# AN INTEGRATED MODELING APPROACH FOR RISK ASSESSMENT OF HEAVY METALS IN SOILS

Cristina DUMITRESCU[1], Diana M. COCÂRȚĂ[2], Adrian BADEA[3]

*Lucrarea prezintă un model matematic dezvoltat pentru evaluarea riscului asupra sănătății umane asociat solurilor contaminate. Funcționalitatea modelului este exemplificată prin intermediul unui studiu de caz - un sit contaminat cu metale grele (în special Be, Cd, Ni, CrVI şi Pb) provenite de la o sursă punctiformă de poluare din industria metalurgică. Rezultatele obținute au evidențiat un coeficient de risc de $10^{-5}$, cu un ordin de mărime peste riscul acceptabil de $10^{-6}$ recomandat de către Organizația Mondială a Sănătății. Este ilustrată de asemenea contribuția fiecărui poluant la riscul individual estimat pentru fiecare cale de expunere considerată: ingestie sol şi alimente şi contact dermic. Lucrarea evidențază rolul evlalurăii de risc în alegerea soluției optime pentru remedierea solurilor contaminate, dar şi în planificarea amplasamentelor dedicate zonelor rezidențiale, industriale/comerciale sau agricole.*

*The paper presents a mathematical model developed for human risk assessment associated with contaminated soils. The functionality of the model is shown by a case study – site contaminated with heavy metals (mainly Be, Cd, Ni, CrVI and Pb) originating from a specific pollution source in the metal industry. The results have shown a risk coefficient of $10^{-5}$, one level higher than the $10^{-6}$ acceptable risk recommended by the World Health Organization. Furthermore, it shows the contribution of each pollutant to the individual risk estimated for each exposure pathway: soil and food ingestion and dermal contact. The paper underlines the role of risk assessment in selecting the optimum solution for remediation of contaminated soil, as well as planning sites for residential, industrial/commercial or agricultural areas.*

**Keywords**: risk assessment, soil contamination, heavy metals, oral exposure, dermal exposure

## 1 Introduction

Human risk assessment is an extremely significant instrument for decision making factors for a suitable contaminated soil management. In the last years, in

[1] PhD student, Department of Energy Production and Use, Faculty of Power Engineering, University Politehnica of Bucharest, Romania, cristina.dumitrescu@hotmail.com
[2] Senior Researcher, Department of Energy Production and Use, Faculty of Power Engineering, University Politehnica of Bucharest, Romania, dianacocarta13@yahoo.com
[3] Prof. dr. ing., Department of Energy Production and Use, Faculty of Power Engineering, University Politehnica of Bucharest, Romania, adrian.badea@energ.pub.ro

the current practice, the risk assessment is used both for the identification and selection of the optimum solution for soil remediation and to establish if, depending on the identified level of pollution, the use of the land is in accordance with its selected purpose (agricultural, residential, recreational, commercial, industrial, etc.).

At international level, the first methodology for human risk assessment due to exposure to contaminated soils was developed in the 80s by the Environmental Protection Agency of the United States of America (US EPA) – *Risk Assessment Guidance for Superfund* [1]. Subsequently, due to the increase of concern related to the issue of contaminated soils, other methodologies were developed, such as CSOIL developed in the Netherlands, RBECA developed in Italy, CLEA developed in Great Britain, etc. However, all these methodologies are based on the principles developed by the US EPA methodology.

According to the legal provisions in Romania, i.e. GD 1408/2007 [2], the environmental protection authority decides whether the contaminated sites need to be remediated, as well as the best technology to be used for remediation, based on the geological environment pollution research and assessment studies and risk assessments [art. 24, 25 HG 1408/2007]. At the same time, the legislation envisages that these studies must be carried out in accordance with a framework methodology and content developed by the Ministry of Environment and Forests. Currently, these methodologies are not available, the studies being carried out based on the models developed in other countries, such as those mentioned above.

Furthermore, at the level of the environmental and health authorities, and mainly in Romania, there are no data, expertise and regulation for the development of human health risk assessments.

