults
Age (A)	years	70
Body weight (BW)	kg	70
Exposure frequency (EF)	days/year	30
Exposure duration (ED)	years	21
Average Time (AT)	days	25550

The chosen values of the considered parameters are based on general data used by convention by U.S. EPA and they are kept constant in order to minimize the error for dose estimation [14]. Through dose is measured the exposure to contaminants, which occurs through different pathways of exposure [15]. Doses were calculated using equations provided by U.S. EPA for each considered exposure pathway.

The dose associated to accidentally ingestion of contaminated soil was calculated using (1):

$$D_{si}(mg/kg/day) = (CS \times IR \times CF \times FI \times EF \times ED)/(BW \times AT) \quad (1)$$

where: CS – Chemical Concentration in Soil (mg/kg), IR – Ingestion Rate (mg_{soil}/day), CF – Conversion Factor (10^{-6} kg/mg), FI – Fraction Ingested from Contaminated Source (unitless), EF – Exposure Frequency (days/year), ED – Exposure Duration (years), BW – Body Weight (kg), AT – Averaging Time (days).

Using (2), we estimate the exposure through dermal contact:

$$D_{dc}(mg/kg/day) = (CS \times CF \times SA \times AF \times ABS \times EF \times ED)/(BW \times AT) \quad (2)$$

where CS – Chemical Concentration in Soil (mg/kg), , CF – Conversion Factor (10^{-6} kg/mg), SA – Skin Surface Area Available to Contact (cm^2/event), AF – Soil to Skin Adherence Factor (mg/cm^2), EF – Exposure Frequency (days/year), ED – Exposure Duration (years), BW – Body Weight (kg), AT – Averaging Time (days) [14].

Some parameters considered in doses estimation depends on history of the sites, type of contaminants or human behavior [16].

The effect of the absorbed dose could induce risks to humans that could be carcinogenic or noncarcinogenic and depends of contaminants concentrations in soil and cancer potencies of individual contaminants. The cancer potency is quantified by Slope Factor [17]. Concerning the contaminants analyzed in the present paper study, five of these are known as human carcinogenic; their Slope Factors are presented in the following table (Table V) [18]-[20].

The values for Slope Factors are the same for both pathways of exposure considered in the scenario of this paper study (ingestion of soil and dermal contact), according to OEHHA (Office of Environmental Health Hazard Assessment) [21].

Carcinogenic risk estimations involve multiplying the chronic daily intake - CDI (estimated doses for soil ingestion or for dermal contact) with Slope Factor - SF. Using (3) we calculated the human health risk considering two exposure pathways [22].

$$Carcinogenic\_Risk = CDI(mg/kg/day) \times SF(mg/kg/zi)^{-1}(a\,dimensional) \quad (3)$$

TABLE V
SLOPE FACTORS FOR IDENTIFIED METALS IN THE CONTAMINATED SOIL

Contaminants	Slope Factor $(mg/kg/day)^{-1}$
As	1.50×10^{0}
Cd	1.50×10^{1}
Cr^{VI}	4.20×10^{-1}
Ni	9.10×10^{-1}
Pb	8.50×10^{-3}

III. RESULTS AND DISCUSSION

Carcinogenic risk related to human exposure to soil contaminated with crude oil (particularly contamination with heavy metals due crude oil pollution) was assessed for the two sites from where the soil samples were coming. The IR assessed in case of the first site (Site 1) was 8.61×10^{-6}, while for the second site was 1.11×10^{-5} (Site 2). Both values exceeded the acceptable risk (10^{-6} suggested by the World Health Organization – WHO), but the risk is higher in case of the second site. The obtained results concerning the human carcinogenic risk, specific to each exposure pathways and considering every single carcinogenic contaminant are presented in the following table (Table VI).

