TECHNICAL UNIVERSITY OF CIVIL ENGINEERING BUCHAREST
FACULTY OF HIDROTECHNICS

Doctoral School

RISK ANALYSIS, A DEPOSIT MANAGEMENT TOOL FROM DECOMMISSIONED INDUSTRIAL WAREHOUSES

PhD Thesis Summary

2021

CONTENT

LIST OF FIGURES

LIST OF TABLES

1 INTRODUCTION AND OVERVIEW

Soil pollution is an important and topical issue in Europe, having a direct impact on the quality of soil, subsoil, water, air, biodiversity and last but not least on climate change.

The technical report on contaminated sites in Europe in 2018 [4] estimates approximately 650,000 sites registered in the national and regional inventory showing polluting activities that have taken place or are taking place. More than 76,000 new sites have been registered since the last progress in the management of contaminated sites in Europe, respectively in 2014. According to the same publications, it is worth mentioning that Spain, Germany, France, Hungary, the Netherlands and Slovakia have reduced the number of sites. registered on which polluting activities have taken place or are taking place. This can happen based on inventory dynamics in some countries, such as France, where once a site has been investigated and remedied (if necessary), it is removed from the inventory.

2 CURRENT LEGISLATION IN THE FIELD

Romania has transposed the requirements of European environmental legislation through laws, decisions, government decisions, national directives. The specific national and international legislation for contaminated sites was presented.

3 SYNTHESIS REGARDING THE PARTICULARITIES OF THE CONTAMINATED SITES ACCORDING TO THE ACTIVITY CARRIED OUT

Chapter 3 presented representative locations in the country, based on practical situations, related to the distribution - storage - transport component of the mining and oil industry.

Usually, each site has a uniqueness in terms of surface, positioning and size of buildings, technology used, types of products, specific activities, management of damage situations, etc., all with implications on the phenomena of pollution of environmental factors. This uniqueness of the site also characterizes the underground environment through the particularity of geomorphological, geological, hydrogeological, geochemical conditions that favor more or less the infiltration and migration of the pollutant.

The particularities of the contaminated sites presented and synthesized in this chapter take into account the natural environment and the activity carried out that contributed to the pollution. These aspects will be necessary to understand the sources and causes that generate pollution at the specific site and to allow a critical analysis in choosing the method and methods of investigation and assessment of pollution and subsequently methods of limiting and remedying depending on the particularities of contaminated sites.

4. PERFORMANCES AND LIMITATIONS OF METHODS AND TECHNIQUES FOR INVESTIGATION OF UNDERGROUND POLLUTION

The presentation of direct prospecting methods for taking samples from the underground environment, specific to environmental protection works allowed a critical look at the conditions of application, advantages and limitations, disadvantages of applying direct methods, necessary to establish and age the appropriate drilling type for a particular location, taking into account the particularities analyzed in chapter 3.

The investigation program is established by choosing the method of execution, the depth at which it is possible to meet contamination, the lithology of the formations, the way of recovering the samples and the drilling location model. In the case of equipping drilling in piezometers, it is necessary to establish the way of capturing the layer, the direction in which the drilling is performed in relation to the central drilling or in relation to the direction of water flow, possible experimental pumping.

The data obtained will allow an optimal characterization of the location in ensuring the assessment of pollution and risk (source-path and receiver connection) and the identification and feasible choice of the remediation option.

For the drilling to investigate the geological environment in the field of environmental protection works, it is necessary to meet the following conditions, which I propose necessary based on the works analyzed and followed so far:

- the drilling execution is without drilling fluid (in dry system);
- any layer encountered can be identified immediately and allows performing qualitative particle size analysis to choose the filter slot and the sort of pearl gravel; in some cases it does not allow the clogging of the aquifers;
- in the conditions of drilling without drilling fluid there is the possibility to obtain water samples during drilling for the analysis of samples in the laboratory;
- for the execution of drilling and sampling to recommend protective piping in order to avoid pollution (cross) between soil layers and deep pollution of soil and groundwater;
- in the case of monitoring wells (piezometers) the material used for piping must be from the category of PVC and HDPE, which affects to a small extent, respectively the environment;
- also in the case of piezometers, the groundwater level to fluctuate permanently in the filter section, in order to identify the existence of the free phase of the oil product and possibly the measurement of its thickness (NAPLs).

For environmental protection studies, direct investigations are corroborated with indirect investigations by geophysical methods. Indirect investigation methods allow a much more efficient application of the investigation plan by direct methods and complement the results obtained by drilling. Through a comparative study of the investigation methods, the advantages, disadvantages as well as the applicability and limitation of these types and modalities of investigation are presented.

5 CONCEPTUAL MODEL OF CONTAMINATED SITES. COMPONENT ELEMENT

The objective of developing a sampling plan is to establish the nature and extent of horizontal and vertical pollution for a site.

The sampling strategy starts from the complex knowledge of the general information of the location, if they exist, such as: location, existing facilities on the site, the technological process, materials used for the activity, etc. The investigation requirements of the site must also take into account the budget requirements before finalizing the model adopted for the site investigation.

An important factor that helps to obtain relevant information in the case of the investigation model is the application of indirect methods (geophysical methods) and the use of equipment for on-site measurement of contaminants, respectively analytical measurements.

A sampling and investigation program cannot be defined in a complete and rigorous way, as it will be dimensioned according to the size and complexity of the site. Four models of location of sampling points specific to contaminated sites over time were studied, of which the most important are:

- the model based on judgment / objective - judicial
- systematic - systematic model
- stratified model
- random model.

6 MANAGEMENT OF CONTAMINATED SITES

The management of contaminated sites falls within the criteria, conditions, rigors of the general management of an activity, for which legislative norms, guidelines and implementation methodologies are elaborated. The management of potentially contaminated and contaminated sites aims to adopt a set of measures through which the current and future management of the contaminated area to be done through minimal efforts while ensuring the reduction of risks posed by the contaminated area to levels where adverse effects on human health and the environment to be within acceptable limits.

For potentially contaminated or contaminated sites, in accordance with the national legislation in force, it is recommended to complete the following steps: preliminary and / or detailed investigation of potentially contaminated and contaminated sites, environmental risk assessment, adoption of safe management measures of the declared site contaminated, including the adoption and implementation of remedial measures, if required, post-remedial monitoring.

The stages and steps regulated at European level regarding the management of contaminated sites are approached and implemented relatively similarly within the member countries. [4].

In situ and ex situ remediation measures are equally applicable at European level according to Figure 6.1, which shows the common methods of remediation of contaminated soil in Europe. Regarding the decontamination of groundwater, ex situ physical and / or chemical remediation methods are the most common and applicable (37%) [89].

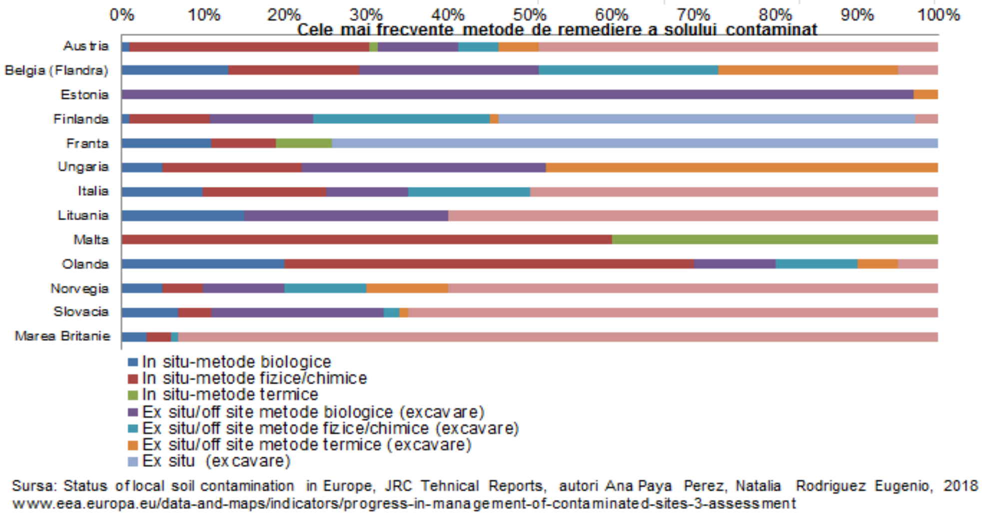

Figure 6.1 The most common methods of remedying contaminated soil in Europe

7 HIERARCHY OF THE IMPORTANCE OF PARAMETERS IN THE RISK ASSESSMENT OF POPULATION HEALTH AND THE ENVIRONMENT THROUGH THE RBCA TOOLKIT CALCULATION MODEL

Risk assessment of population health can be defined as a characterization of potential adverse effects on population exposure to hazards, and ecological risk assessment can be defined as a process of estimating the potential impact of chemical or physical agents on an ecological system (Markus & Mc Bratney , 2001). Risk assessment models involve following the elements contained in the conceptual model of the location, transport and migration of contaminants, the level of exposure in order to assess the quantitative and qualitative risk of the receptors.

Risk assessment on human health and the environment can be done both qualitatively and quantitatively. Regardless of the method chosen, risk characterization involves the assessment of exposure (probability of danger) and toxicity (severity).

In this chapter, attention will be paid to the quantitative assessment of the risk on human health, respectively on the carcinogenic and non-carcinogenic risk. This type of assessment requires a high degree of knowledge of the area, by collecting the information necessary to define the contaminated site. [79].

To quantify carcinogenic risk, the IOWA Department [90] has defined the following general formula:

Risk = f (Dose & Toxicity)

The dose is defined by the amount of the substance to which an individual is exposed (for carcinogenic risk it is dependent on its weight and size) and the period of time in which a person is exposed to the risk (the usual indicator is 70 years). The unit of dose is mg / kg per day.

In the thesis for risk assessment, the RBCAToolkit software is used, the facilities of which are presented below.

Dose calculation formula:

$$\text{Dose} = (C \times ER \times EF \times ED \times CF) / BW / At_c \times 365 \text{ days, where:}$$

SYMBOL	EXPLANATION
C	concentration of the substance (mg/kg)
ER	exposure rate of one person per day (h/ event)
EF	the frequency of exposure of a person in a year (day/year)
ED	exposure time (year)
CF	conversion factor, depending on the environmental factor (soil, water, air)
BW	body weight of an adult / child (kg)
ATc	average period of exposure to carcinogenic risk (70 year)

Theoretical tolerance for non-carcinogenic risk is equal to or less than 1. If the index of non-carcinogenic risk is greater than 1, there is a risk to public health, exposure to contaminants is acute or chronic. Depending on the method of risk quantification, it is considered that the acute exposure is short-term, and can be considered from 2 weeks, and the chronic exposure is for a longer period, considered from 1 year or more.