In this context, the research project **"Multicriteria decision system for the remediation of soils contaminated with toxic and persisten pollutants in large industrial areas**" was initiated within the University Politehnica of Bucharest. This project is financed by the European Union under the Operational Programme "Increase of Economic Competitiveness" (SOP IEC). The project initiated in 2010 is currently under impelemntation and is to be finalised in 2013. The main objective of the research is the development of a multicriteria system allowing the selection of the best solution for the remediation of soils contaminated with toxic and persistent pollutants, considering the human health risk assessment as a decision making criterion, together with two other significant criteria, namely: the soil pollutant remediation level and the level of costs associated with the proposed remediation (electro-chemical treatment methods, biological treatment methods and thermal treatment methods: incineration and pyrolysis).

The objective of the article is on one hand, the presentation of the mathematical model for risk assessment developed within the research project and on the other hand, its parameterization (the contextualization of the assessment), an essential aspect for a correct and comprehensive risk assessment. The functionality of the programme was verified through a case study, respectively a risk assessment for a site located in the central part of Romania, contaminated with heavy metals (Be, Cd, Cr VI, Ni and Pb) originating from a specific pollution source in the metal industry. The analysis of the soil samples taken from the site has shown that the level of concentration of these pollutants exceeds by far the intervention level for sensitive use established by the Romanian legislation [3]. Thus, it is needed to carry out some detailed studies, including the development of a risk assessment to determine the impact of the contaminated soil on the environment and health of the population to identify the best measures required to be taken to reduce the potential impact to the accepted limit.

Furthermore, another objective of the paper is to present the results obtained pursuant to the applying of the mathematical model for risk assessment, namely the quantifying, analysis and assessment of the human health risk due to exposure to soil contaminated with heavy metals.

## 2 Mathematical model developed for carcinogenic risk assessment

The mathematical model for risk assessment is carried out in Excel and mainly contains 2 types of sheets. One sheet summarises tens of specific parameters, types of pollutant, receivers and exposure pathways, the site for which the assessment is developed, etc. and the other one which contains the formula for the assessment of the exposure and risk coefficient. The mathematical model was mainly based on the methodology developed by the Environmental Protection Agency of the United States of America – *Risk Assessment Guidance for Superfund: Volume I – Human Health Evaluation Manual* [1]. Furthermore, during the research, risk assessment models developed in Netherlands (CSOIL, 1994) [4], [5] and Canada (PQRA, 2004) [6] were additionally consulted in order to carry out the best estimation of the risk coefficient associated with contaminated soils. However, these methodologies were analysed and read from the perspective of the particularities in Romania which sometimes are significantly different to other developed countries, such as those considered as reference. Examples are the food ingestion rate, the type of consumed food of vegetal or animal origin, etc.

The mathematical model is based on the general scheme for risk assessment developed by the US EPA 98, shown in Figure 1.

As shown in the General scheme for risk assessment, presented in Figure 1, the first stage is the *Data Assessment* which generally targets the identification and analysis of the chemical substances to be found in the studied area with a potential impact on the environment and human health. Generally, this stage means collection of all data required for the characterization of the site and taking of samples to identify those chemical substances which exceed the concentration threshold.

The next two stages consisted in the *Exposure assessment* (dosage assessment) and *Toxicity Assessment* (effect assessment). If in terms of exposure assessment there are mathematical models which lead to its identification, in terms of toxicity exposure, the toxicological properties of the analysed substance must be established, which actually means the intrinsic ability of the chemical element to cause adverse effects. For example, a chemical compound may be hepatotoxic, mutagenic, carcinogenic, teratogenic, allergenic, etc. However, this sequence does not inform us if the pollutants shall produce these effects under any circumstances, but solely identifies the main hazards which shall be considered in the assessment to be carried out.

