TECHNICAL UNIVERSITY OF CIVIL ENGINEERING BUCHAREST
FACULTY OF HIDROTECHNICS

Doctoral School

ASSESSMENT POLLUTION FROM WASTE DISPOSALS

Research report no. 3

Content

1. METHODS AND MODELS OF SOIL SAMPLING

1.1. Introduction

The objective of the sampling plan is to establish the nature and extent of pollution, both horizontally and vertically.

The stages preceding the field investigation are the following:

- obtaining the necessary authorizations from all the competent authorizations involved at project level in the county where the investigation action is carried out;
- revision of the preliminary investigation plan, from the office documentation phase by visual evaluation of the soil;
- presentation of sampling equipment specific to environmental applications;
- calibration of field equipment, if applicable;
- knowledge of occupational health and safety protection measures during the investigation works.

The sampling strategy will require detailed knowledge of the historical information of the site, if it exists, such as: location, depth, type and source of contamination, etc.

An important factor that helps to apply the sampling model is the use of indirect methods of investigation (geophysical surveys) and the use of equipment for on-site measurement of contaminants, analytical measurements. These devices must be properly calibrated and require specialized personnel, through which the information taken to be interpreted according to the specifications and findings in the field.

Steps followed in carrying out the contamination assessment on a site, according to the specialized literature are [5]:

- determining hot spots;
- determining the arithmetic mean of contaminant concentrations;
- determining the percentage by which the degree of contamination of the site is presented.

The sampling program of the investigation phase, in general, depending on the specifics of each site should include the following [5]:

- soil test:
- groundwater samples;
- surface water and sediment samples;
- soil vapor samples, if information is available that they are volatile contaminants.

An important stage that defines the characterization of the location is the choice of the investigation method through which to determine the areas where the samples will be taken, their number and at what time intervals.

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

For all investigation techniques it is necessary to establish the number of samples, their type and positioning to allow the identification of contamination in as much detail as possible, on the entire site.

1.2. Types of strategies for positioning sampling points

The presentation of the methods and models of investigation is made on the basis of numerous specialized publications of a scientific nature that establish guidelines on the methods and models of location of sampling points for contaminated sites.
In this sense, the main specialized sources are mentioned:

On the U.S. website The EPA presents the agreed methods of investigation [5], which detail the methods of investigation mentioned above.

a) Strategy for judgemental positioning

The sampling points of the investigation plan are selected based on previous knowledge from the investigator's database on the area, technological objects and probable distribution of contaminants on the site, visible spots of surface pollution.

The quality of the positioning of the sampling points depends on the experience of the investigator and the availability of historical information. It is mentioned that this model is not used in case of validation of the contamination of the entire site.

b) Strategy for random positioning

Sampling points are randomly selected on site. It is useful when we do not know any information about the location or possible contaminated area.

The random process ensures the choice of any location of sampling points having an equal chance to be selected as an investigation point.

It is not recommended for determining hot spots because it is an impartial statistical model.

In the case of sites contaminated over time, this strategy of positioning sampling points is very rare.

c) Strategy for systematic positioning

This type of investigation involves a uniform and equidistant selection of the position of the investigation points. No point groups are generated and it is much more useful compared to random strategy.

It has the shape of a grid, often square in shape. The usual method of establishing the sampling points are the grid nodes, respectively the intersection points obtained on the entire grid.

If there are existing constructions, the intersection points for investigation will be moved so as to allow their execution in the field.

d) Strategy for stratified positioning

The first step in such a strategy is the division into sub-areas taking into account several aspects: geological and geographical conditions, nature of contaminants, historical source of pollution on the site.

Each area will be treated individually and with a different concentration of sampling points in that sub-area. This model requires a complex statistical analysis.

In the absence of site requirements, Table 1.1 [5], [6] may guide the establishment of the recommended number of sampling points for the characterization of the site:

Table 1.1 Recommendation of the number of investigation points depending on the surface of the site

Site size (ha)	No. of sampling points	Orientation diameter hot spot (m)
0,05	5	11,8
0,1	6	15,2

0,2	7	19,9
0,3	9	21,5
0,4	11	22,5
0,5	13	23,1
0,6	15	23,6
0,7	17	23,9
0,8	19	24,2
0,9	20	25,0
1,0	21	25,7
1,5	25	28,9
2,0	30	30,5
2,5	35	31,5
3,0	40	32,4
3,5	45	32,9
4,0	50	33,4
4,5	52	34,6
5,0	55	35,6

- In the guide on the assessment and management of contaminated sites in New Zealand [5] some general guidelines are suggested:

- defining the potentially contaminated area based on historical information;
- adopting the strategies for positioning the target - sampling points, in areas where the existence of contamination is known, the probable concentration of the contaminant and the spatial distribution of the contamination;

The same publication presents differentiated the two models of investigation: systematic (systematic) and target. The target prediction model is similar to the objective / judgment-based model defined by other research in the literature.

a) Strategy for systematic positioning:

- useful in identifying hot-spots in areas where they are not expected to be contaminated;
- estimates the average concentrations in the contaminated area;
- as a rule, a grid distance of 10 m - 30 m is recommended;
- it can have a flexible character, considering the change of the location of the sampling points due to the obstacles encountered on the field.

b) Strategy for judgemental positioning:

- the model of positioning the sampling points depends largely on the degree of knowledge from the historical information;
- usually, this type of sampling strategy is performed in combination with the systematic model;
- the depth of sampling depends on the nature of the contaminant and the location of the source of contamination, so: in the vicinity of surface facilities, the depth of samples is recommended up to 2 m and in heavily contaminated areas undisturbed samples will be taken so as not to contaminate water. underground.