The computational relationships used in the RBCA Toolkit [71] to establish and quantify non-carcinogenic risk are similar to carcinogenic risk.

Dose calculation formula:

$$\text{Dose} = (C \times ER \times EF \times ED \times CF) / BW / At_n \times 365 \text{ days, where:}$$

SYMBOL	EXPLANATION
C	concentration of the substance (mg/kg)
ER	exposure rate of one person per day (h/ event)
EF	the frequency of exposure of a person in a year (day/year)
ED	exposure time (year)
CF	conversion factor, depending on the environmental factor (soil, water, air)
BW	body weight of an adult / child (kg)
ATn	average period of exposure to non-carcinogenic risk (duration of exposure varies depending on the route of exposure)

For petroleum products, the RBCA methodology was implemented in the United States by the American Society for Testing and Materials (ASTM) 1739-1995 (Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sutes).

This methodology aims to help establish processes, manage or remedy sites contaminated with various chemicals, including petroleum products. The procedure follows several stages, depending on the complexity applicable to the risk assessment on a specific location, based on three levels of risk quantification: level 1, 2 and 3.

The general criteria used at the level of a specific location to perform a carcinogenic and non-carcinogenic risk assessment using the RBCA Toolkit software (table 7.1.):

Table 7.1 RBCA software input and output data

Input data	**Output data**
• The proposed routes of exposure are: air (volatilization of air in open spaces) and groundwater; • Identification of receptors: sensitive; • Distance from receivers: (between 50 ÷ 1000) m, equidistance of 50 m; • Defining the contaminated source / environment with impact on the soil and groundwater: contaminated soil and infiltration of soil pollutant into groundwater; groundwater contamination; • Definition of pollutants: TPH, Benzene, MTBE; the concentrations of the indicators show a significant pollution; • Geological characteristics, specific to a location; • Hydrogeological characteristics, specific to a location; • Location characteristics, specific to a location.	• Calculation of individual and cumulated risk, depending on the routes of exposure and the characterization of the contaminated area; • Risk calculation, depending on the model of transport of pollutants through environments: soil, subsoil, groundwater and air; • Establishing remedial limits to eliminate the risk to receptors.

Using the RBCA software, an analysis of the influence of various parameters used by this software in quantifying the risk was performed. The parameters taken into account are summarized in tables 7.2 and 7.3. Variable parameters are: average annual rainfall, soil type, hydrogeological parameters, airflow parameters.

Constant parameters are: type and nature of chemicals, characteristics of the source of contamination, receptors.

Table 7.2 Variable parameters used to calculate the risk

Alternative risk assessment	**Variable parameters**
1. Average annual rainfall	400 mm/an 500 mm/an
2. Hydraulic conductivity	k (sand) = 4709 cm/zi k (clay) = 4,70 cm/zi k (sandy clay) = 470,9 cm/zi
3. Hydraulic gradient	i=0,05 i=0,001
4. Soil types	Sand Clay Sandy clay
5. Atmospheric air speed	vaer=1 m/s; 1.25 m/s vaer=2 m/s; 2.25 m/s vaer=3 m/s; 3.25 m/s
6. The height of the contaminated air	hair=1 m hair=2 m

Table 7.3 Constant parameters used to calculate the risk

Characteristics	**Constant parameters**
1.Chemical substances	TPH Benzene MTBE
2. Effective porosity	37%
3. The thickness of the saturated area	1 m
4. Depth of contaminated water	4.5 m
5. Depth of contaminated soil	4.5 m
6. Distance from receivers	(50÷1000) m
7. The length of the contaminated soil parallel to the direction of groundwater flow	(50, 100, 150, 200, 300, 500) m

The geological, hydrogeological and hydraulic parameters are considered specific to the potentially contaminated and contaminated sites in Romania, being analyzed following the sampling both in the field and through analyzes in specialized laboratories. The actual porosity was not varied, because during the running of the scenarios at the software level, no scenarios were obtained that would substantially change the risk values, compared to the rest of the various parameters presented by the study.

Following the running of the RBCA Toolkit software for the input data taken in the analysis, the distribution of the risk level in relation to the distance from the source of contamination was obtained. The results are presented in graphical form as it results from the subprograms attached to the mentioned software.

The general conclusions that emerge from the analysis of these results are:

- The values of the carcinogenic / non-carcinogenic risk for the air transmission path in open spaces, is higher and even exceeds the allowed limit for carcinogenic (10-5) / non-carcinogenic risk (1) in the case of non-cohesive soil (sand) under the conditions of volatilization of petroleum compounds light in atmospheric air compared to a cohesive (clayey) soil, impermeable or poorly permeable; this highlights that in addition to the route of transmission, the characteristics of the contaminated area (in this case the soil), influence the level of risk;
- In this case, it can be observed that the structure of the permeable, non-cohesive soil allows volatile petroleum substances to easily reach the atmospheric air, contaminating it;
- The value of the carcinogenic risk is high in the vicinity of the source of contamination, this being dependent on the size of the length of the contaminated area on the direction of groundwater flow;
- The risk values for the way of transmitting the contaminated air in open spaces are higher the closer the front of the contaminated air (with vapors released by the contaminated area) is (1m, 2 m) and the wind speed is lower (h = 1 m / s, 2 m / s, 3 m / s). In other words, the carcinogenic risk is higher the closer the receptors are to the volatilization zone at the level of the contaminated area and

the wind speed does not allow a dispersion of pollutants in the atmosphere and remains concentrated in the vicinity of the source;

- The degree of volatilization depends on the contact surface in the contaminated area and the characteristics of the unsaturated area (density, groundwater depth, contaminated soil depth, volume of water in the soil), pollutant vapor pressure, Henry constant;
- This behavior is influenced by the permeability coefficient and the Darcy speed; in the case of soil-groundwater contaminant transfer for less permeable clay soil type, the risk of carcinogenic / non-carcinogenic is higher compared to sandy, permeable soil;
- The carcinogenic / non-carcinogenic risk values for the groundwater transmission path are higher the higher the amount of precipitation falling on a site; in this situation, the specific influence parameter is the leaching factor considering the precipitation infiltration rate;
- The hydraulic gradient is another important hydrogeological parameter that influences the values of carcinogenic or non-carcinogenic risk for the groundwater transmission path. We can see that the slope of the free surface or the small, smooth piezometric level also determines a higher risk. In such conditions, we can appreciate that the contaminated area at the water level remains for a longer period of time and there is no dilution / dispersion printing a health risk for the receptors;
- The general mechanisms that contribute to groundwater pollution are infiltration and direct migration.

8 ASSESSMENT OF THE RISK GENERATED BY CONTAMINATED SITES. CASE STUDIES

8.1. Investigation and evaluation of the degree of contamination and the risk of the "A" site polluted with petroleum products. Case study no. 1

8.1.1 Location description

The case study is performed for a location where activities for storage, storage and distribution of petroleum products were carried out.

Possible pollutants to be identified at the site are in the category of petroleum products, total petroleum products, volatile aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene), heavy metals, substances used to increase the octane number of gasoline (eg MTBE, TAME) .

Direct investigation methods were used, soil / subsoil investigation drillings were performed hydraulically, in a dry system, with protection pipe. In order to identify the utilities, largely avoiding the situation of piercing pipes, buried cables, the indirect, electromagnetic investigation method was used both in the site area and later in the residential area.

The soil investigation boreholes were located in the area of constructions with pollution potential and with easy access (figure 8.1.1). These were located in the area of the railway ramp (F1, F4), in the area of the tanks located in the northern part of the site (F2), the decanter area - car loading ramp (F3) and the area of tanks south - car loading ramp line (F5)).

Soil samples and groundwater samples were taken from these boreholes (F3 borehole). Soil and water samples were transported for analysis of soil and groundwater pollutant concentrations for total aliphatic hydrocarbons (TPH) and volatile aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene). The results of laboratory analyzes, referring to the provisions of Order 756/1997 on the assessment of environmental pollution, using as a limit the concentration of the intervention threshold for "less sensitive use".

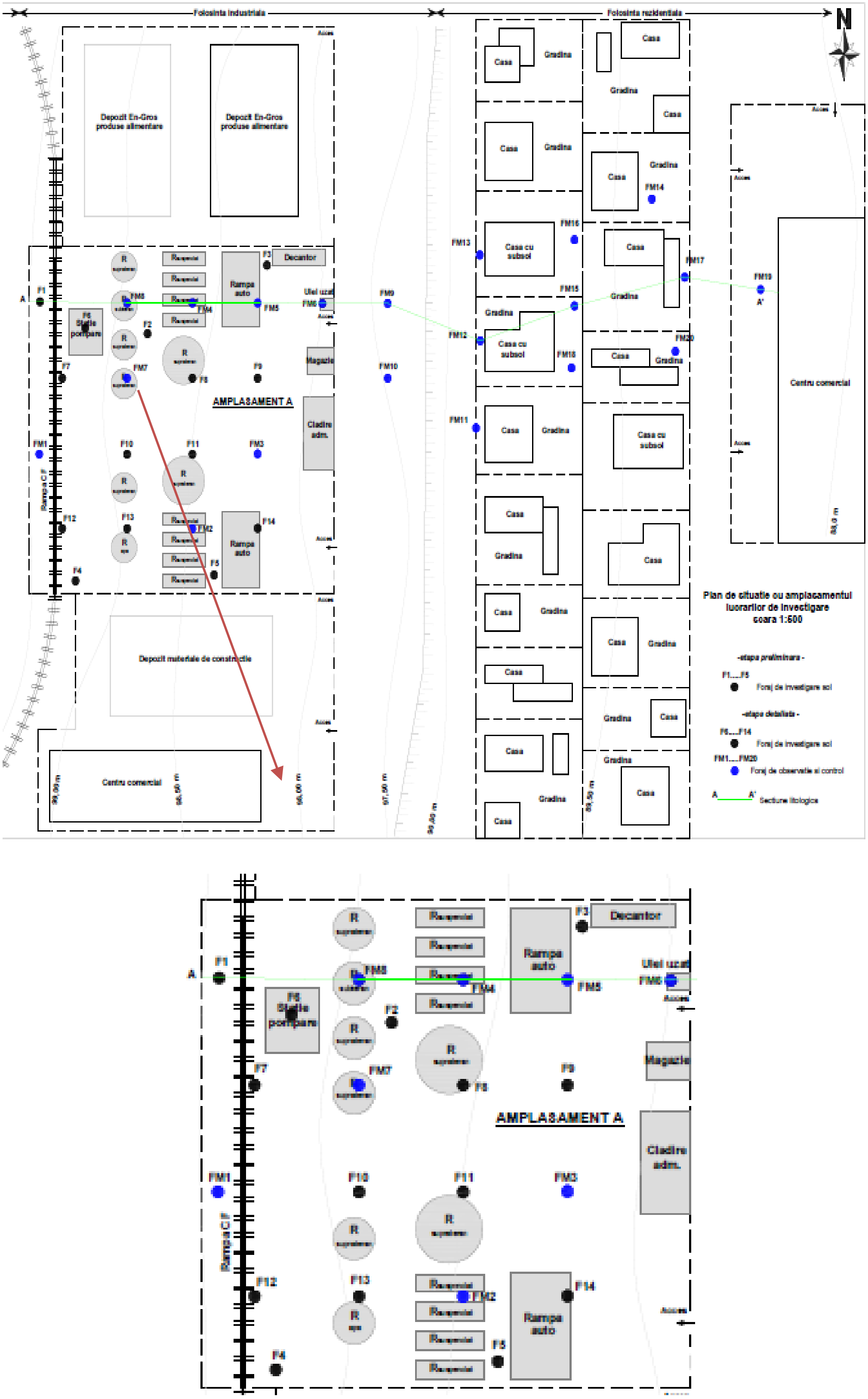

Figure 8.1.1 Site investigation plan

The image of a significant contamination of the soil with total petroleum hydrocarbons, TPH, was highlighted and outlined in the samples taken from the northern part of the site, in the area of the tanks (F2) and the car loading ramp, decanter (F3); in the case of the groundwater sample, no alert threshold for the TPH and benzene indicator was identified. Soil samples were taken from depths of 0.30 m, 1.0 m and then from meter to meter to a depth of 5.0 m, depending on the organoleptically identified contamination.

