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HUMAN HEALTH RISK ASSESSMENT: A CASE STUDY INVOLVING POLYCYCLIC AROMATIC HYDROCARBONS SOIL CONTAMINATION AND HUMAN EXPOSURE

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Abstract- The present study investigates human health risks of Polycyclic Aromatic Hydrocarbons (PAHs) contaminated soils. The research was performed within a project co-funded by the European Regional Development Fund. In the framework of the study, the crude oil artificially contamination of soil was realized using soil from an area historically polluted with heavy metals. This area is located Central Romania, close to a specific pollution source – non-ferrous industry. Sixteen individual PAHs were identified in the 12 sampling points from the investigated area, but the attention was mainly focused on ΣPAHs and Benzo(a)Pyrene (BaP) known as human carcinogens. The evaluated exposure pathways were ingestion (soil ingestion and food) and dermal contact. According to the established exposure scenario, the results revealed a risk factor of PAHs contaminated soil six times higher than the acceptable risk (10^{-6}) suggested by the World Health Organization. The most important exposure pathway revealed in the present work was food ingestion (particularly vegetable products ingestion) which contributed 99 % of the total risks (exposure to PAHs from contaminated site via inhalation pathway was considered negligible).

Keywords- BAP, Exposure Pathways, Pahs, Risk Assessment, Soil Pollution.

I. INTRODUCTION

Soil pollution implies the existence of chemicals which have harmful effects on biological, biochemical and biophysical processes. Given that the soil is one of the environments involved in the food chain, soil contamination will lead to contamination of plants, animals and negative effects on humans [1], [2].
Soil pollution with oil products may have several causes such as oil and gas leakage resulting from exploitation, pipeline cracks, improper storage of waste, etc. [3]. Related to these kinds of pollution there are two types of contaminants that could be identified organic and inorganic. Concerning the first category, a special attention must be focused on Polycyclic Aromatic Hydrocarbons (PAHs), dioxins and furans (PCDD/F), polychlorinted biphenyls (PCBs) and BTEX (benzene, ethylbenzene, toluene and xylene) as these are known as human carcinogens.

Present paper focuses on PAHs, which are an important group of hydrocarbons resulted generally after an incomplete combustion [4]. The impact on soil produced by PAHs is influenced by the initial soil properties. The biodegradation is influenced by the physico-chemical properties of each hydrocarbon, such as solubility, molecular size or structure [5]. In soil, generally, could be found PAHs congeners as anthracene, benzo[a]anthracene, benzo[a]fluoranthene, benzo[k]fluoranthene naphthalene, indeno[1, 2, 3 - cd]pyrene, benzo[a]pyrene [4].

An important and toxic compound from the PAHs group of contaminants is Benzo[a]pyrene (BaP) known as being resulted generally from incomplete combustion of organic matters. The sources of pollution for BaP are various like vehicle exhaust, smoke from burning coal and oil, smoking tobacco, the fumes from industrial processes, etc. The effects of BaP on human health are harmful; it can cause cancer, skin or reproductive diseases.

The contaminants reach to the soil and then are absorbed into plants. A path for human exposure to the PAHs, and especially to the BAP, is the ingestion of contaminated vegetables or contaminated animal products [6], [7].

II. DETAILS EXPERIMENTAL

2.1. Material and methods

Soil used in the present study comes from Central Romania, near a metallurgical industrial site contaminated with heavy metals, but used for agricultural purposes. With the aim of the present study, the soil was excavated by 20 cm depth and transported to a waterproofed. After this it was stretched on a surface of about 280 m^2 and it was ridged (0.2 m thickness layers). It was artificially contaminated with crude oil. So, pollution with PAHs was obtained artificially. Next paragraph is presenting the analytical procedure used in order to determinate the PAHs concentration in soil.

2.2. Analytical procedure

Twelve soil samples were collected from the investigated area and characterized from the PAHs contamination point of view before and after the artificial pollution. These were collected from the experimental platform according to STAS 7184/1-75 [8]. In order to use a homogenous mass, the soil was size-fractionated by a cutting mill [9]. The existing standard methods used with the aim of identifying the concentration levels for PAHs were SR EN 14039 (2005), EPA 8270 (1998), EPA Method 3540 (1996) [10], [11]. First, the solid samples were passed through a sieve of approximately 2 mm openings in thickness. The Soxhlet extractions were done using the 6 benches Soxhlet equipment. In the order of 20 g fraction of contaminated soil was extracted with 250 ml of HPLC grade petroleum ether solvent. The extract was concentrated to a low solvent volume using Heidolph rotary evaporator and eluted with hexane. After concentration step samples were clean-up, if necessary, or were transferred to a capped and sealed vial for gas-chromatographic analysis. For qualitative and quantitative analysis a GCMS QP2010 Shimadzu Gas Chromatograph with a mass spectrometer detector was used. ΣPAHs and BaP concentrations in soil samples were identified by a combination of retention time and spectral mass match against the calibration standards (Agilent Technologies 2008 and 2009) [12], [13].