  In case of groundwater sampling, the following aspects are recommended:
- the number of samples and their location depend on the complexity of the site;
- for LNAPL type pollutants, the pollutant concentration on different depths will be monitored;

- during the preliminary investigations, the selection of monitoring wells will be considered in order to characterize the aquifer.

The investigation of groundwater, regardless of the method or strategy of sampling, will be aimed at determining the depth of water, its direction and speed of movement, determining the contamination that may be in groundwater (both on site and off site), the type and form of contaminants (eg LNAPL).

- The website of the New Zealand Ministry of the Environment presents three categories of strategies for establishing sampling points:

a) Strategy for judgemental positioning

This type of model requires knowledge of historical information about the contaminated site (figure 1).

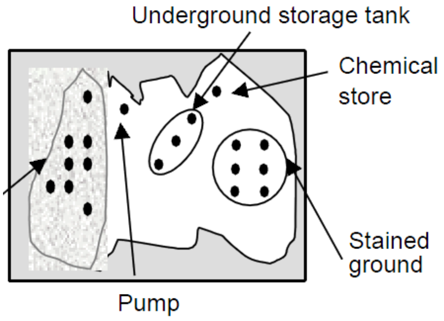

Figure 1 Justified sampling model [5]

The sampling procedure is the most used method, especially in the case of former sites contaminated for a long time (history).

The location of these sampling points is established based on historical information about the source of contamination of the site / site and can be used for:

- confirmation of the presence of pollutants on the site based on historical activities;

- confirmation of the presence of a level of contamination above the admissible limit for the specific site (eg intervention threshold, according to the specifications of the regulations in force in Romania);

- providing future information to establish future data for validation of contamination and completion of detailed site investigations.

The advantage of this type of strategy is the much lower cost compared to designing a statistical model for the location of sampling points and can be easily implemented.

The major limitation of the judgment-based strategy is the site's historical database.

The objective type of strategy cannot be used to validate contamination on a site, therefore it is recommended to continue the location of statistical sampling points.

b) Strategy for systematic positioning

The plan allows the positioning of sampling points at equal intervals as distance, the first location of the investigation point is random to reduce subjectivism (US EPA, 2002) (figure 2).

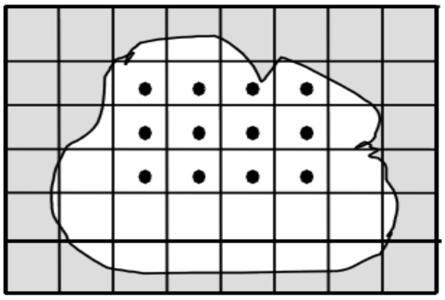

Figure 2 Systematic sampling model [5]

The strategy is based on a grid model to define the location of sampling points on the contaminated site. It starts from equal distances to achieve the grid on the entire surface of the site with the position of the first sampling location randomly.
The shape of the sampling points for these grids is triangular, rectangular or zig-zag chosen based on the size of the site and the data about the size / geometry of the hot spots.
The main disadvantage is the large number of samples and implicitly the costs.

c) Strategy for stratified positioning

The site area is divided into subzones with sample point positioning in each of these areas (figure 3).

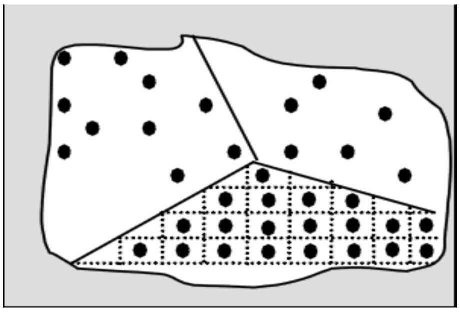

Figure 3 Model stratified sampling [5]

This type of strategy involves dividing the site into three sub-areas with different density and positioning of sampling points. The cause of the division into the 3 areas depends mainly on the behavior of the contaminant.

The number of sampling points in each sub-area is conditioned by its size as well as by:

- Geological characteristics
- Existing constructions or activity on site;
- Site history;
- Vertical or horizontal distribution of the contaminant;
- Future development of each subzone.

The strategy of positioning the sampling points of stratified type is often found when the surfaces of the sites are large and complex or when the level of contamination on the site can be anticipated (based on historical data).

1.3. Calculation procedures for establishing the number of investigation points

The investigation methods presented in [5] describe the guidelines on the strategies for locating the investigation points presented as well as different procedures for identifying hot spots.

i. The procedure for determining the number of sampling points required for the detection of a hot spot is referred to [6].