The detailed investigation followed the vertical and horizontal detailing of soil and groundwater pollution in all potentially contaminated and contaminated area, its delimitation in space depending on depth, identification of nature and intensity of pollution, link between pollutants and geological environment structure, migration routes and transportation of pollution, risk assessment.

All the information regarding the characterization of the underground environment conditions and the contamination of the site served to achieve the hydrogeological profile of the site (figure 8.1.2).

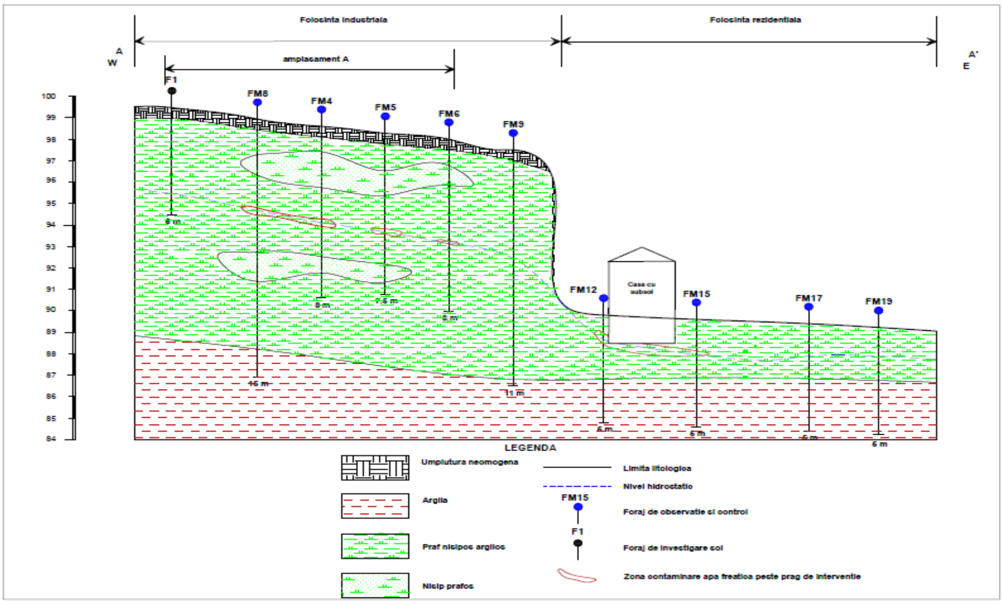

Figure 8.1.2 Hydrogeological profile of site A

8.1.2 Results of the field investigation

Figure 8.1.3 shows the values of TPH concentrations relative to the alert threshold and the intervention threshold for less sensitive uses at the level of all investigation boreholes.

In the case of drillings performed in the residential area, the laboratory analyzes on the soil samples for total hydrocarbon concentrations in oil fall within the range of normal values or below the alert threshold.

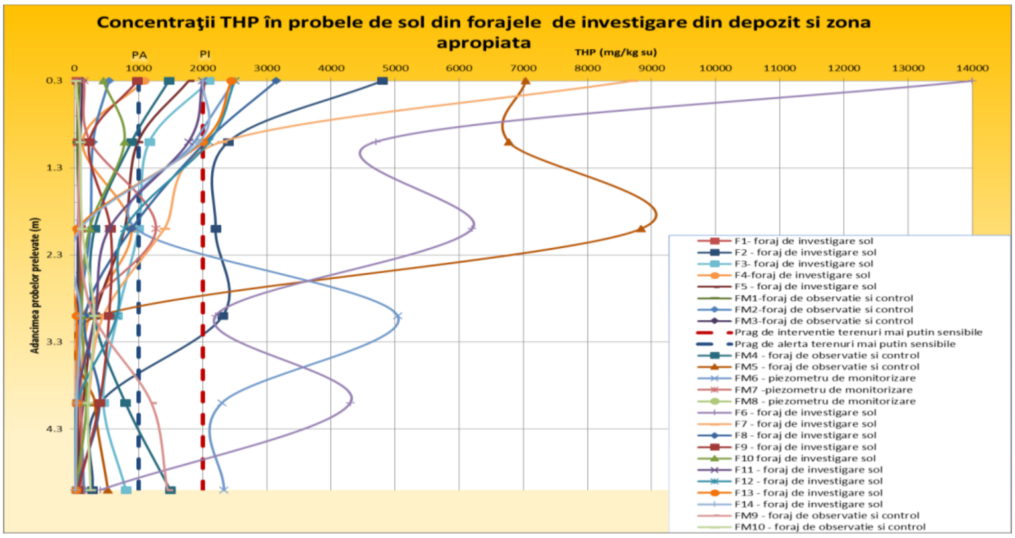

Figure 8.1.3 TPH concentrations in soil samples from investigation wells in the warehouse / site and nearby area

The analytical determination, the processing of the resulting data highlighted the soil contamination at a depth of 4m ÷ 5 m, thus being possible the transport of the identified pollutants to the groundwater through the percolation process.

The results of the laboratory analyzes showed the contamination of the groundwater both in the area of the site and downstream of it in the residential area in the direction of the groundwater flow. TPH values in groundwater above the intervention threshold (0.60 mg / l) were identified in the observation and control boreholes FM8 and FM4 (reservoir area north of the site), FM5 (car ramp), FM6 (waste oil storage area) and FM12 in the residential area. TPH values in groundwater above the alert threshold (0.10 mg / l) were identified in most observation and control boreholes except those located in the southern part of the site (FM1, FM2 and FM3), F3 and those in residential area FM14 and FM19 (figure 8.1.4).

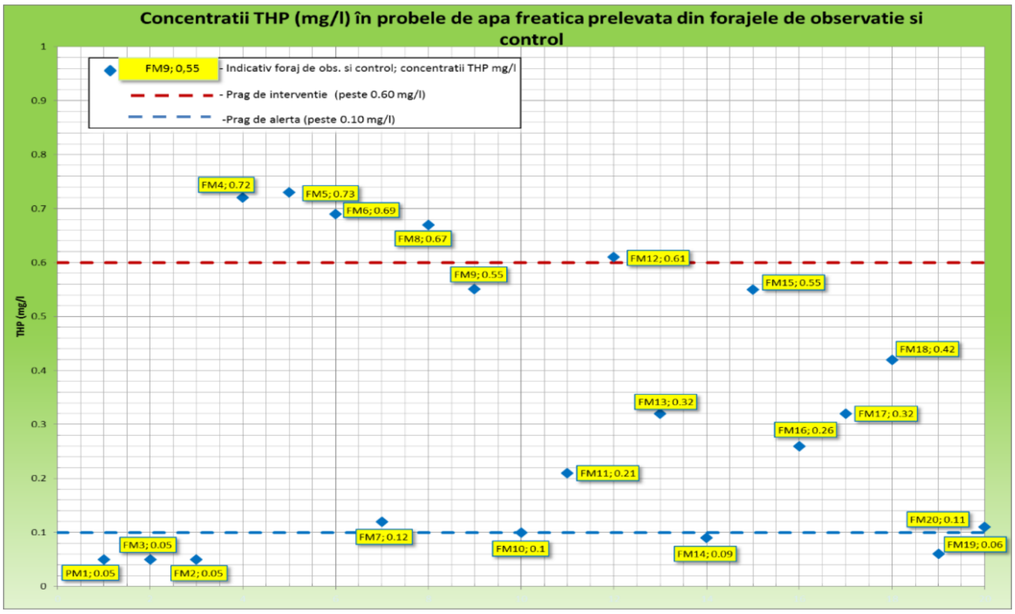

Figure 8.1.42 TPH concentrations in groundwater samples taken from well drillings

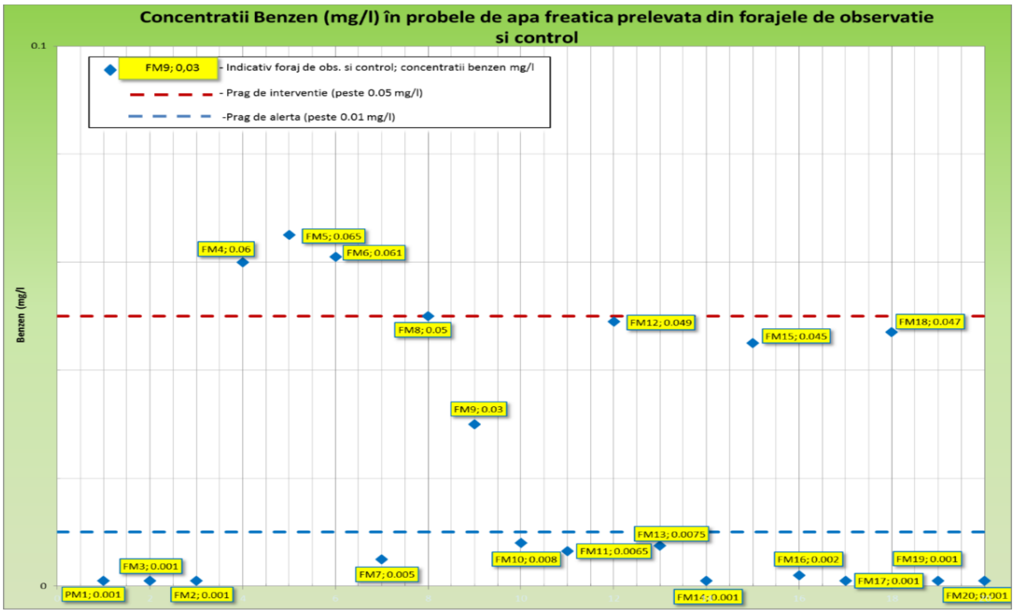

Figure 8.1.53 Benzene concentrations in groundwater samples taken from well drillings

The form of TPH isoconcentrations in groundwater highlights the infiltration of the pollutant in the northern area of the site and its migration in the direction of the groundwater flow and an extension of the pollutant wedge to the residential area (figure 8.1.6).