TABLE VI
IR DUE TO SOIL INGESTION AND DERMAL CONTACT EXPOSURE PATHWAYS

	Contaminant	IR due soil ingestion	IR due dermal contact
Site 1	As	5.25×10^{-9}	1.94×10^{-6}
	Cd	1.43×10^{-8}	6.28×10^{-9}
	Cr^{VI}	4.44×10^{-10}	1.95×10^{-9}
	Ni	3.56×10^{-7}	6.27×10^{-6}
	Pb	3.11×10^{-9}	1.37×10^{-8}
	Contaminant	IR due soil ingestion	IR due dermal contact
Site 2	As	8.77×10^{-9}	3.24×10^{-6}
	Cd	1.59×10^{-7}	6.98×10^{-8}
	Cr^{VI}	4.44×10^{-10}	1.95×10^{-9}
	Ni	4.08×10^{-7}	7.19×10^{-6}
	Pb	1.08×10^{-8}	4.76×10^{-8}

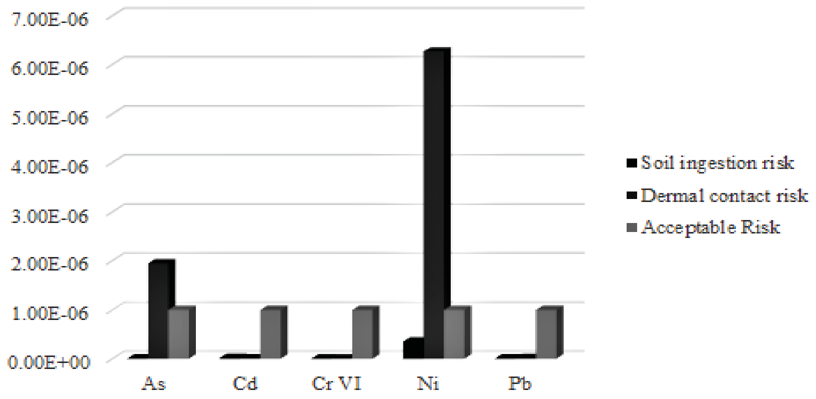

Fig. 4 (a) IR related to the specific exposure pathways (Site 1)

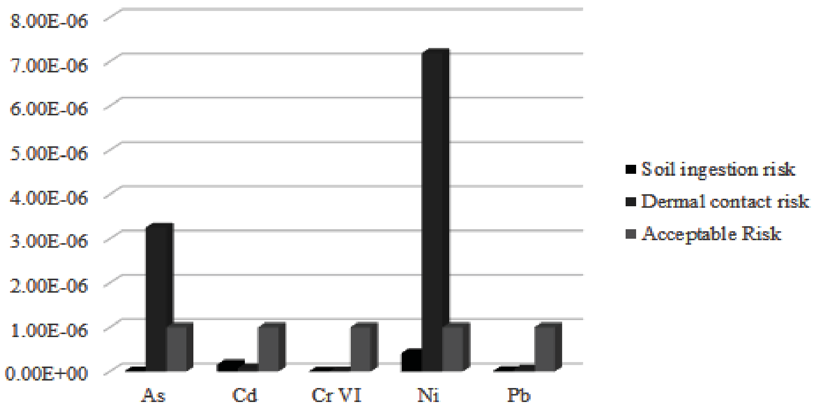

Fig. 4 (b) IR related to the specific exposure pathways (Site 2)

In order to identify the most relevant hazard related to a specific compound or exposure pathway, we evaluated the obtained results considering also every single contaminant and the specific exposure pathways. It was observed that for both sites the exposure through soil ingestion do not lead to an overcome of the acceptable risk. Concerning the exposure through dermal contact, the carcinogenic risk due to the presence in soil of As and Ni for both sites was observed (Figs. 4 (a) and (b)); in both study cases, the IR for these contaminants are overcoming the acceptable risk.

Open Science Index, Environmental and Ecological Engineering Vol:11, No:5, 2017 publications.waset.org/10007768.pdf

If we are evaluating the obtained results for both sites, it could be observed that the IR determined for Site 2 (considering the contamination with heavy metals due crude oil pollution) is higher comparing to Site 1: 1.11×10^{-5} respect to 8.61×10^{-6}. It is evidenced in this way a correlation with regard to crude oil pollution and risks induced by heavy metals because the contamination generated by this kind of pollution.

Concerning the individual exposure pathways and assessed risk could be noticed that in case of human exposure through accidentally soil ingestion, the identified risk does not exceed the acceptable one even if it is about the site for which was determined higher or less crude oil contamination: 3.79×10^{-7} for Site 1 and 5.87×10^{-7} for Site 2. So, these determined IR do not exceed the individual acceptable risk of 10^{-6}, which means that the carcinogenic risk is given preponderantly by human exposure through dermal contact.