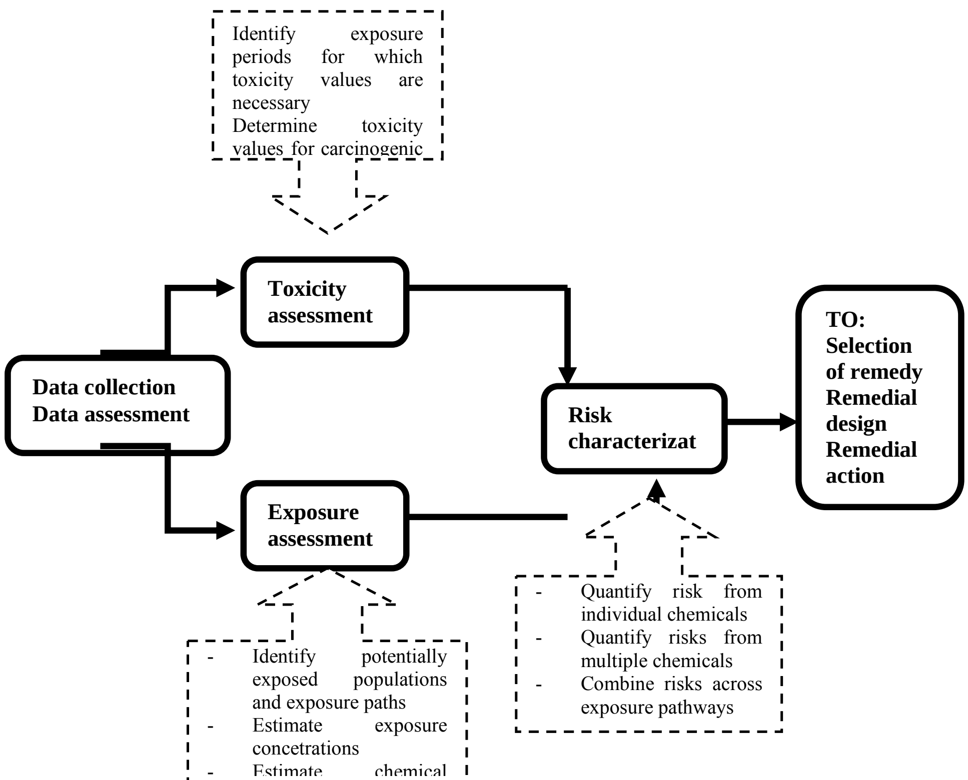


Figure 1. General scheme for risk assessment (adjustment after the US EPA, 1998)

The results obtained after the *Exposure Assessment* and *Toxicity Assessment* are the basis for the *Risk Characterization.* The scope of the risk assessment is to determine the potential adverse impact on the health of the population as per exposure to a contaminated soil in default of control or pollutant reduction measures. Thus, the results of the risk assessment are used to: i) determine the magnitude of the risk and the primary causes of this risk, ii) determine whether it is needed to apply remediation measures to reduce the contamination level in order not be a risk factor anymore depending on the use of the land.

## 2.1 Exposure assessment

The risk assessment is carried out to estimate the type and magnitude of the exposure compared to the chemical elements present in the soil. According to the US EPA methodology, the exposure is the contact of the human body with a chemical element or physical agent. The exposure magnitude is determined by measuring or estimating the concentration/quantity of the chemical element during a certain period of time. Thus, the exposure assessment is the determination or estimation (qualitative or quantitative) of the magnitude, frequency, duration and exposure pathway (source USA EPA 98).

Exposure characterization

The first stage of exposure is the identification and characterization of general elements relative to the exposure of the population to the chemical elements identified on a site, respectively, the physical characteristics of the site, as well as of the population to be found on site or in the vicinity. Thus, during this stage, the following are carried out:

- general characterization of the site respectively, information concerning: the climate (rainfall, temperature, wind speed, wind direction), flora, geology (type of soil, pH, etc.) and hydrology (underground water level and flow direction), surface water identification and characterization, etc.;
- characterization of the population potentially exposed to the risk, respectively information concerning: the distance from the residential areas to the studied area, identifying the households located the closest to the site, identifying of the population which may be, in the future, exposed to the risk due to pollutant migration, feeding habits;
- current and future/planned use of the site respectively, information concerning the activities of the potentially exposed population. Generally, within risk assessments, 3 categories of land use are considered: agricultural, residential and commercial/industrial.

Exposure pathways identification

During this stage of the assessment, the pathways the population may be exposed to contamination with pollutants found in the soil, are identified. The exposure pathways are identified considering the source, type and location of the pollutants in the soil. The exposure assessment is carried out for each identified exposure pathway.

The main exposure pathways, to which the majority of the models for exposure assessment within the specific literature make reference to, are the following: i) oral exposure through ingestion (soil ingestion, ingestion of products of vegetable or animal origin, etc.), ii) exposure through indoor and outdoor inhaling, iii) exposure through dermal contact.