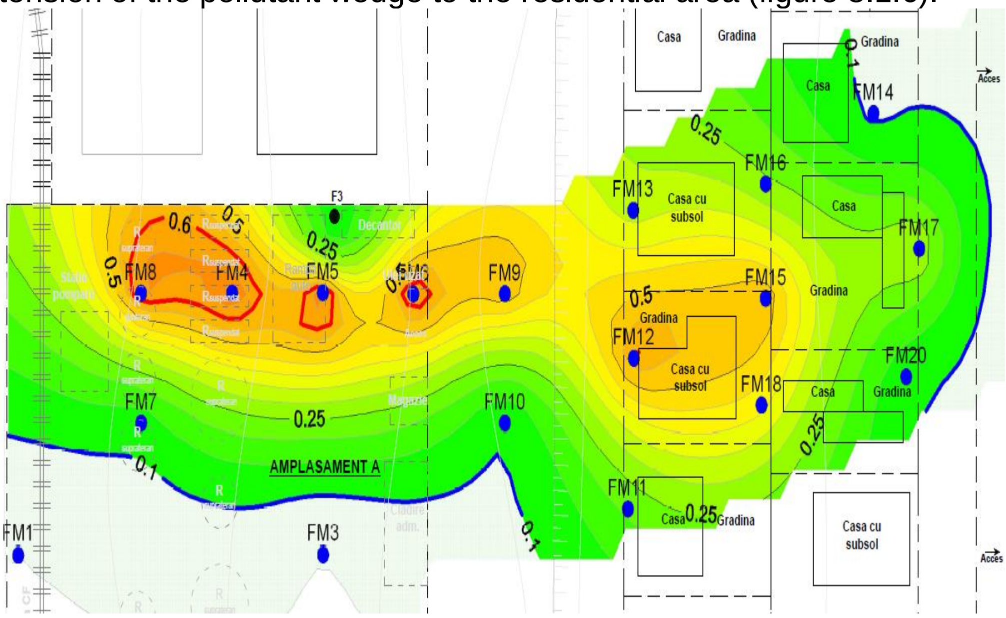

Figure 8.1.6 Distribution of TPH contamination in groundwater

Among the BTEX indicators, the values resulting from the laboratory analyzes showed exceeding the intervention threshold for benzene (over 0.05 mg / l) in the observation and control boreholes/well drillings FM4 (reservoir area north of the site), FM5 (car ramp) and FM6 (used oil storage area) and in the residential area between FM12, FM15 and FM18 observation and control boreholes/ well drillings.

Soil contamination on the site affects an area of approximately 5890 m2 (approx. 34% of the total area of the site) and an estimated volume of contaminated soil of approximately 29450 m3. Based on the soil analyzes performed for the TPH and BTEX indicators, there was a significant pollution with petroleum products up to a depth of 5 m in the tank area, the area for loading / unloading petroleum products, used oil storage.

The analysis of the groundwater showed a significant pollution with petroleum products (TPH, benzene) at the site, and this contamination migrates outside the site, to the residential area.

The contamination of the aquifer on the territory of the site covers an area of approximately 10,602 m2 (approx. 61% of the total area of the site).

8.1.3 Risk assessment (source-path-receiver identification) using the RBCA Toolkit

Quantitative risk assessment was chosen using the RBCA Toolkit for Chemical Releases software version 2.6, applying the ASTM E-2081-00 Standard Guide for Risk-Based Corrective Action (ASTM 2004) and ASTM E-1739-95 Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites. This procedure aimed at defining the reference target values taking into account the characteristic receptors inside (on site) and outside (off site) of site A.

The results of this modeling show that the risk limits are exceeded at the level of receptors identified for airways in open spaces and groundwater, through dermal contact with soil and contaminated groundwater, accidental ingestion of contaminated soil / water, release of vapors / dust, emissions. The potential recipients affected are: the workers on the site or the inhabitants of the area, located downstream, on the direction of groundwater flow or on the predominant direction of the wind.

The conclusions of this modeling reveal that for the carcinogenic risk none of the routes of exposure exceeds the maximum values administered, but for the toxic effects (non-carcinogenic risk) it is found that the exposure by air transport outside (2.7E + 0) exceeds the imposed limits.

According to ASTM E-2081-00 and ASTM E-1739-95 (Standards Guide for Risk Based Corrective Action), the acceptable value for carcinogenic risk is 10-5 (HCRQ = 10-5) and in the case of non-carcinogenic risk the risk value is 1 (HRQ = 1).

Return	Print Sheet	RBCA SITE ASSESSMENT	Baseline Risk Summary-All Pathways
Help		Completed By: Ana Date Completed: 01.01.2020	1 of 1

BASELINE RISK SUMMARY TABLE

	BASELINE CARCINOGENIC RISK					BASELINE TOXIC EFFECTS				
	Individual COC Risk		Cumulative COC Risk		Risk	Hazard Quotient		Hazard Index		Toxicity
EXPOSURE PATHWAY	Maximum Value	Target Risk	Total Value	Target Risk	Limit(s) Exceeded?	Maximum Value	Applicable Limit	Total Value	Applicable Limit	Limit(s) Exceeded?
OUTDOOR AIR EXPOSURE PATHWAYS										
Complete: ■	1.9E-8	1.0E-5	1.9E-8	1.0E-5	☐	2.7E+0	1.0E+0	2.7E+0	1.0E+0	■
INDOOR AIR EXPOSURE PATHWAYS										
Complete: ■	4.7E-8	1.0E-5	4.7E-8	1.0E-5	☐	6.1E-1	1.0E+0	6.1E-1	1.0E+0	☐
SOIL EXPOSURE PATHWAYS										
Complete: ■	7.9E-10	1.0E-5	7.9E-10	1.0E-5	☐	5.0E-1	1.0E+0	5.0E-1	1.0E+0	☐
GROUNDWATER EXPOSURE PATHWAYS										
Complete: ■	7.8E-6	1.0E-5	7.8E-6	1.0E-5	☐	5.6E-1	1.0E+0	8.8E-1	1.0E+0	☐
SURFACE WATER EXPOSURE PATHWAYS										
Complete: ☐	NA	NA	NA	NA	☐	NA	NA	NA	NA	☐
CRITICAL EXPOSURE PATHWAY (Maximum Values From Complete Pathways)										
	7.8E-6	*1.0E-5*	*7.8E-6*	*1.0E-5*	☐	*2.7E+0*	*1.0E+0*	*2.7E+0*	*1.0E+0*	■
	Groundwater		*Groundwater*			*Outdoor Air*		*Outdoor Air*		

Figure 8.1.7 Calculation of the basic risk of both carcinogenic and non-carcinogenic

The results presented in figure 8.1.7 require the taking of measures to reduce the risk in case of exposure to contaminated air and to contaminated groundwater, respectively. This can be done by decontaminating the site to reduce pollutant concentrations in soil and groundwater.

Based on the characterization of the site through the specialized software in RBCA risk assessment, there was a non-cancerous (toxic) risk at the level of the air transport route as well as at the groundwater level for the receptors identified on site (workers during remediation works) but also off site , downstream of location A (persons in the residential area).

The recommended measures for reducing or eliminating the sources of soil pollution are chosen in a feasible way by applying ex-situ and / or in-situ methods, reaching acceptable values of pollutants and possibly being achieved simultaneously for soil and groundwater remediation.

8.2. Investigation of the geological environment and assessment of the specific risk of a location in the distribution and storage component using the RBCA Toolkit and RISC 5 software. Case study no. 2

8.2.1. Location description and characteristics of the underground environment

Contaminated site B is an industrial area located in the meadow of a river. For a recent period, on the site, activities for storing petroleum products in storage and distribution tanks were carried out. The constructions left after the cessation of the activity are the loading / unloading ramp, tanks, decanter, pumping stations, technological pipes.

To assess the degree of contamination of the site, a number of 20 soil / subsoil investigation boreholes were drilled (points identified on the plan as red, example FY19) (figure 8.2.1), of which 5 drillings were transformed into well monitoring (points identified on the plan having the color blue, example FYP1) for time monitoring of groundwater quality.

The presentation of all the above information as well as the evaluation of the geological environment pollution for site B was systematized by the afferent lithological profile (figure 8.2.2).

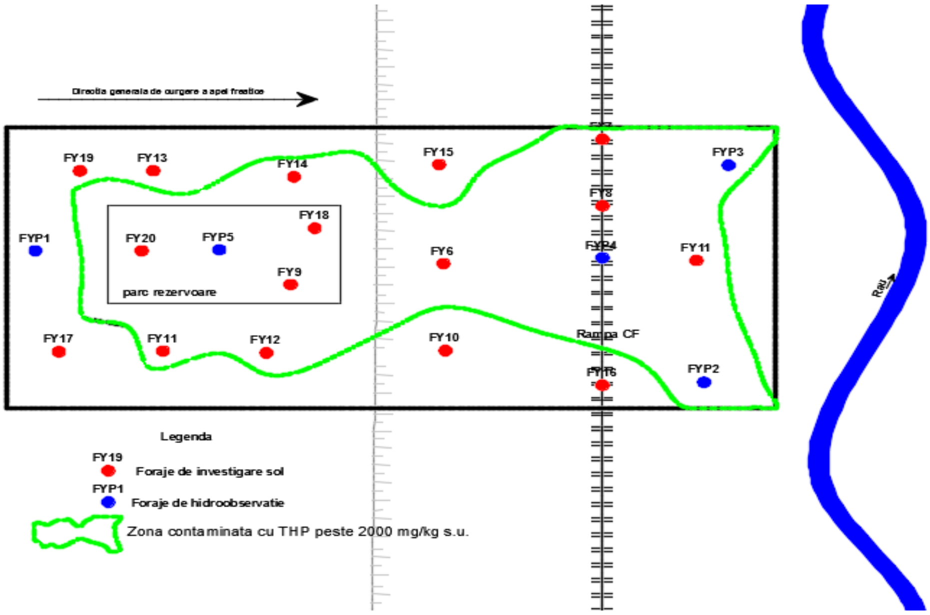

Figure 8.2.1 Spatial delimitation of the contaminated area at site "B"