The method involves detecting a hot spot using the grid method of dividing the site. The calculation relations are relatively simple, the difficulty is the choice of the calculation parameters. With the help of the first calculation relation, the sampling scheme will be determined by calculating the grid size starting from the size of the hot-spot area defined by its radius. The second calculation relation (n) determines the number of monitoring wells.

Calculation method:

$$G = R / 0.59$$

$$n = A / G^2$$

SIMBOL	EXPLICATIE
n	the required number of wells or sampling points
A	site area, (m^2)
G	distance between two sampling points, grid size, (m)
R	radius of the smallest hot spot, the subject of this action (m)
0.59	factor resulting from the probability of prediction (in this case 95%), having a circular shape of the contaminated area (hotspot)

Procedure:

-determining the radius of a hot spot, R

-calculation of the grid size, G

-determining the number of sampling points or wells, n, necessary for the identification of the contaminant.

Note: The larger the hot spot radius, the greater the distance between the grid and the smaller the number of boreholes.

Determining the number of wells, for certain ideal cases, can also be done using basic data on the size of the contaminated area (hot-spot) (ME, 2011):

Table 1.2 Sampling points depending on the area of the area

Hot-spot diameter detectable with 95% confidence	The size of the grid G (m)	surface area A (m^2)	Minimum number of sampling points N
11.8	10.0	500	5
15.2	12.9	1000	6
21.5	18.2	3000	9
23.1	19.6	5000	13
30.5	25.8	20,000	30
35.6	30.2	50,000	55

i. Another procedure is to determine the number of sampling points required for the detection of the average concentration, has as reference [80].

The method of determining the number of sampling points is a validation method, where the mean concentration and standard deviation can be estimated for the initial results.

Calculation method:

$$n = (6.2 \times \sigma^2) / (c_S - \mu)$$

SIMBOL	EXPLICATIE
n	the required number of wells or sampling points

σ	estimation of the standard deviation, (mg/kg)
μ	estimating the average concentration, (mg/kg)
c_s	limit concentration, acceptable (mg/kg)

Procedure:

1. μ is estimated based on data from previous investigations;
2. estimation of σ based on initial sampling data; when no data are available it is calculated as follows:
   - estimation of the lowest concentrations in the investigated area, cL
   - estimation of the highest concentrations in the investigated area, cH
   - calculation equation: $\sigma = (cH - cL) / 6$
3. determination of the maximum permissible concentration;
4. application of the calculation method, according to the formula.

1.4. Conclusions

Based on the information presented in detail but also on other scientific articles on the methods of positioning the sampling points on a specific location, a critical analysis of these site investigation models can be presented in terms of their applicability, advantages, disadvantages and limitations. investigation methods.

a) Application

JUDGMENT-BASED INVESTIGATION METHOD

- confirms the contamination on a site, following the historical activity carried out;
- provides further information for the detailed investigation phase;
- it is usually used together with the method of systematic investigation to validate the contamination on a site;
- applicable for sites about which previous information is known regarding possible accidents or former potentially polluting facilities (storage tanks, decanters, landfills), etc .; including visual contamination from the soil surface, may determine the positioning of sampling points.

SYSTEMATIC INVESTIGATION METHOD

- detects hot-spots or heavily polluted areas validating the site as contaminated, including in situations where hot spots are identified in areas where it was not expected;
- use in case of limited information about site contamination;
- estimation of average concentrations of contaminants;
- the general characterization of the site in the absence of adequate information about its history (usually, distances between points of 10-30 m, but it depends on the facilities on the site and its characteristics).

STRATIFIED RESEARCH METHOD

- sampling model suitable on large sites with a complex distribution of contaminants;
- knowledge in detail of the location as well as of its historical data;
- correlation of the situation regarding the stratification of the layers: in case of the existence of clay it can be correlated with the amount of contaminant reached in the soil;
- division of the site to be investigated according to the expected level of contamination and its characteristics.

RANDOM INVESTIGATION METHOD

- evaluation of average values of the characteristics of polluting substances
- they are used with good results in the conditions of a homogeneous contamination
- can be applied in the first or last part of the sampling.

b) Benefits

JUDGMENT-BASED INVESTIGATION METHOD

- selective character;
- efficient and easy to implement;
- taking samples from sources known to be contaminated;
- limiting unnecessary random sampling costs;
- lower costs compared to statistical and selective models.

SYSTEMATIC INVESTIGATION METHOD

- practical and easy to use for surveying sampling locations compared to random model;
- allows the identification of hot spots;
- does not generate groups of sampling points;
- characterizes the site as a whole, in the absence of information about the history of the activity carried out;
- probabilistic method;
- utility when it is known that possible contamination can migrate anywhere on the site;
- validates the contamination of the site reducing the subjectivity of the method.

STRATIFIED RESEARCH METHOD

- probabilistic method;
- user friendly;
- much higher accuracy of estimating the average value of pollutant concentrations, compared to the random method;
- closer study sites can be grouped to minimize investigation time and related costs;
- limiting the samples depending on the knowledge of the location data.