In the particular case of the case study shown by this paper, considering that i) the analysed chemical elements (Be, Cd, Ni, CrVI, Pb) were accumulated in the soil through dispersion from air to soil and ii) the source of generation of the pollutants in the air does not exist anymore, only the oral exposure through ingestion (soil ingestion and food ingestion) and exposure through dermal contact have been considered for the human health risk assessment.

Exposure assessment

The potential human health risk from heavy metals in the site was assessed taking into account all levels of concentrations identified in the analyzed area. For every exposure pathway, doses were estimated using the following expressions:

- Exposure through dermal contact

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

The exposure through dermal contact $I_1$ has been 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

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

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 × IR × FI × EF × ED] / [BW × AT] (3)

*CF = (Cdep) × (GRAF) + Ctrans* *(3.1)*

*Cdep = 0 in our case; Ctrans = Cs × UF* *(3.2)*

The exposure through food ingestion has been calculated taking into account: ingestion of vegetables $I_3$ considering data related to ingestion rate (IR) and fraction ingested from the contaminated source (FI). The contaminant concentration in vegetables has been estimated considering the concentration due to the direct deposition of contaminants is zero, and the concentration due to translation from the roots is based on root uptake factor (UF) and concentration of contaminant in soil (Cs).

It was considered that 100% of the territory is dedicated to the cultivation of crops (corn), the real context. Concerning diet, 10% of the corn was considered to be used from the contaminated area. These are assumed percentages, considering the local context. Other parameters used for dose exposure evaluation are listed in Table 1. Values of parameters listed in Table 1 are parameters suggested by the US Environmental Protection Agency for this type of assessment.

*Table 1*

**Parameters used in the mathematical model for exposure assessment**

| **Exposure pathway** | **Parameter** | **Value** | **UM** |
|---|---|---|---|
| Site specific | Exposure frequency | 120 | d/y |
| Site specific | Total exposure time | 30 | y |
| Site specific | Adults exposure time | 21 | y |
| Site specific | Children exposure time | 9 | y |
| Site specific e | Total days of exposure period | 2550 | d |
| Site specific | Adults body weight | 70 | Kg |
| Site specific | Children body weight | 30 | kg |
| Soil ingestion | Soil ingestion rate | 100 | mg/d |
| Soil ingestion | Fraction ingested from contaminated source | 0.2 a | |
| Dermal abortion | Skin surface area available for contact | 4700 | $cm^2$/event |
| Dermal abortion | Soil to skin adherence factor | 1.45 | |
| Vegetable ingestion | Corn daily consumption | 0.17 | kg/meal |
| Vegetable ingestion | Root uptake factor | Metal specific | adim |
| Vegetable ingestion | Corn ingested from the contaminated area | 15 | % |

## 2.2 Carcinogenic risk characterization

For the characterization of potential carcinogenic effects, the probability that an individual develops cancer during the exposure period, beginning from the daily intake or dosage calculated within the previous stage and information concerning the specific dosage – response for each chemical element, is estimated.

$$Risk = I * SF \quad (4)$$

where, I= chronic daily intake (mg/kg-day) and SF=slope factor (mg/kg/day)

In case the risk is determined by several pollutants, the risk is calculated as the sum of the risk generated by each pollutant for each exposure pathway:

$$Risk_{Total} = \Sigma Risk_i \quad (5)$$

where $Risk_i$ is the estimated risk for each substance

Total exposure cancer risk = risk $_{total}$ (exposure pathway 1)+ risk $_{total}$ (exposure pathway 2) +.....$_{risk\ total}$ (exposure pathway i) (6)

## 3 Reading of the results of the risk assessment

Using the mathematical model developed based on the methodology described above, both the individual carcinogenic risk due to the exposure to each of the 5 studied heavy metals – Be, Cd, Cr VI, Ni, Pb – for each exposure pathway – soil ingestion, dermal contact and vegetable ingestion – as well as their sum have been estimated in order to determine the total risk. The results are presented in table 2.