In order to determine the contaminated soil moisture content, a laboratory oven-drying was used. After the soil sample has been weighted, it was kept in oven-drying for 24 hours at 105°C and after weighted again in order to determine the moisture quantity: 4.64% [9].

ΣPAHs and BaP determined concentration levels in soil for the analysed 12 samples are illustrated in Figure 1 with an average of about 135 $mg/kg_{d.m.}$.

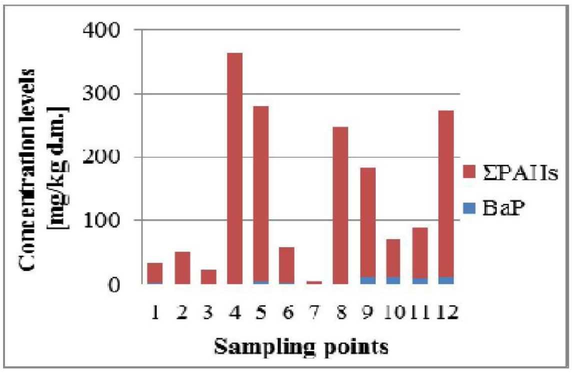

Fig. 1. ΣPAHs and BaP concentrations in soil

The obtained results were compared with the thresholds established by the Romanian regulation (Ministerial Order 756/1997 in force) [1] according to the land use types (sensitive land use or less sensitive land use). MO 756/1997 establishes the normal, alert and intervention thresholds in soils for different kinds of pollutants. The land use for the present study is sensitive as the site is agricultural.

Table 1 is illustrating the thresholds established by MO 756/1997 concerning the investigated contaminants.

Table 1: Maximum concentration levels of ΣPAHs and BaP in soils allowed by the Romanian regulation

Chemical	Normal value (mg/kg_{su})		
		Warning level (mg/kg_{dm})	Intervention level (mg/kgd_m)
		Sensitive land use	Sensitive land use
BaP	0.02	2	5
ΣPAHs	0.1	7.5	15

2.3. Data analysis

2.3.1. Exposure assessment

The human exposure to contaminated sites occurs by different ways. The routes of exposure are: ingestion, inhalation and dermal contact. The exposure pathway could be through ingestion of contaminated soil (especially in case of the children exposure), ingestion of contaminated vegetables or animal products. The inhalation can occur in case of volatile compounds from soil or from water. Dermal contact with chemicals is represented by the direct contact with contaminated soil, contaminated dust or contaminated water [14].

In order to assess exposure and human health risk different methods and models were developed. These have the purpose to evaluate the sources of pollution, to determinate the optimal method for decontamination, the exposure pathways, to estimate the absorbed doses and to determine the toxicological or carcinogenic effect on human health. Before the appearance of human health risk assessment concept, were the methods for decontamination. The most popular are HRS (Hazard Ranking System) Method (EPA, 1980), Baden – Württemberg Method (1983), National Classification System for Contaminated Sites (The Canadian Council of Ministers of the Environment's, 1992), etc. [15].

The first model was developed by U.S. EPA in 1980's. In the last years there were developed several other models for the human risk assessment: CLEA, CSOIL, RBCA, UMS, etc. These are structured on various exposure scenarios and pathways, with which can be assessed the exposure risk, the level of concentration of pollutants in soil or it can be performed physico - chemical analyses and toxicological studies for the human body [16].

Human health risk assessment involves to determinate the individual risk of each substance to which the human can be exposed and the carcinogenic or not effects on human health. The acceptable individual risk suggested by World Health Organization is 10^{-6} [17].

Because the large number of sources and multiple pathways of exposure to PAHs, the human health risks are high. On the other hand, it was also found that the variety of PAHs, such as BaP, and more than 40 chemicals are known or suspected to be human carcinogens [18].

2.3.2. Dose estimation

Cancer risk estimation of chemicals as PAHs existing in contaminated soils supposes the dose evaluation. Dose addition to assess cumulative risks from exposures to multiple chemicals is one of the essential steps for the human health assessment from contaminated sites. As the investigated routes of exposure related to the present study case were dermal contact, soil ingestion, vegetables ingestion and animal products, the evaluated chemical doses were: dose of dermal absorption and ingestion (contaminated soil, vegetables and animal products). According to the United States Environmental Protection Agency (US EPA, 1997), the considered equations were:

- Exposure through dermal contact

$$I_1 = [CS \times CF \times SA \times AF \times ABS \times EF \times ED]/[BW \times AT] \quad (1)$$

The exposure through dermal contact I_1 is calculated taking into account the chemical concentration in soil (CS), the conversion factor (CF), the skin surface area available for contact (SA), the absorption factor (ABS), the exposure frequency (EF), the exposure duration (ED), the body weight (BW) and the mean time (AT).