RANDOM INVESTIGATION METHOD

- protects against subjective situations, guaranteeing the choice of random samples, if no historical data about the location are known;
- the way of choosing the samples is simple, without initial calculations;
- easy to understand and implement.

c) Disadvantage

JUDGMENT-BASED INVESTIGATION METHOD

- biased, subjective character;
- may introduce errors due to the structure of the model;
- quality of results depending on the experience of the investigation staff and the knowledge of the location information.

SYSTEMATIC INVESTIGATION METHOD

- large number of sampling points.
- an expensive method, sometimes due to additional levies;
- the sampling points can be modified due to the above-ground and underground facilities

STRATIFIED RESEARCH METHOD

- needs a complex statistical analysis
- expensive method.

RANDOM INVESTIGATION METHOD

- the results are not as representative as the other sampling methods

d) Limitation

JUDGMENT-BASED INVESTIGATION METHOD

- prior knowledge of the site;
- it is not a statistical method;
- requires specialized personnel;
- specific to locations with pollution over time (history);
- data validation depends on the degree of knowledge of the site and the professional training of the investigator;
- the method is not recommended as a model for validating contamination on a site.

SYSTEMATIC INVESTIGATION METHOD

- cannot be as accurate as the judgment-based or stratified method, if prior information is not available;
- qualified personnel for the realization of the investment plan and for the interpretation of the data.

STRATIFIED RESEARCH METHOD

- qualified personnel for the realization of the investigation plan and for the interpretation of the data;
- knowing the information about the location and the history of contamination data.

RANDOM INVESTIGATION METHOD

- does not present a uniform distribution of sampling points;
- there is the possibility of not identifying the hot spots or the shapes / sizes and concentrations of the contaminated areas

2 HEALTH AND ECOLOGICAL RISK ASSESSMENT

2.1. Introduction

Soil and groundwater pollution due to accidental spills of hazardous products is a problem for the environment and health for all countries. Strategies are needed to quantify and address pollution, and many states have developed or are developing risk assessment and management procedures for these contaminated sites. [5].

The risk assessment is performed when a site proves to be significantly polluted, respectively the concentrations of site-specific chemicals are higher than the maximum allowable concentrations for the type of use of the site, according to the regulations of the legislation in force. The risk assessment is presented in the form of the risk assessment study requested at the request of the competent authority.

At national level, according to the Order of the Ministry of Waters, Forests and Environmental Protection no. 184/1997, the risk assessment is of two types:

- Health assessments;
- Ecological assessments.

The general objective of the risk assessment is to control the risks coming from a location, by identifying (Order 184/1997):

- pollutants or the most important hazards;
- resources and receptors exposed to risk;
- the mechanisms by which the risk is realized;
- important risks that appear on the site;
- the general measures needed to reduce the degree of risk to an "acceptable level".

Risk assessment can be defined as the process of estimating the potential impact of chemicals on ecosystems and / or the population, based on specific conditions (Guidelines for Assessing and Managing Petroleum Hydrocarbon. Contaminated Sites in New Zeeland, 1999).

In this procedure it is necessary to make a complex connection between the source (specific pollutants or presumed to exist on site) - pathway (the pathway through which toxic substances reach the receptor and have harmful effects) - receptor (target, on which the harmful effects act : human beings, animals, plants, water resources, etc.).

A toxic agent, at a specific concentration, administered over a period of time is a source. In principle, if the concentrations of pollutants, respectively of the reference chemical agents (COC) are below the legal limits, the additional remedial / decontamination actions are no longer necessary.

The route (s) of exposure involves the transport of the contaminant by means of the exposure medium, groundwater, air, soil.

The specialized literature presents three ways of risk:

-inggestion / inhalation, dermal contact or direct and / or indirect contact and percolation / solubilization of pollutants in groundwater.

Receptors or targets can be classified into human receptors that often, in specialized software are broken down by age groups (children, adult), ecological receptor can be animal or plant population and physical receptor such as property limit, etc. .

The risk assessment, in accordance with the legislation in force, represents the analysis of the probability and severity of the main components of the impact on the environment.

2.2. Risk assessment

Risk assessment procedures are constantly evolving and it depends on two factors:

- the analysis of the contaminants on the site, respectively the identification and analysis of the pollutant and the impact on the health of the population, on the water resources and of other receptors of the environment;
- the relationship between soil and contaminated water.

Soil and groundwater pollution cannot be described by a set of fixed parameters, and over time the parameters can degrade, disperse and transform (Risk assessment for contaminated sites in Europe, chapter 9).

The risk assessment can be performed both quantitatively and qualitatively, and the establishment of the necessary data for these assessments must allow an investigation as detailed as possible on the contaminated site and to fully assess all information obtained from the field, present and historical.

The biggest influence related to the risk assessment process is the U.S. National Research Center. (U.S. National Research Council, NRC), which describes the procedure in 4 essential steps (Risk Assessment for Contaminated Sites in Europe, 1998):

- Hazard identification - identification of pollutants, which can cause adverse effects;
- Source (dose) - response relationship - estimating the relationship between the degree of exposure and the effect obtained (or toxicity assessment);
- Exposure assessment - estimation of the intensity, frequency and duration of exposure to dangerous substances;
- Risk characterization - the conclusion of the specialists, which should include a description of the risk distribution on the exposed receptors.