In order to determine the carcinogenic risk to which population can be exposed during the entire life, it is necessary to estimate the IR induced by the exposure to all metals identified in soil and known as carcinogenic. So, the IR takes into account in this case both considered exposure pathways and all the investigated chemical compounds as evidenced in the next table (Table VII).

TABLE VII
IR FOR EACH CONTAMINANT AND FOR BOTH SOIL SITES

Contaminant	Site 1	Site 2
As	1.95×10^{-6}	3.25×10^{-6}
Cd	2.05×10^{-8}	2.28×10^{-7}
Cr ^{VI}	2.40×10^{-9}	2.40×10^{-9}
Ni	6.62×10^{-6}	7.60×10^{-6}
Pb	1.68×10^{-8}	5.85×10^{-8}
As; Cd; Cr ^{VI}; Ni; Pb	8.61×10^{-6}	1.11×10^{-5}

In order to evidence the IR assessed for both sites, the obtained results were compared with the acceptable risk as shown in Fig. 5. It could be noticed that even if it was about higher or slower contamination of soil with crude oil, the heavy metals presence in soil generated risks above the acceptable one.

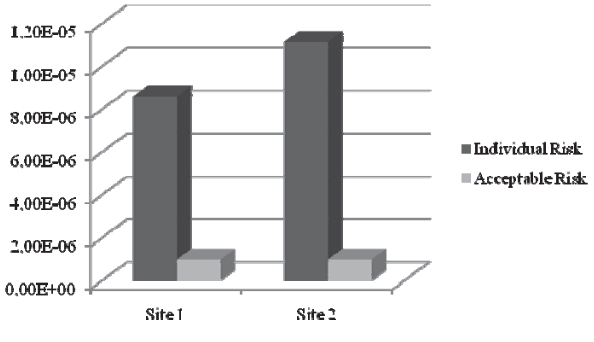

Fig. 5 IR for Site 1 and Site 2 comparing with the acceptable IR

IV. CONCLUSIONS

Results illustrated in the present work evidenced that the human health risk could be higher that the acceptable one even if the concentrations for metals in soil samples do not exceed the alert or intervention thresholds (for less sensitive use of soil in the presented study cases). The main important exposure pathway between the analyzed exposure pathways was the dermal contact, which driven to the carcinogenic effects on population health. The obtained results showed that, even if the contamination degree with heavy metals in soil was not so high, from the remediation point of view, a special attention must be given also to As and Ni. For both cases, the IR was driven by As (IR Site 1 = 1.95×10^{-6} and IR Site 2 = 3.25×10^{-6}) and Ni (IR Site 1 = $6.62\times10^{-6}$and IR Site 2 = 7.6×10^{-6}). The results showed that soil from both sites has a harmful effect on human health, although the contaminants concentrations are not so high. With this regard, the soil must be proposed for remediation.

ACKNOWLEDGMENT

The work was supported by the PNII-RU-TE2014-4-2348/ REMPET project, ctr. no 354/01.10.2015, SOP IEC POSCCE-A2-O2.1.2.-2009-2, RECOLAND ID519, SMIS-CSNR: 11982, ctr. 182/18.06.2010 and the Erasmus+Programme, EnvyJobs project, contract no 2015-1-RO01-KA203-015089 and EduLabFrame project, contract no 2014-1-RO01-KA203-002986.

REFERENCES

[1] EEA, “Progress in management of contaminated sites”, *European Environment Agency*, Sep. 2015.

[2] C. Cojocaru, D.M. Cocârţă, I.A. Istrate, and I. Crețescu, “Graphical Methodology of Global Pollution Index for the Environmental Impact Assessment Using Two Environmental Components”, *Sustenability*, vol. 9 (4), Apr. 2017.

[3] J.Pinedo, R. Ibanez, J.P.A. Lijzen, and A. Irabien, “Assessment of soil pollution based on total petroleum hydrocarbons and individual oil substances”, *Journal of Environmental Management*, vol. 130, pp. 72-79, Nov. 2013.