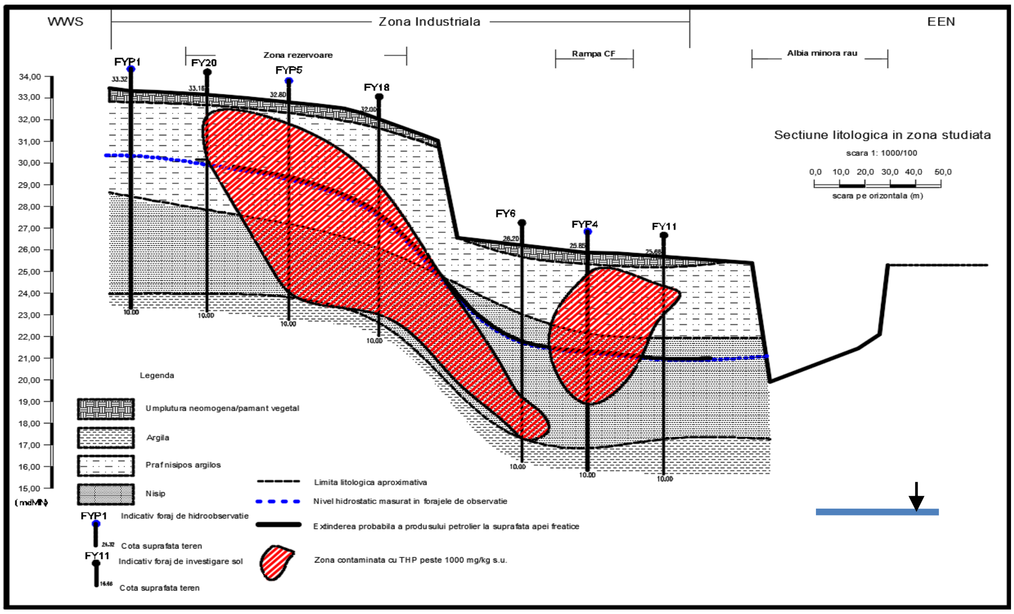

Figure 8.2.2 Lithological profile with evidence of contaminated area

8.2.2. The situation of contamination at the level of the environmental factor - soil

The graphs below show TPH concentrations, grouped by areas with potential sources of pollution. Their variation in depth is highlighted for each of the boreholes belonging to the respective area. For each graph, the alert threshold and the intervention threshold specific to the less sensitive activities were presented (Order 756/1997).

For the drilling area executed upstream of the oil storage tanks, the TPH concentrations were below the values of the intervention threshold, respectively 2000 mg / kg. The exception is the F17 borehole which has exceeded the alert threshold between the depths of 6.0 - 8.0 m.

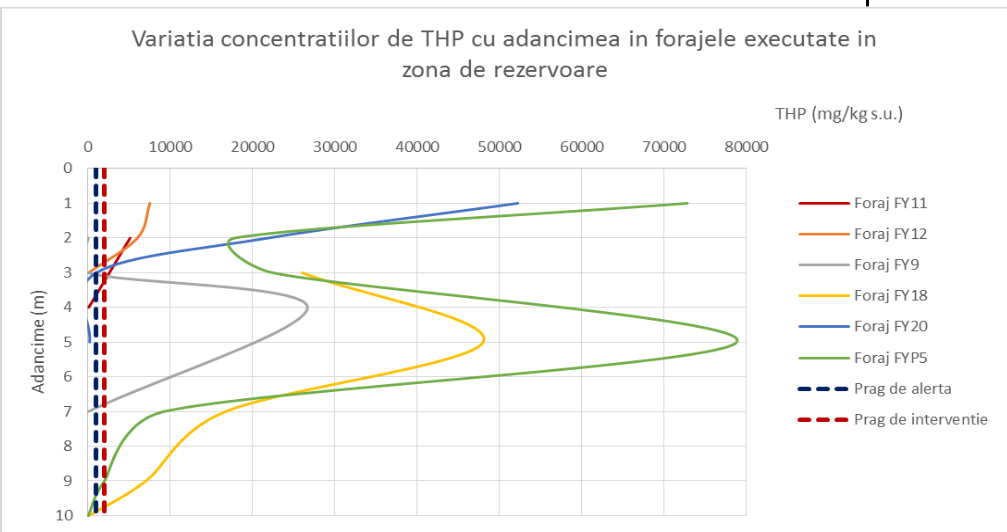

Figure 8.2.3 The variation of TPH concentrations relative to the depth of the drillings executed in the reservoir area

In the case of the reservoir area, most TPH concentrations were above the values of the intervention threshold, respectively 2000 mg / kg (figure 8.2.3). The maximum TPH concentration identified in this area is 78800 mg / kg in FYP5 drilling at a depth of 5.0 m.

For the area between the storage tanks and the CF ramp, the TPH concentrations were above the values of the intervention threshold, respectively 2000 mg / kg, in the case of FY6 drilling between the depths 5.0 - 9.0 m.

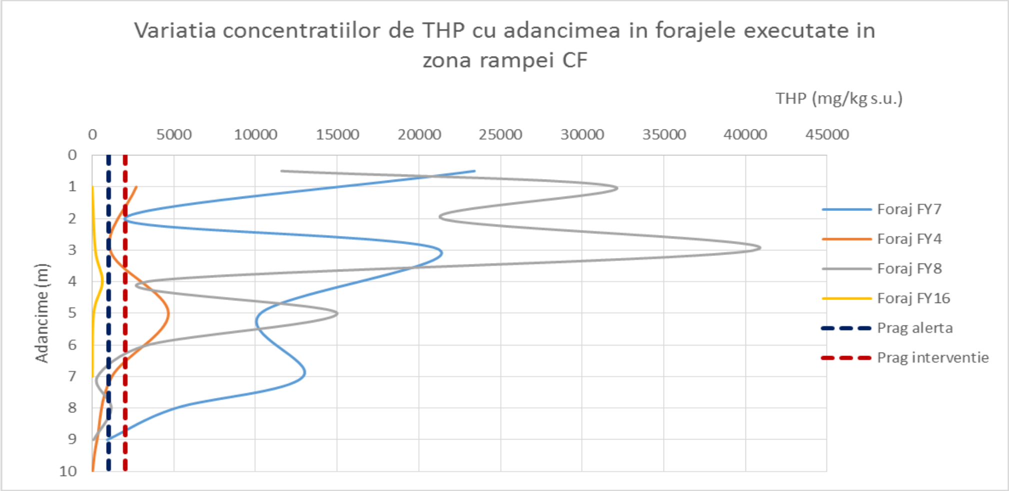

Figure 8.2.4 Variation of TPH concentrations relative to the depth of the drillings made in the railway area

In the case of the CF ramp area, most TPH concentrations were above the values of the intervention threshold, respectively 2000 mg / kg (figure 8.2.4). The maximum TPH concentration identified in this area is approximately 40,600 mg / kg in the FY8 borehole at a depth of 3.0 m. The only borehole in this area, FY16, does not exceed the alert threshold, respectively 1000 mg / kg.

For the area between the CF ramp and the river, most of the TPH concentrations were above the values of the intervention threshold, respectively 2000 mg / kg, identifying a significant pollution with TPH.

Below are the concentrations of benzene (mg / kg s.u.) determined on the samples from each investigation borehole and reported at the alert and intervention thresholds for less sensitive uses (figure 8.2.5).

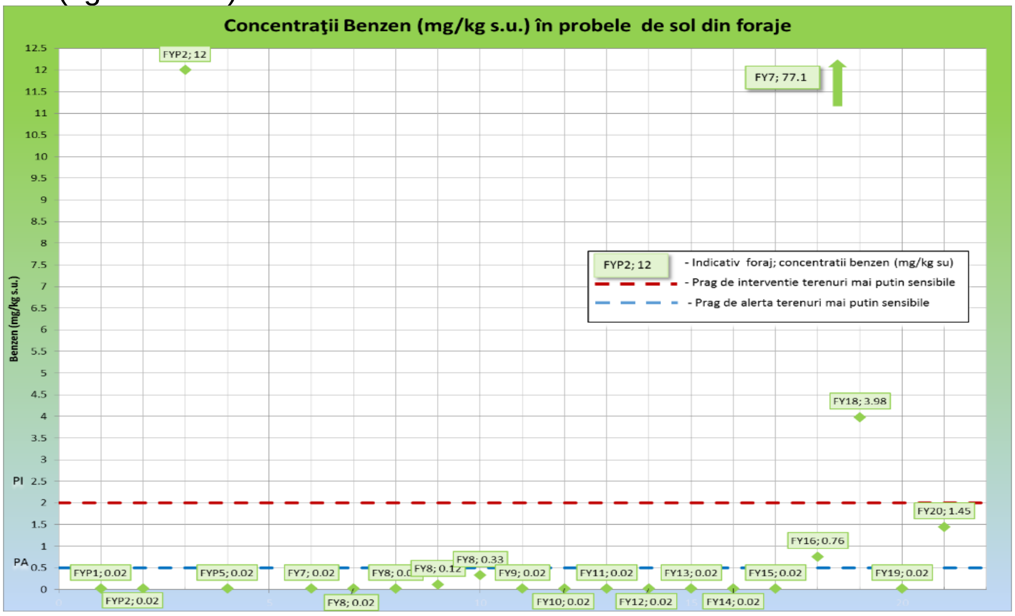

Figure 8.2.5 Benzene concentrations in soil samples from drillings

Therefore, it can be seen that the values of the benzene indicator, in most cases are below the alert threshold, only occasionally exceed the values of the alert threshold (FY16 and FY18) and the intervention threshold (FYP2-12 mg / kg, FY7-777, 1 mg / kg, FY18- 3.98 mg / kg).

The xylene concentrations (mg / kg s.u.) determined on the samples from each investigation borehole and reported at the alert and intervention thresholds for less sensitive uses.

For the ethylbenzene indicator, contamination was identified in a single borehole, with a value of 122 mg / kg in the FYP2 borehole.

In conclusion, the investigation works showed a significant pollution of the soil with petroleum products (TPH, benzene, ethylbenzene, xylene) up to a depth of 9 m.

8.2.3 The situation of contamination at the level of the environmental factor - groundwater

Next is presented the spatial distribution of TPH concentrations in groundwater (figure 8.2.6) at the level of hydro-observation boreholes. It can be concluded that significant TPH pollution is mainly identified in FYP4, FYP5 boreholes that exceed approximately 13 ÷ 22 times the TPH values of the intervention threshold.