Environmental factors at the level of historical contamination of hazardous product deposits are soil / subsoil and groundwater.

The establishment of the maximum admissible concentrations for the environmental factor SOL, for the type of sensitive or less sensitive use, applicable to dangerous polluting substances is evaluated by Order no. 756/1997 for the approval of the regulation regarding the evaluation of the environmental pollution.

In the case of the environmental factor UNDERGROUND WATER, the establishment of the maximum allowable concentrations applicable to hazardous pollutants is presented by H.G. no. 53/2009 for the approval of the National Groundwater Protection Plan against pollution and damage completed and modified by H.G.449 / 2013.

The degree of risk depends on the identification of risk factors, the nature of the impact on the receptor and the probability of its manifestation.

Through DEFRA, 2002 (Department for Environment, Food and Rural Affairs, UK) the steps involved for quantifying the risk assessment on a specific site are presented:

a. defining the conceptual model;

b.collecting the characteristics of human exposure and data on the transport of contaminants;

c. establishing the concentrations of soil contaminants based on investigations;

d. quantitative exposure modeling;

e. comparing human exposure with limit values on health;

f. risk assessment on the health of the population when the admissible values are exceeded.

Through the investigation stage, the specific environmental methods for sampling will be taken into account, so that through analyzes to identify the dangerous or potentially dangerous chemicals present on the site.

Samples of soil, air, groundwater, sediments are collected from the site and / or around the site.

In order to understand the stage of hazard identification, several deposits of historically contaminated petroleum products were analyzed.

In order to facilitate the knowledge of the dangers, it is necessary to present the activity objective: - supply / storage / sale, over time, of gasoline of different types, diesel, light liquid fuel (CLU), oil, LPG bottles (liquefied petroleum gas).

The presentation of the activity objective allows the identification of these existing hazards within the petroleum products warehouse following the historical activity carried out:

- supply (by rail or road) and unloading in storage tanks of petroleum products from refineries in the country;
- storage / storage of petroleum products in storage tanks (including waste oils, slam);
- loading in tank trucks in the car ramp of the petroleum products stored in the storage tanks in order to be sold through distribution stations;
- occasionally, there were activities of gasoline ethylation, supply / storage of hydrocarbon by-products: paraffin, greases and canning of mineral oils.

The premises of the warehouses of dangerous products were occupied by:

- constructions specific to the activity objective;
- municipal and fuel networks;
- concrete platforms;
-green spaces

.

The triggering causes regarding the potential source of pollution during the activity carried out on the site were divided into three categories [16]:

losses on the route of underground or above-ground technological pipes through the joints of pipe sections, reinforcements and cracks;
- deterioration of the transport networks in time, first of all due to the chemistry

Technical causes	of the circulated waters (aggressiveness on the pipes depending on the temperature of the discharged waters); - leaks of petroleum products from the storage tanks during the filling period as well as during the stationary period; - losses of petroleum products at the level of loading / unloading facilities for tankers, tank wagons and tankers; - the joints at the level of the railway ramp for unloading the tank wagons; - failures of technological installations that may cause losses of oil product as a result of revisions and repairs not performed on time or superficially; - lack or damage of the restraint system for possible accidental leaks.
Human causes	- handling of petroleum products, in case of: loading / unloading of petroleum products; the action of emptying and cleaning the tanks and of the technological installations for storing the petroleum products; - during the decommissioning, demolition of the technological installations.
Natural causes	-the nature of the underground environment can favor rapid contamination through lithological composition and hydrogeological characteristics.

2.3. Methods for characterizing the risk assessment

By applying a model of risk assessment on the health of the population for a certain location, taking into account its specifications, it is possible to evaluate as complex and detailed as possible the effects of the risk manifested at the level of the population and the environment [6].

The route of exposure is an important component in assessing the risk to human health and the environment. The route or routes of exposure involve the transport of contaminants by means of a means of exposure, transferring them from the source to the receiver or receivers.

The characterization elements of the routes of exposure, presented in the literature, are: the concentration of contaminants to environmental factors, the path of penetration, frequency, duration and dose applied and / or absorbed [6].

The Guide to the Assessment and Management of Contaminated Sites in Australia and New Zealand classifies the routes of exposure of the population as follows [6]:

- ingestion of contaminated soil;
- inhalation of contaminated dust particles;
- dermal contact;
- ingestion of vegetables, contaminated plants, surface water or groundwater.

In [5] contaminated soil can reach the human body in 3 ways:

- soil ingestion, affects, in particular, children who come into contact with contaminated soil when playing;
- inhalation of soil / dust particles during soil mobilization (eg during agricultural works, excavations);
- dermal contact, absorption.

Another way of impacting the soil contaminated with the effects on the health of the population and the environment is the mobilization of soil contaminants in the water bodies (underground, mainly).