[4] T. Joy, and Ch. VanCantfort, “User Guide for Risk Assessment of Petroleum Releases”, *West Virginia Division of Environmental Protection Office of Environmental Remediation*, Nov. 1999.

[5] D.M. Cocârţă, S. Neamțu, and A.M. Reșetar Deac, “Carcinogenic risk evaluation for human health risk assessment from soils contaminated with heavy metals”, *International Journal of Environmental Science and Technology*, vol. 13 (8), pp. 2025-2036, Aug. 2016.

[6] U.S. EPA, “Risk Assessment - Human Health Risk Assessment*”, United States Environmental Protection Agency*, Oct. 2016.

[7] U.S. EPA, “Risk Assessment - Conducting a Human Health Risk Assessment*”, United States Environmental Protection Agency*, Jul. 2016.

[8] S. Gupta, P. Pandotra, A.P. Gupta, J.K. Dhar, G. Sharma, G. Ram, M.K. Husain, and Y.S. Bedi, “Volatile (As and Hg) and non-volatile (Pb and Cd) toxic heavy metals analysis in rhizome of Zingiber officinale collected from different locations of North Western Himalayas by Atomic Absorption Spectroscopy”, *Food and Chemical Toxicology*, vol. 48 (10), Jul. 2010.

[9] H.H. Li, L.J. Chen, l. Yu, Z.b. Guo, C.Q. Shan, J.Q. Lin, Y.g. Gu, Z.B. Yang, Y.X. Yang, J.R. Shao, X.M. Zhu, and Z. Cheng, “Pollution characteristics and risk assessment of human exposure to oral bioaccessibility of heavy metals via urban street dusts from different functional areas in Chengdu, China”, *The Science of the Total Environment*, vol. 586, pp. 1076-1084 Feb. 2017.

[10] S. Ata1, S. Tayyab1 and A. Rasool1, “Analysis Of Non-Volatile Toxic Heavy Metals (Cd, Pb, Cu,Cr And Zn) In ALLIUM SATIVUM (Garlic) And Soil Samples ,Collected From Different Locations Of Punjab, Pakistan By Atomic Absorption Spectroscopy”, *EDP Science*, vol. 1, Apr. 2013.

[11] R. Goyer, and M. Golub, “Issue Paper on the Human Health Effects of

Metals", *U.S. Environmental Protection Agency Risk Assessment Forum*, Draft, Aug. 2003.

[12] National Toxicology Program, "Report of Carcinogens", *U.S. Department of Health and Human Services,* Twelfth Edition, 2011.

[13] M.O. 1997*,* "Ministry Order No. 756 from November 3, 1997 for approval of Regulation concerning environmental pollution assessment", *Official Monitor,* No. 303/6, Nov.1997.

[14] U.S. Environmental Protection Agency, "Risk Assessment Guidance for Superfund", *Office of Emergency and Remedial Response,* vol. I Human Health Evaluation Manual, part A, Dec.1989.

[15] ATSDR, "Glossary of Terms", *Agency for Toxic Substances and Disease Registry*, Jan. 2016.

[16] T.K. Boguski, "Human Health Risk Assessment*", Environmental Science and Technology Briefs for Citizens*, 1999.

[17] European Commission, "Introduction to Risk Assessment - Children's Health and the Environment", *DG Health and Food Safety*, 2003.

[18] NJDEP, "Toxicity Factors", *New Jersey Department of Environmental Protection*, Sep. 2009.

[19] Health Canada, "Slope Factors for Carcinogens", *Federal Contaminated Site Risk Assessment in Canada,* part I and II, 2008.

[20] U.S. EPA, "Slope Factors for Carcinogens", *United States Environmental Protection Agency*, 2007.

[21] R. Blaisdell, J.F. Collins, D.E. Dodge, G. Harris, and M.A. Marty, "The Air Toxics Hot Spots Program Guidance Manual for Preparation of Health Risk Assessment", *Office of Environmental Hazard Assessment,* Aug. 2003.

[22] J. Anderson, A. Levine, J. Peterson, M. Poulsen, P. Seidel, and S. Turnblom, "Human Health Risk Assessment Guidance", *Oregon Department of Environmental Quality*, May 2010.

Open Science Index, Environmental and Ecological Engineering Vol:11, No:5, 2017 publications.waset.org/10007768.pdf