Contaminarea apei subterane cu THP in forajele de hidroobservatie

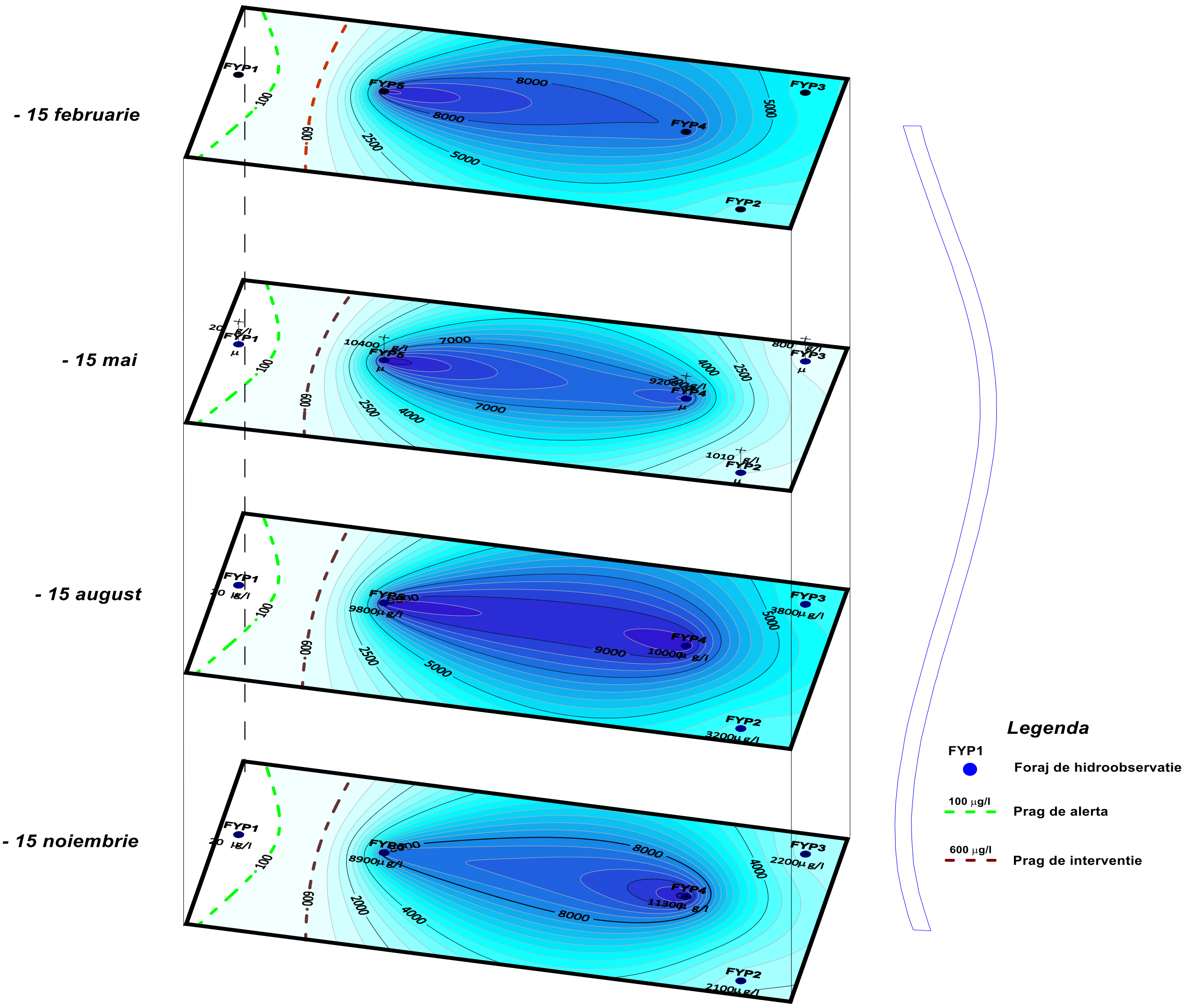

Figure 8.2.6 Spatial distribution of TPH contamination in groundwater during monitoring campaigns

From the analysis of TPH isoconcentrations in groundwater, the migration of pollutant from FYP5 to FYP4, respectively from the terrace area to the meadow area with the possibility of migration of the pollution feather outside the site to the neighboring river on the groundwater flow direction. .

Upstream and downstream water samples were taken from the river in the direction of groundwater flow in the area of site B and the results obtained from the sampling do not exceed the values of the alert thresholds of the oil products indicators.

In the same way it is presented the spatial distribution of benzene concentrations in hydro-observation boreholes in the 4 monitoring campaigns. At the level of groundwater pollution assessment, it is observed for both benzene and TPH that the pollutants are significantly identified in the FYP2, FYP3, FYP4 and FYP5 boreholes and with the possibility, in the future, to exceed the site limits.

At the site level, pollutant wedges were identified in the central area of the site, both in the terrace and meadow area, respectively in the area of railway unloading of petroleum products and in the area of the tank park.

Observing the contaminated areas, it can be concluded that the horizontal dispersion of the pollutant to the depth of the groundwater is reduced, but reaching this depth, the pollution spreads, influenced by the level of seasonal fluctuations of the groundwater level.

The investigations and analytical determinations performed on the studied site revealed a significant pollution of the underground environment with petroleum products such as TPH and BTEX up to a depth of 9 m.

The investigations highlight the existence of the following sources of contamination: tank area, pumping station, CF ramp area, oil products loading / unloading area.

Soil contamination on the site covers an area of approximately 7890 m2 (about 67% of the total area of the site) and an estimated volume of contaminated soil of approximately 31,500 m3.

Analyzes of groundwater samples also show significant pollution with petroleum products (TPH and BTEX). The dynamics of groundwater reveal that these pollutants migrate from the site to the river in its vicinity.

The contamination of the aquifer on the territory of the site covers an area of approximately 10,783 m2 (about 82% of the total area of the site).

8.2.4. Quantifying the potential risk on the human factor - using the RISC 5

The calculations regarding the estimation of the risk on the population based on the input data in the RISC 5 program demonstrate a non-carcinogenic risk for the soil environmental factor through the exposure routes: soil ingestion and dermal contact with the contaminated soil considering the high TPH concentrations.

Regarding the carcinogenic risk generated by the concentrations of the compounds identified following the site investigation, respectively benzene, ethylbenzene, xylene, the risk does not exceed the standardized limit value (figure 8.2.7).

SUMMARY OF CARCINOGENIC RISK
Receptor 1:
Construction Worker - Upper Percentile

Chemical	Ingestion of Soil	Dermal Contact with Soil	Ingestion of Irrigation Water	Dermal Contact with GW	Inhalation of GW Spray	Inhalation of Outdoor Air	Inhalation of Particulates	TOTAL
Benzene	3.7E-07	1.2E-06	0.0E+00	2.9E-36	4.0E-37	3.3E-09	1.7E-20	**1.6E-06**
Ethylbenzene	4.7E-07	1.5E-06	0.0E+00	0.0E+00	0.0E+00	1.1E-09	3.5E-20	**2.0E-06**
TPH Aliphatic C10-12	ND	ND	ND	ND	ND	ND	ND	**ND**
Xylenes (total)	ND	ND	ND	ND	ND	ND	ND	**ND**
TOTAL	**8.4E-07**	**2.7E-06**	**0.0E+00**	**2.9E-36**	**4.0E-37**	**4.4E-09**	**5.2E-20**	**3.6E-06**

SUMMARY OF HAZARD QUOTIENTS
Receptor 1:
Construction Worker - Upper Percentile

Chemical	Ingestion of Soil	Dermal Contact with Soil	Ingestion of Irrigation Water	Dermal Contact with GW	Inhalation of GW Spray	Inhalation of Outdoor Air	Inhalation of Particulates	TOTAL
Benzene	5.9E-02	1.9E-01	0.0E+00	4.5E-31	5.9E-32	4.9E-04	2.6E-15	**2.5E-01**
Ethylbenzene	1.5E-02	4.8E-02	0.0E+00	0.0E+00	0.0E+00	1.6E-05	4.9E-16	**6.3E-02**
TPH Aliphatic C10-12	2.4E+00	7.8E+00	0.0E+00	0.0E+00	0.0E+00	5.3E-09	7.8E-14	**1.0E+01**
Xylenes (total)	1.9E-03	6.0E-03	0.0E+00	0.0E+00	0.0E+00	4.7E-05	1.2E-15	**8.0E-03**
TOTAL	**2.5E+00**	**8.0E+00**	**0.0E+00**	**4.5E-31**	**5.9E-32**	**5.6E-04**	**8.2E-14**	**1.1E+01**

Figure 8.2.7 Assessment of carcinogenic and non-carcinogenic risk in the unsaturated area - RISC 5

The risk generated for contaminated groundwater based on RISC 5 program input data are shown in Figure 8.2.8, demonstrating a carcinogenic and non-carcinogenic risk by exposure to dermal contact with contaminated groundwater due to high TPH concentrations.

SUMMARY OF CARCINOGENIC RISK
Receptor 1:
Construction Worker - Upper Percentile

Chemical	Ingestion of Irrigation Water	Dermal Contact with GW	Inhalation of GW Spray	Inhalation of Outdoor Air	TOTAL
Benzene	0.0E+00	3.7E-05	5.1E-06	1.3E-08	**4.2E-05**
Ethylbenzene	0.0E+00	0.0E+00	0.0E+00	0.0E+00	**ND**
TPH Aliphatic C10-12	ND	ND	ND	ND	**ND**
Xylenes (total)	ND	ND	ND	ND	**ND**
TOTAL	**0.0E+00**	**3.7E-05**	**5.1E-06**	**1.3E-08**	**4.2E-05**

SUMMARY OF HAZARD QUOTIENTS
Receptor 1:
Construction Worker - Upper Percentile

Chemical	Ingestion of Irrigation Water	Dermal Contact with GW	Inhalation of GW Spray	Inhalation of Outdoor Air	TOTAL
Benzene	0.0E+00	5.9E+00	7.7E-01	2.0E-03	**6.6E+00**
Ethylbenzene	0.0E+00	0.0E+00	0.0E+00	0.0E+00	**ND**
TPH Aliphatic C10-12	0.0E+00	3.3E+01	2.7E-02	3.3E-02	**3.3E+01**
Xylenes (total)	0.0E+00	0.0E+00	0.0E+00	0.0E+00	**ND**
TOTAL	**0.0E+00**	**3.9E+01**	**7.9E-01**	**3.5E-02**	**3.9E+01**

Figure 8.2.8 Assessment of carcinogenic and non-carcinogenic risk at groundwater level - RISC 5

8.2.5 Quantify the potential risk to the human factor - using the RBCA Toolkit SOFT

The second software used in risk assessment is the RBCA (Risk Based Corrective Action) Toolkit for Chemical Releases Version 2.6. The evaluation 2/3 was used, respectively the definition of the characteristics afferent to the interior and exterior of the site, of the receivers and of the target values specific to the site.