A specialized study [5] presents the main routes of exposure for representative receptors (table 2.1.), As follows:

Table 2.1 Routes of exposure for representative receptors

The main routes of exposur	Residential receivers		Industrial receivers	
	Soil surface	The underground environment	Soil surface	The underground environment
Ingestion of contaminated soil	✓		✓	
Consumption of contaminated products	✓			
Absorption through the skin	✓		✓	
Inhalation of vapors		✓		✓
Inhalation of dust particles	✓		✓	

The routes of exposure for major petroleum products are presented in the specialized reports of the U.S. Environmental Protection Agency. according to the following classification (table 2.2):

Table 1.2 Exposure routes for the main petroleum products

pollutant	Path of exposure
THP	Ingestion *, inhalation **, absorption through skin ***
BENZENE	Ingestion *, inhalation of vapors **, absorption through skin ***, dermal contact and / or eye contact
TOLUENE	Ingestion *, inhalation of vapors **, absorption through skin ***, dermal contact and / or eye contact
ETILBENZENE	Ingestion *, inhalation of vapors **, dermal contact and / or eye contact
XILENE	Ingestion *, inhalation of vapors **, absorption through skin ***, dermal contact and / or eye contact
MTBE	Vapor inhalation **, absorption through skin ***, dermal and / or eye contact

* Ingestion: consumption of contaminated products / water that comes from soils contaminated with petroleum products
** Inhalation: inhalation of contaminated air / dust, contaminated water vapor
*** Absorption: dermal contact with soil, water, air, immersion in contaminated water.

Assessing the degree of toxicity is the identification of direct or indirect effects that hazardous substances may have on the health of the population. By establishing the toxicity of a substance, one can know the relationship between the dose of a chemical and the response, more precisely, the effect it had on the health of the receptor or receptors, taking into account the routes of exposure that favored this connection.

The effects on the health of the receptor are defined by regulations, but especially at the international level, carcinogenic risk and non-carcinogenic risk are taken into account. According to the U.S. Environmental Protection Agency, it has been reported that the effects of hazardous products have tartaric effects and immediate effects [6].

According to the same source [6], the main substances specific to the petrochemical industry and analyzed in this paper (table 2.3.) By soil and groundwater analyzes are:

Table 2.2 The potential carcinogenic / non-carcinogenic character of pollutants in the petrochemical industry

Poluant	Potential Cancerigen	Potential necancerigen
THP		✓
BENZENE	✓	✓
TOLUENE		✓
ETILBENZENE		✓
XILENE		✓
MTBE	✓	✓
LEAD		✓

2.4. Models for quantifying risk assessment

In order to assess the risk in case of contaminated soil, it is important to determine [5]:

- if there are human receivers on-site and off-site (eg part-time, full-time workers, workers who will carry out their activity during the works, workers during maintenance, residential, recreational area)
- extension of contaminants on-site but also off-site;
- migration or infiltration of soil contaminants into groundwater.

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).

According to research Cheng & Nathanail, 2009, in which the input data and scenarios considered differ from one model to another (Poggio et al., 2008) 17 risk assessment models have been identified at European and global level (table 2.4.).

Table 2.3 Risk assessment models identified in the literature (Cheng&Nathanail, 2009)

Model	*Developer*
CETOX - human	DHI Water and Environment and Danish Toxicological Centre
CLEA 2002	DEFRA
CSOIL	RIVM, Netherlands
JAGG	Denmark
LUR	LABEIN Technological Centre, Spain
Fara nume	INERIS, France
Fara nume	Kemarkta Konsult AB, Sweden
RBCA Toolkit	ASTM, SUA
Report 4639	Sweden
RISC	SUA
RISC-HUMAN	Van Hall Instituut, Netherlands
Risc Assistant	Hampshire Research Institute, SUA
ROME	ANPA, Italy
SFT 99:06	Norway
SNIFFER	Land Quality Management, UK
UMS	Germany
Vlier -Humaan	VITO, Belgium

Quantification of carcinogenic risk

The acceptable value for carcinogenic risk starts from 1 x 10-6, respectively a case of disease per 1,000,000 people during life. The carcinogenic risk approach is the probabilistic estimate that the receptor will develop cancer during life as a result of exposure to hazardous chemicals.

Theoretical lifetime tolerance for contaminated sites for carcinogenic risk is between 10-4 and 10-6 (Netherlands and Denmark). In the case of Germany, Italy, and Australia, New Zealand and the U.S.A. the value of the carcinogenic risk is 10-5 [5].

To quantify carcinogenic risk, the IOWA Department [6] 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:

Dose = (C x ER x EF x ED x CF) / BW / At_c x 365 days, where:

SIMBOL	EXPLICATIE
C	substance concentration (mg / kg)
ER	exposure rate of one person per day (time / event)
EF	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 cancer risk (70 years)

Toxicity depends on the specific dose of each substance to have an adverse effect. The toxicity factor for carcinogenic risk assessment is slope factor (SF), used to estimate risk by oral exposure (ingestion and inhalation).

Quantification of non-cancer risk

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 [5] to establish and quantify non-carcinogenic risk are similar to carcinogenic risk.