*Table 2*

**Individual and total risk assessment**

| **Exposure pathway** | | **Be** | **Cd** | **Cr VI** | **Ni** | **Pb** | Individual risk for each exposure pathway |
|---|---|---|---|---|---|---|---|
| | | **1** | **2** | **3** | **4** | **5** | (1+2+3+4+5) |
| Soil ingestion | a | 8,23E-08 | 2,05E-05 | 7,23E-07 | 1,27E-06 | 1,95E-06 | 2,44E-05 |
| Dermal contact | b | 3,74E-08 | 7,28E-06 | 8,02E-08 | 1,28E-06 | 2,82E-06 | 1,15E-05 |
| Vegetable ingestion | c | 4,13E-08 | 3,91E-06 | 6,51E-08 | 1,08E-06 | 2,14E-07 | 5,26E-06 |
| Individual risk for each element | a+b+c | 1,61E-07 | 3,17E-05 | 8,69E-07 | 3,63E-06 | 4,98E-06 | - |
| **TOTAL risk** | | | | | | | **4,12E-05** |

Comparing the values obtained both for the individual risk for each exposure pathway, as well as for the total risk, it is found that these exceed the value indicated by the World Health Organization (WHO) as being an acceptable risk ($10^{-6}$, being one cancer case at each 1 million persons).

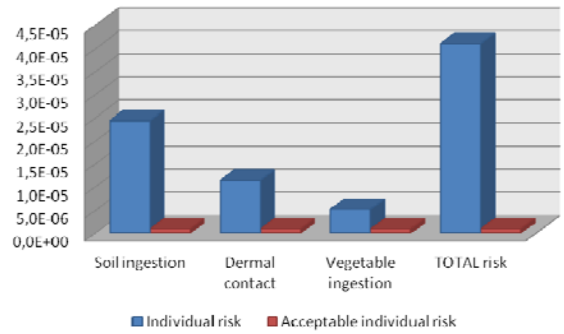


Fig. 2. Individual risk for each analysed exposure pathway compared to the value proposed by WHO

This result confirms the expectations considering that the level of heavy metal concentrations identified in the studied soil exceeds by far the intervention threshold established by the in force Romanian legislation. Furthermore, the analysis of the obtained results shows that from the studied 3 exposure pathways, soil ingestion is the pathway with a major contribution on the human health, following by the dermal contact and finally, the ingestion of food (in this case, corn).

Although the total risk exceeds the recommended threshold, the adjacent figure shows that the individual risk in case of Be and Cr VI is within the acceptable threshold. Cd presents the highest risk, followed by Pb and Ni, although the initial level of concentrations of Pb in the soil was identified as being the highest one. This is explained by the high value of the slope factor for Cd (1.5E+1), which is much higher compared to the rest of the studied metals (Be:8.4 E+0, CrVI: 5.1E+2, Ni:9.1E-1, Pb4.2E-2) – values published in the Toxic Air Contaminant Document, Office of Environmental Health Hazard Assessment [8].

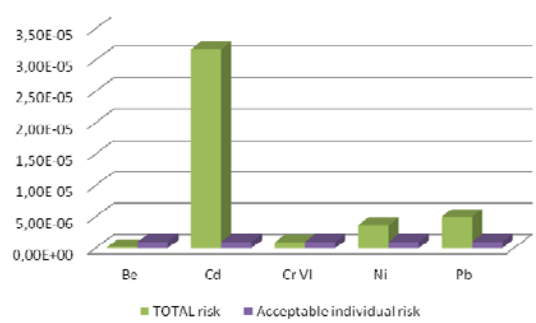


Fig. 3. Individual risk for each of the 5 metals, accumulated for all exposure pathways compared to the value recommended by WHO

Analyzing the individual behaviour of each metal in relation with the human health risk, depending on the exposure pathway (Fig.4), it may be seen that, if in the case of Be, Cd and CrVI the exposure pathway with the highest share in the total risk is determined by soil ingestion, this is not applicable for Ni and Pb for which the significant share is determined by the dermal contact. In case of Pb, the major exposure is the dermal contact and soil ingestion. Exposure through ingestion of food is not significant and this may be explained by the fact that the Pb absorption ratio in corn and, generally, in plants is low. In case of Ni, the risk share for the 3 exposure pathways is approximately the same. For Cd and Be the behaviour is similar, soil ingestion representing approximately 50 % of the total risk.