The results are structured on the one hand by risk categories, respectively carcinogenic risk and toxic or toxicity risk (non-carcinogenic) and on the other hand by exposure routes defined at the level of exposure routes. The data highlight the following aspect (figure 8.2.9): carcinogenic risk is highlighted for exposure by air (in open spaces) respectively for exposure through groundwater; The risk generated by toxicity is highlighted for the air exposure pathway (in open spaces), the soil exposure pathway and the groundwater exposure pathway.

Return | Print Sheet | RBCA SITE ASSESSMENT | Baseline Risk Summary-All Pathways

Help | Completed By: Ana | Date Completed: 01.01.2020 | 1 of 1

BASELINE RISK SUMMARY TABLE

	BASELINE CARCINOGENIC RISK					BASELINE TOXIC EFFECTS				
	Individual COC Risk		Cumulative COC Risk		Risk	Hazard Quotient		Hazard Index		Toxicity
EXPOSURE PATHWAY	Maximum Value	Target Risk	Total Value	Target Risk	Limit(s) Exceeded?	Maximum Value	Applicable Limit	Total Value	Applicable Limit	Limit(s) Exceeded?
OUTDOOR AIR EXPOSURE PATHWAYS										
Complete: ■	1.9E-5	1.0E-5	1.9E-5	1.0E-5	■	3.3E+1	1.0E+0	3.3E+1	1.0E+0	■
INDOOR AIR EXPOSURE PATHWAYS										
Complete: □	NA	NA	NA	NA	□	NA	NA	NA	NA	□
SOIL EXPOSURE PATHWAYS										
Complete: ■	2.0E-7	1.0E-5	2.0E-7	1.0E-5	□	2.8E+0	1.0E+0	2.8E+0	1.0E+0	■
GROUNDWATER EXPOSURE PATHWAYS										
Complete: ■	4.0E-3	1.0E-5	4.0E-3	1.0E-5	■	1.9E+2	1.0E+0	2.1E+2	1.0E+0	■
SURFACE WATER EXPOSURE PATHWAYS										
Complete: ■	1.6E-15	1.0E-5	1.6E-15	1.0E-5	□	1.1E-10	1.0E+0	1.3E-10	1.0E+0	□
CRITICAL EXPOSURE PATHWAY (Maximum Values From Complete Pathways)										
	4.0E-3	*1.0E-5*	*4.0E-3*	*1.0E-5*	■	*1.9E+2*	*1.0E+0*	*2.1E+2*	*1.0E+0*	■
	Groundwater		*Groundwater*			*Groundwater*		*Groundwater*		

Figure 8.2.91 Assessment of carcinogenic and non-carcinogenic risk through the RBCA Toolkit

In the case of site "B", the carcinogenic and non-carcinogenic risk is significant in several ways of exposure through the RBCA software compared to the carcinogenic and non-carcinogenic risk through the RISC 5 software.

To explain this situation, the similarities and differences between the two software are further presented starting from the characteristic input and output data.

The study defined the risk by establishing the sources of risk, the transport routes and the level of pollutant concentrations at the receptors.

Risk management is the process of analyzing and implementing decisions to minimize them to acceptable levels or eliminate them.

Both programs used respectively RBCA and RISC 5 highlight a high risk on the health of the population and on the environment both for the groundwater exposure route and for the soil exposure route.

The modeling results allow the implementation of risk management measures by eliminating the sources of contamination, respectively the application of adequate decontamination solutions, taking into account the identified sources of contamination and the physico-chemical characteristics of pollutants (volatility, solubility, degradability).

Taking into account the existing pollution, at the level of soil and groundwater the following measures are required:

- continuous monitoring of the evolution in time and space of the polluting front;
- continuation of the investigation studies of the contaminated area in order to define all the characteristics necessary to carry out the feasibility study for the decontamination of the area;

Based on this study, it will then be possible to carry out the technical project for the management of contamination in this location.

9 CONCLUSIONS

9.1. General conclusions

The doctoral thesis "Risk analysis, a tool in the management of decommissioned industrial waste landfills" aims to analyze the risks generated by decommissioned industrial waste landfills.

The doctoral thesis is structured in 9 chapters.

The first chapter - Introduction and overview, presents the existing situation and the evolution of potentially contaminated and contaminated sites in accordance with the main polluting activities in Romania, mainly petrochemical and mining industry, which generated a significant form of contamination on environmental factors. These sites are numerous and imprint a unique and complex character through the specifics of the activity carried out, of the pollutants circulated and of the natural and location conditions.

The second chapter - Current legislation in the field - presents the concern regarding environmental protection found at the level of national and international regulations. Romania has transposed the requirements of European legislation through a series of laws, directives, government decisions on soil, groundwater, air, waste management and the management of contaminated and potentially contaminated sites.

The third chapter of the thesis - Synthesis on the particularities of contaminated sites depending on the activity - presents representative sites for the oil industry, respectively battles, treatment plants, oil depots, refineries and for the mining industry, respectively tailings dumps and tailings ponds. These sites are specific to the distribution - storage - transport component for raw materials, industrial wastewater and solid waste. In addition to the sites representative of these industries, the urban component represented by non-compliant landfills and related wastewater was also analyzed.

During the chapter, a description was made of the activity carried out, of the component constructive elements that allowed the general identification of the causes and specific pollution sources for each of the 6 types of sites. At the end of chapter three, this information was summarized in the form of a table for each type of site by surface area, raw materials and waste, potential contaminants, potentially contaminated areas, sources of contamination and the mechanisms that trigger contamination. In addition to the analysis of each type of site, data were collected on the specific geological and hydrogeological particularities specified at the country level.

All the information used and synthesized in this chapter is necessary for the development of the following stages of investigation, risk assessment and site remediation.

In chapter four - Performances and limitations of the methods and techniques of investigating the pollution of the underground environment - the main methods and modalities of investigation specific to the environmental protection works were selected and analyzed. A retrospective of the literature was conducted on the direct methods of investigating the geological environment by taking disturbed and undisturbed samples: manual and hydraulic drilling (rotary drilling method, drilling method, tubular drilling method and Direct method Push). In the case of indirect methods for investigating the geological environment, the following were chosen: vertical electric sounding method, seismic method, georadar method, electromagnetic method, Direct-Push method.

Following the synthesis of each investigation method, the conditions of applicability and limitation were characterized, the advantages and disadvantages of these methods to have a clear and complete picture in choosing the investigation method depending on lithology, nature of pollutants, conditions to limit the investigation.

The fifth chapter of the thesis - Conceptual model of contaminated sites. Components - are presented the models and methods of investigation specific to environmental works and potentially contaminated and contaminated sites. An important stage presented in the chapter is the choice of the investigation methodology to establish the location of the sampling points, the number and depth of samples from the geological environment to be collected. This information can be obtained as concretely as possible by applying the methodologies: the random method, the judgment-based or objective method, the systematic method and the stratified method. For each of these methods, their advantages, disadvantages, limitations and applicability were evaluated to assess the degree of pollution of contaminated sites.

The conceptual model of the site includes all the data obtained from the above stages, namely geological, hydrogeological characteristics, distribution of contaminants, contamination mechanisms, characteristics of contaminants, routes of exposure, potential receptors and assembles them into a comprehensive image allowing a detailed understanding of the site. . It is improved as new data or information characterizing the area and the site is obtained. The conceptual model is important for the choice and development of feasible remedial scenarios.

Chapter six - Management of contaminated sites - describes, in the first part, the situation of contaminated sites at European level, their situation in terms of soil and groundwater contaminants applicable to the topic of interest of the thesis (contaminants in the oil and mining industry: heavy metals, petroleum hydrocarbons, oils). Below are presented the perspectives of land planning, the management measures of the contaminated sites and the applicability of the measures for decontamination of the underground environment depending on the chemicals, duration, geological and hydrogeological conditions.

In chapter seven of the thesis - Ranking the importance of parameters in assessing the risk to public health and the environment through the RBCA Toolkit calculation model - a parametric study was performed on the factors that influence the amplitude of cancer and non-cancer risk using RBCA software.

All the information introduced in the risk assessments are often used in the locations discussed in the thesis (oil product depots, refineries) but also in the case studies detailed in the next chapter of the thesis. The characterized chemicals are petroleum hydrocarbons with carcinogenic risk, benzene and MTBE and non-carcinogenic risk, TPH. Chemical concentrations have high values defining a significant contamination at the site. The variable input data in the software are the average annual precipitation, the hydraulic conductivity related to the evaluated soil type, the hydraulic gradient, the soil type and the atmospheric air speed in the analyzed contaminated area. Constant parameters are: type and nature of chemicals (benzene, MTBE and TPH), characteristics of the source of contamination (depth, length, width of the contaminated area), receptors (sensitive), exposed environmental factors (open air and groundwater). The actual porosity was not varied, because during the running of the scenarios through the software used, no results were obtained that would substantially change the risk values, compared to the rest of the various parameters presented by the study.

Geological, hydrogeological and hydraulic parameters are considered specific to potentially contaminated and contaminated sites in Romania, being analyzed after sampling both in the field and by analysis in specialized laboratories.

The running of the data and the parameters introduced allowed the modeling and forecasting of the carcinogenic and non-carcinogenic risk on a given distance from the source of contamination and the way of its variation.

The degree of volatilization of pollutants in the geological environment depends on the contact surface in the contaminated area and the characteristics of the unsaturated area (density, groundwater depth, contaminated soil depth, volume of water in the soil), pollutant vapor pressure, Henry constant. The permeable soil (sand, sand-clay) analyzed allows volatile substances to evaporate easily into the atmospheric air in open and closed spaces contaminating it.

The carcinogenic and non-carcinogenic risk by transferring contaminants between soil and groundwater is higher for clay soil compared to sandy, permeable soil. This behavior is influenced by the permeability coefficient and the Darcy speed. Higher rainfall on a contaminated site increases the risk of cancer and non-cancer on the receptors; this parameter influences the leaching factor of the pollutant from soil to subsoil and groundwater considering the rate of precipitation infiltration.

Another important aspect is that the risk of carcinogenic and non-carcinogenic increases in the case of impermeable, clayey soils compared to sandy soils. If the wind speed is lower, the risk is increased, thus not creating conditions for a dispersion in the atmospheric air of the pollutant at the level of the pollution source.

The shape or shape of the graphs for carcinogenic and non-carcinogenic risk is similar, respectively the risk values increase in the immediate vicinity of the contaminated source (around 50 m) and subsequently decrease with the removal of the source. In the case of carcinogenic risk, it is observed that its values depend on the length of the contaminated source and the risk increases with the increase of this source. For the path of air exposure in open spaces, unlike the other situations, the non-carcinogenic risk (for sandy, sand-clay and clay soils) has the same value not being influenced by the size of the contamination source.