Dose calculation formula:

Dose = (C x ER x EF x ED x CF) / BW / At_n x 365 days, where:

SIMBOL	EXPLICATIE
C	substance concentration (mg / kg)
ER	exposure rate of one person per day (time / event)
EF	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)

Toxicity for non-cancer risk depends on the dose, established by standards; in case of water and / or soil ingestion, the toxicity factor defining the reference dose for the pollutant (RfD).

2.5 Conclusions

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.

In the risk assessment procedure it is necessary to make a complex link between the source (specific pollutants or presumed to exist on site) - pathway (the pathway through which toxic substances reach the receptor and have harmful effects) - receptor (target, on which acts harmful effects: human beings, animals, plants, water resources, etc.).

A toxic agent, at a specific concentration, administered over a period of time is a source. In principle, if the concentrations of pollutants, respectively of the reference chemical agents (COC) are below the legal limits, the additional remedial / decontamination actions are no longer necessary.

The route (s) of exposure involves the transport of the contaminant by means of the exposure medium, groundwater, air, soil.

The specialized literature presents three ways of risk:

-inggestion / inhalation, dermal contact or direct and / or indirect contact and percolation / solubilization of pollutants in groundwater.

Receptors or targets can be classified into human receptors that often, in specialized software are broken down by age groups (children, adult), ecological receptor can be animal or plant population and physical receptor such as property limit, etc. .

3 CASE STUDY

Investigation and evaluation of the degree of contamination of the "A" site polluted with petroleum products.

3.1 Location description

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

Location A is positioned in the built-up area of a locality, in the industrial area, having as neighborhoods both residential areas, upstream and downstream, as well as commercial areas, in the north and south (figure 4).

The main activity objective of the warehouse was the supply by means of railway and road transport, storage in vertical and horizontal tanks, above ground and underground as well as the sale of petroleum products (such as gasoline, diesel, oil). In order to ensure the development of the entire activity, the site had the following facilities: mainly, specific constructions: loading / unloading ramp to ensure the transfer of products, storage tanks, pumping stations, decanter or separator of petroleum products, transport pipes between technological objects, urban networks, product storage and storage spaces, concrete platform, administrative constructions, green spaces.

3.2 Geological data

From a geomorphological point of view, the location is located in a terrace area, close to its contact with the meadow area.

In the area of the site, the land has a slight slope that decreases from west to east (altitude in the area of interest between 100 mdMN and elevation 97.50 mdMN), followed by a slope with a height of about 7.00 m that connects with the area of meadow. In this area the slope of the land is much smoother from 90 mdMN to 89 mdMN. A characteristic of the area is given by the slope breaks that make the transition from industrial use to the residential area downstream of the A location.

On the occasion of specialized studies, from a geological point of view, the terrace area is made up of a layer of 0.50 m thick under the ground, under which a semi-cohesive formation develops mainly made of clayey sandy powders where lenses meet. of clayey sands. This formation has an important thickness of about 10 m. Under this layer develops the formation of the base rock, impermeable, consisting of marly clays.

In the meadow area, a layer of vegetal soil develops on the surface of the land, under which the semi-cohesive formation appears, made up mainly of clayey sandy powders with a thickness of approximately 2.50 m.

3.3 Hydrogeological data

From a hydrogeological point of view, the presence of a groundwater aquifer with a free level located in the semi-cohesive formations is noticeable. The groundwater level in the terrace area is about 4.50 m deep, and in the meadow area it is at depths of 1.60 m. The groundwater aquifer is fed mainly by precipitation. During periods of intense rainfall, the presence of springs at the base of the terrace is noticeable. The measurements performed in drilling allowed, by interpolating the hydrostatic level values, the determination of the general flow direction of the groundwater aquifer from west to east as well as values between 0.02 - 0.021 for the hydraulic gradient of the groundwater aquifer.

The climate is temperate continental, with average temperatures of about 9.80C, average annual rainfall is 450-500 mm. The predominant wind direction is from the West, West-East, East-South.

3.4 Description of investigations

The known information allowed the elaboration of a preliminary investigation plan of the soil, the subsoil at the site level, referring me to the potential sources of pollution and to the areas visibly to be contaminated, applying in this case the objective or justified investigation method. Within this plan were included 5 soil investigation boreholes with a depth of 5 m, executed according to the preliminary investigation situation plan (figure 4).