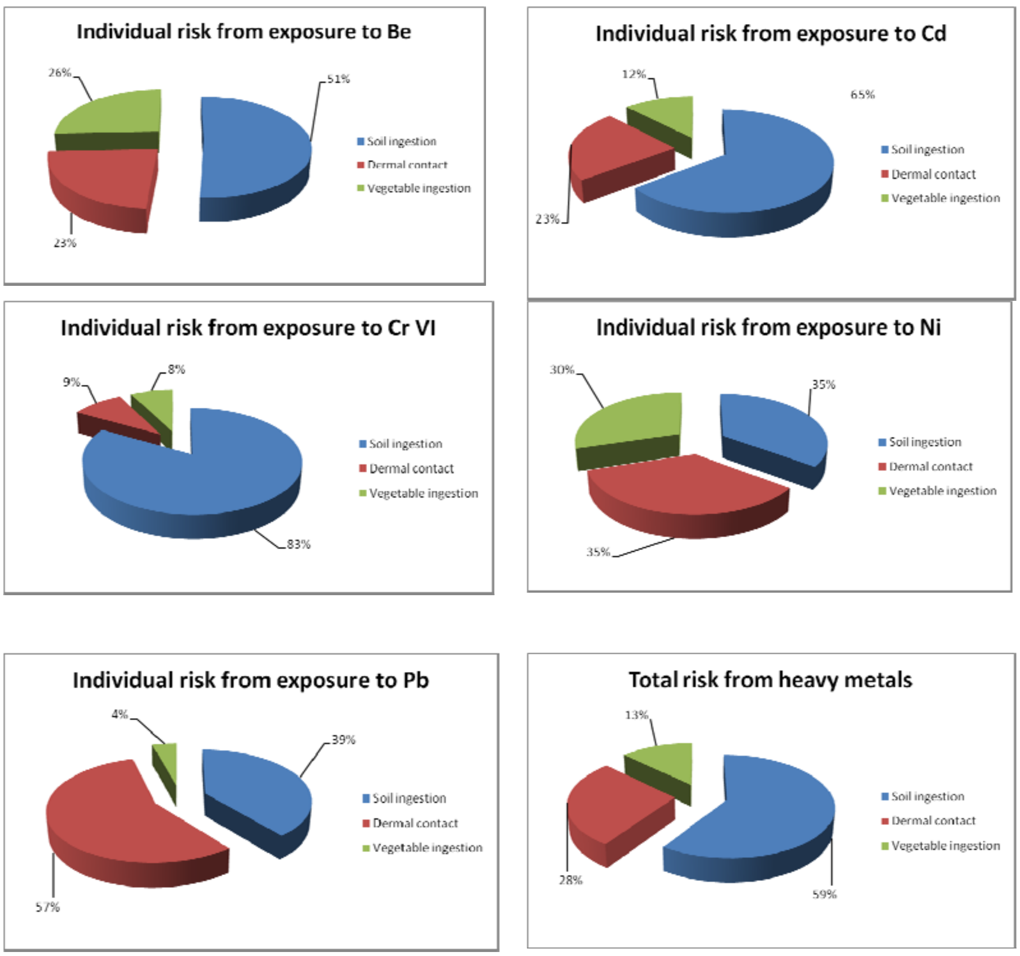


Figure 4. Individual and total human health risk due to contamination with heavy metals

## 4 Conclusions

1. This paper presents the mathematical model developed for risk assessment. The model is based on the risk methodology proposed by the US EPA, 1998 with the customization of the assumptions and parameters to the conditions in Romania, so that the obtained results reflect as accurately as possible the local conditions. However, an issue is the lack of data and parameters at national level.

2. The risk coefficient estimated for the analyzed area of interest ($10^{-5}$ compared to the acceptable risk of $10^{-6}$) leads to the necessity to carry out contaminated soil remediation activities in the respective area. The results of such an analysis are an essential element for the decision making factors in terms of the management of contaminated sites and for the selection of the best remediation solution so that it generated the lowest impact on the population and the environment.

3. Although the total risk is the one which is read when estimating the impact on the human health due to exposure to contaminated soil, the present study underlines that also the individual reading of the behaviour of each chemical element is an extremely significant element for the determination of the best contaminated site remediation solution.

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