- Soil ingestion

$$I_2 = [CS \times CF \times IR \times FI / BW] \times [EF \times ED / AT] \quad (2)$$

For the calculation of the exposure through soil ingestion I_2, date related to the ingestion rate (IR) and fraction ingested from contaminated source (FI) were considered.

- Food ingestion

$$I_3 = [CF \times IR \times FI \times EF \times ED]/[BW \times AT] \quad (3)$$

$$CF = (C_{dep}) \times (GRAF) + C_{trans} \quad (3.1)$$

$$C_{dep} = 0 \text{ in our case; } C_{trans} = Cs \times UF \quad (3.2)$$

The exposure scenario, according to the local context, is defined by the parameters illustrated in Table 2 that are known as influencing the exposure. The risk was estimated both for adults and children as environmental factors can affect children's health quite differently from adults' health [19].

Table 2: Parameters related to the exposure scenario

Parameters	Children	Adults
Fraction ingested from contaminated source	0.1	0.3
Exposure frequency for dermal contact risk type (days/years)	15	30
Exposure frequency for soil ingestion risk type (days/years)	15	15
Exposure frequency for vegetables ingestion risk type (days/years)	256	256
Exposure frequency for animal products risk type (days/years)	256	256
Exposure duration (years)	5	21
Averaging time (days)	2555	25550

2.3.3. Risk assessment

Contaminated sites assessment for the reduction of environmental pollution by risk-based approach could really define in a proper manner the requirements for and the extent of remedial measures for polluted sites. Quantitative health risk assessment is a site-specific complex procedure requiring evaluation of all possible pathways [20].

In the framework of the present study, mathematical model used is mainly based on the methodology developed by US EPA [21]. Additionally, risk assessment models developed by specific authorities from Netherlands [22], [23] and Canada [24] were taken into account. In is way, risk assessment particularities for the Romanian context was pointed out [17]. The software tool used for the human health risk assessment from contaminated soil with PAHs was developed in the framework of a more complex research within a European project (RECOLAND v1.0) [25].
According to the analyzed twelve soil samples, the lifetime cancer risk was assessed.

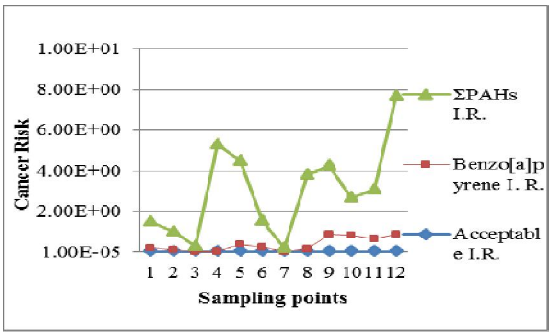

Fig. 2. Cancer risk following exposure to PAHs related to the twelve soil samples

Concerning the estimated risk, taking into consideration pollution with PAHs, starting from the concentration levels in soil because of the crude oil contamination, results as presented in Figure 2 were achieved. The ΣPAHs individual risk associated to the contaminated soil is higher than the acceptable value of 10^{-6} (the average risk that is characterizing the investigated are is six time higher the than acceptable risk: 1.01 x 10^{+0} respect to 10^{-6}).

Furthermore, the BaP individual risk is also higher than the acceptable value in the investigated area (3.64 x 10^{-1}). Results are underlying in this way the necessity for remediation works being in the same time an example of contaminated sites assessment for the reduction of environmental pollution by risk-based approach.

III. RESULTS AND DISCUSSION

Comparing with the limits regulation in force in Romania related to for PAHs in soil, the results showed that the concentration levels of BaP and ΣPAHs has exceeded threshold values both for warning and intervention levels (Figure 3). Consequently, according to MO 756/1997, involves decontamination in order to avoid risks for humans.