Chapter eight - Risk assessment generated by contaminated sites - includes two case studies that describe the entire process of identification, investigation, evaluation and management of contaminated sites in Romania taking into account the entire flow of information and applications considered in the thesis chapters.

The first case study - Investigation and assessment of the degree of contamination and risk of site "A" polluted with petroleum products - presents a detailed analysis, interprets and presents the results of field investigations for a potentially contaminated site in the country, having an activity carried out in time for storage, storage and transport of petroleum products by car and rail. The entire investigation of the analyzed location "A" was presented in stages, in a detailed and complex way, following the evaluation of the degree of contamination. The site is characterized by dusty clayey sandy soils, groundwater level located at about 4.5 m and contaminants such as petroleum products: TPH, benzene in the geological environment.

Following the finding of significant contamination on the geological environment and the specific features of these types of sites (information contained in chapter three of the thesis) but also particular for site "A", the degree of quantitative risk on population health was assessed for receptors at the site and those in the vicinity of site "A" (at relatively short distances from the source of contamination, 30 m and 100 m). In this case, the receivers are people in residential areas (adults, children), kindergartens, commercial spaces.

Mathematical modeling for risk assessment was performed using RBCA software and shows the risk limits exceeded at the level of receptors identified for airways in open spaces and groundwater, by dermal contact with soil and contaminated groundwater, accidental ingestion of contaminated soil / water, vapor / dust release, emissions. The potential recipients affected are: the workers on the site or the inhabitants of the area, located downstream, on the direction of groundwater flow or on the predominant direction of the wind.

The conclusions of the modeling related to the "A" site reveal that for the carcinogenic risk none of the routes of exposure exceeds the maximum values administered, but for the toxic effects (non-carcinogenic risk) it is found that the exposure via outdoor air transport / open spaces (2.7E + 0) exceeds the imposed limits.

In this way, the results obtained from the quantitative risk assessment require measures to reduce the risk in case of exposure to contaminated air and contaminated groundwater, respectively. This can be done by decontaminating the site to reduce pollutant concentrations in soil and groundwater.

In the case study no. 2 - Investigating the geological environment and assessing the specific risk of a site in the distribution and storage component using RBCA Toolkit and RISC 5 software - presents in addition to the stages of investigation and assessment of groundwater pollution for site "B" and quantitative risk assessment on public health through 2 constantly used software worldwide, RBCA Toolkit and RISC 5. The location analyzed "B" is similar to the location "A" in the first case study, the similar aspect being only the type of activity carried out at their level, supply, storage-distribution and transport of petroleum products in the country. The "B" location is found in urban areas, having in the vicinity sensitive receptors, in this case, the river. In addition to presenting the way of investigating the site by choosing the methods and models of investigation, an interpretation of the results was made to obtain a characterization of the degree of pollution for the geological environment. For this purpose, the Surfer software was used, through which all the information was integrated and the spatial distribution of the site contamination for soil and groundwater for petroleum hydrocarbons, benzene, xylene, ethylbenzene resulted. The geological conditions are similar to the storage and transport sites, respectively clayey sandy powders. The specificity of the location "B", from the point of view of the receivers is to be in the vicinity of a river, which allowed an analysis of the interconnection of water level (in hydro-observation wells) and river level, based on data processed from monitoring quarterly for 1 year.

The contamination of the site is significant, therefore it required the assessment of the degree of risk on the receivers.

The estimation of the degree of risk on the population based on the input data in the RISC 5 program determines a non-carcinogenic risk for the soil environmental factor through the exposure routes: soil ingestion and dermal contact with the contaminated soil considering the high TPH concentrations. Regarding the carcinogenic risk generated by the concentrations of the compounds identified following the site investigation, respectively benzene, ethylbenzene, xylene the risk does not exceed the standardized limit value (1.0E-5).

The risk generated by the contaminated groundwater based on the data entered in the RISC 5 program presents a carcinogenic and non-carcinogenic risk by exposure to dermal contact with it given the high concentrations of TPH, benzene.

As a result of the risk assessment obtained, it is necessary to carry out decontamination works on the site and groundwater to reduce the concentrations of pollutants so that both the carcinogenic risk and the toxic / non-carcinogenic risk are reduced to acceptable levels for public health and for the environment.

Also, analyzing the carcinogenic and non-carcinogenic risk assessments through the two software, RBCA Toolkit and RISC 5, differences were found in the results obtained. In the case of site "B", the carcinogenic and non-carcinogenic risk is significant in several ways of exposure through the RBCA software compared to the carcinogenic and non-carcinogenic risk through the RISC 5 software.

To explain this situation, the similarities and differences between the two software were analyzed starting from the characteristic input and output data. One of the most important similarities is that both software have in the database the types of chemicals analyzed and that allowed the introduction of the same concentrations. Also, both softwares take into account the homogeneous conditions in the field, present the database with the properties of the chemical substances, with the geological, hydrogeological conditions, toxicity and if the user considers necessary certain indicators can be modified.

In this way, it is important to define in a complex and concise way the sources, the transmission routes and the receivers of the specific location in order to evaluate the appropriate quantitative risk and to respond to the real situation in the field.

9.2. Personal contributions

The multidisciplinary research carried out to solve the topic proposed by this doctoral thesis has facilitated the formulation of new approaches that can be considered as personal contributions to the knowledge of this field.

Of these, the most important are:

- synthesis and analysis of the legislation at national and international level regarding the management of potentially contaminated and contaminated sites from the activities carried out in the mining field, storage and distribution services of petroleum products, urban component;
- evaluation of the particularities of the industrial sites for the distribution, storage and transport activities, the influence of the natural environment, of the types of pollutants specific to them and of the forms of contamination generated. The analysis allowed the optimization of the application of the methods of investigation and evaluation of the pollution but also of the identification of the risks generated by these locations;
- critical analysis of the performances, limitations, advantages and disadvantages of the techniques and modalities of direct and indirect investigation of the pollution of the underground environment;
- analysis and updating of the management of contaminated sites in the context of the field of study of this thesis, respectively mining, oil and fuel distribution areas;
- identifying the routes of exposure and the methods and models for quantifying the risk specific to a site focused on risk assessment on the health of the population and the environment;
- parametric analysis of influencing factors in calculating carcinogenic and non-carcinogenic risk taking into account the specifics of general geological conditions (sand, clay, clayey sand), hydrogeological and natural conditions identified in the sites applying the calculation method of RBCA Toolkit software;
- detailed analysis of two contaminated sites based on a concrete and complex situation of its location, following the methodology approached in the thesis chapters;
- carrying out a detailed investigation of the contaminated sites defining the geological, hydrogeological, climatic, geographical characteristics of the area;

- realization of a set of 39 investigation boreholes (in case of case study 1) and respectively 20 investigation boreholes (in case of case study 2) for sampling soil and groundwater in order to define the level of pollution;
- analysis and integration of information obtained from the field and laboratory investigation stage in the specialized software (Surfer) for configuring the amplitude of the level of pollution with petroleum products on site both in soil and groundwater, including aquifer flow modeling;
- quantitative assessment of the risk generated by this pollution on human health using 2 high-performance software (RISC 5 and RBCA Toolkit) applicable internationally and interpretation of the results obtained; the similarities and the differences between the 2 software regarding the specific input data for the identification of the sources, exposure routes and receivers were highlighted in order to reproduce as accurately as possible the situation in question;
- adaptation and adoption of risk management tools in the case of site-specific case studies to ensure optimal measures to limit and / or remedy contaminated soil and groundwater, so that the level of carcinogenic and toxic risk is reduced to acceptable values.

9.3. Research directions for the future

The field in which the doctoral thesis was elaborated is topical and represents a major problem of the society, both at present and future level, so that it offers possibilities for further research.

The research directions related to the characterization and evaluation of the management of the potentially contaminated and contaminated sites proposed can be:

- Development and implementation of programs to assess the risk generated by a contaminated site taking into account the background pollution of the environment (contaminated sites in the country, to assess the associated risk to both population and ecosystem health, depending on the nature and assessment of the pollution area and site-specific characteristics);
- Development of techniques for optimizing the conceptual models of the site aiming at minimizing the volume of data collected so as to streamline the investigation of the contaminated area;
- Comparative analysis of management solutions for contaminated sites to reduce the risk generated by these areas by combining remedial solutions with those of breaking migration routes.

REFERENCES EXTRAS

4. Ana Paya Perez, Natalia Rodriguez Eugenio, JRC Technical Reports, 2018.

5. ANZECC / NHMRC, Guidelines for assessing and managing petroleum hydrocarbon contaminated sites in New Zeeland. Ministry for the Environment New Zeeland, 1992.

6. ANZECC, Guidelines for the assessment of on-site containment of contaminated soil. Australia and New Zealand Environment and Conservation Council, 1999.

16. Bica I., Remediation of contaminated sites. University Horizons Publishing House, Timisoara, 2014.

47. Marchidanu, E., Hydrogeology in construction engineering, Technical Publishing House, 1995.

48. ME-Ministry of Environment, Contaminated Land Management Guidelines No. 5: Site Investigation and Analysis of Soils, New Zealand, 2004.

49. ME-Ministry of Environment, Guidelines for Assessing and Managing Petroleum Hydrocarbon Contaminated Sites in New Zealand (Revised 2011), Module 3, Site assessment, New Zealand, 2011.

71. Software Guidance Manual RBCA Tool Kit for Chemical Releases. GSI Environmental Inc.

79. US-Environmental Protection Agency-Handbook of Toxic and Hazardous and Cancinogens, EPA US Integrated Risk Information System 2012.

89. www.eea.europa.eu/data-and-maps/indicators/progress-in-management-of-contaminated-sites-3/assessment.

Petruta, A.M., Bica, I., Particularities of the assessment of land and groundwater contamination in the area of petroleum product warehouses, Agriculture for Life International Conference, Scientific Papers. Series E. Land Reclamation, Earth Observation & Surveying, Environmental Engineering, Vol. IX, 2020, ISSN 2285-6064, ISSN CD-ROM 2285-6072, ISSN Online 2393-5138, ISSN-L 2285-6064 – pag76-81.

Petruta, A.M., Bica, I., Analysis of the pollution degree of the geological environment on a petroleum product storage & distribution site, The 7th Conference of the Sustainable Solutions for Energy and Environment, IOP Conf. Series: Earth and Environmental Science 664, 2021.

Bica, I., Petruta, A.M., The risk assessment, a decision-making tool for the management of contaminated sites, APEEM 2021, E3S Web of Conferences 265.