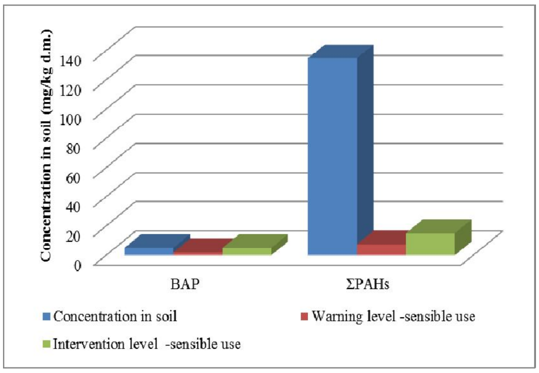

Fig. 3 ΣPAHs and BaP average concentrations in soil

For the quantitative human health risk assessment, according to the local context, the considered exposure pathways were: dermal contact, soil ingestion, vegetables ingestion (protected, exposed, leafy and root) and animal products (beef meat). Consumer behaviour related to vegetable products is presented in Figure 4, while concerning the animal products (beef meat) the is covered by a fraction of 10%.

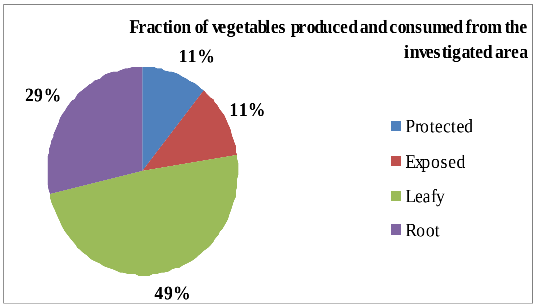

Fig. 4 Consumer behaviour related to vegetable products

For the exposure through ingestion of mother's milk another expression found in the literature was used [26], taking into account the pollutant concentration in mother's milk (C milk), the mother's milk ingestion rate (IngR milk), the average daily maternal intake of contaminant from all routes (Em), the half-life of contaminant in the mother (t1/2) and the fraction of contaminant that partitions to the mother's fat (f1), fraction of mother's weight that is fat (f2) and fraction of fat in the mother's milk (f3) [27]. Table 3 is illustrating results concerning the estimated doses for BaP and ΣPAHs:

Table 3: Exposure pathway and estimated doses

Exposure pathways	Benzo[a]pyrene Dose	ΣPAHs Dose
Dermal contact	$7.6x10^{-6}$	$2x10^{-4}$
Soil ingestion	$9.7x10^{-8}$	$2.56x10^{-6}$
Vegetable ingestion – protected	$6.7x10^{-4}$	$1.8x10^{-2}$
Vegetable ingestion – exposed	$4.5x10^{-2}$	$0.12x10^{-1}$
Vegetable ingestion – leafy	$1.4x10^{-1}$	$0.39x10^{-1}$
Vegetable ingestion – root	$1.1x10^{-1}$	$0.31x10^{-1}$
Animal product – beef	$2.38x10^{-5}$	$6.5x10^{-4}$
Animal product - dairy	10^{-4}	$2.8x10^{-3}$

As soil contamination with ΣPAHs revealed to an unacceptable risk in the investigated area, detailed analysis of the obtained results was done. Figure 5 is showing that the exposure pathway through diet is the most representative, while Figure 6 is illustrating the detailed exposure pathways through vegetable products ingestion.

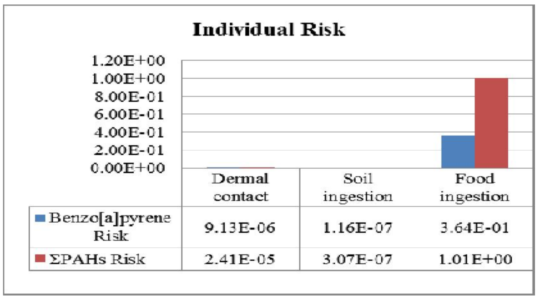

Fig. 5 Individual Risk according to the exposure pathways

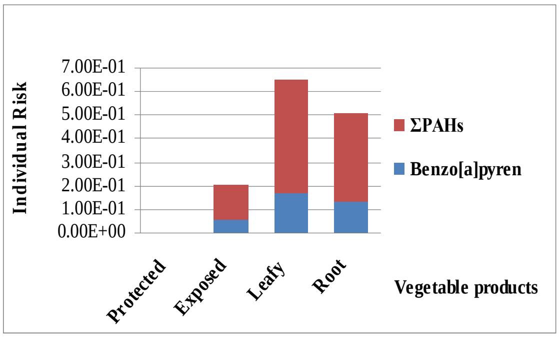

Fig. 6 Individual Risk according to vegetable products exposure pathways

Illustrated result from the research study showed that exposure from ingested food is the main exposure pathway related to the investigated soil contaminated by PAHs.

CONCLUSIONS

Results from the presented work could lead to the improvement of the methodology for assessing human health risk assessment and risk-related practices in the management of contaminated sites. This kind of research should in principle guide to the improvement of site characterization and making better-informed risk management decisions.

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