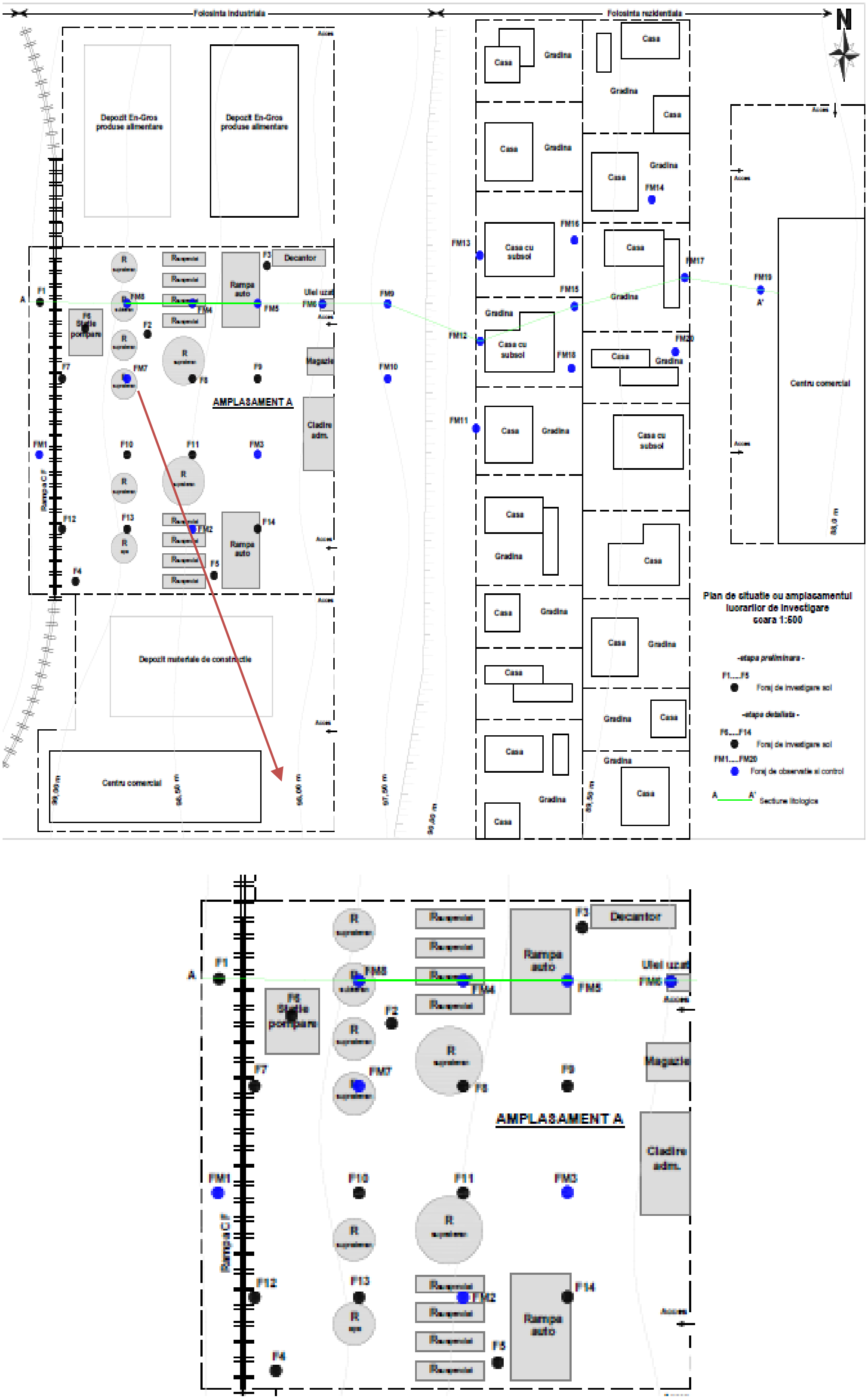

Figure 4 Site investigation "A"

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. 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 (THP) and volatile aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene). The results of the 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".

The image of a significant contamination of the soil with total petroleum hydrocarbons, THP, 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 THP 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 existence of pollution of the underground environment, generated by the activity carried out on site, known based on the preliminary investigation stage, and knowing that the groundwater downstream is contaminated based on iridescence and the smell of petroleum product, the decision was made to conduct a detailed investigation. at the site and downstream, on the direction of groundwater flow. During all this time, the demolition phase of the existing facilities on site A was carried out.

3.5. Detailed investigation and evaluation of the site (stage II)

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, connection between pollutants and geological environment structure, migration routes and transportation of pollution, risk assessment.

The boreholes used (observation and control boreholes, piezometers) were systematically positioned at a distance of approximately 25 m between it both inside and outside the site (figure 4).

The investigation drillings were performed hydraulically with percussion, in dry system, with protection pipe. The drilling method was chosen so as not to allow contamination between various depth intervals and the soil samples to be as representative as possible.

A number of 20 of the investigation boreholes were transformed into piezometers by inserting solid and filtering PVC columns, pearl gravel crown, bentonite, concrete slab in which the protection column and its cover were embedded.

The observation and control boreholes have been dimensioned so that the level of groundwater fluctuation is always in the filter column to allow the measurement of the free phase thickness.

Outside the site, the investigation works were carried out in the areas with the probability of soil and groundwater pollution, taking into account the characteristics of the type of pollutant and the information from the given interpretation phase. At the same time, it is necessary to take into account the accessibility of the personnel, of the equipment in order to execute these works.

The boreholes were located in the area of the ramp (line) CF (FM1, F7, F12, F4), the area of the northern tanks (FM8, F2, FM4, FM7, F8, F9), the ramp (line) car (FM5), pumping station (F3), used oil depot (FM6), central area (F10, F11, FM3), southern reservoir area (F13, FM2), southern car ramp (F14), between location and residential area (FM9, FM10), residential area (FM11 ÷ FM20). 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.

All the information regarding the characterization of the underground environment conditions and of the contamination of the site served to achieve the hydrogeological profile of the site (figure 5).

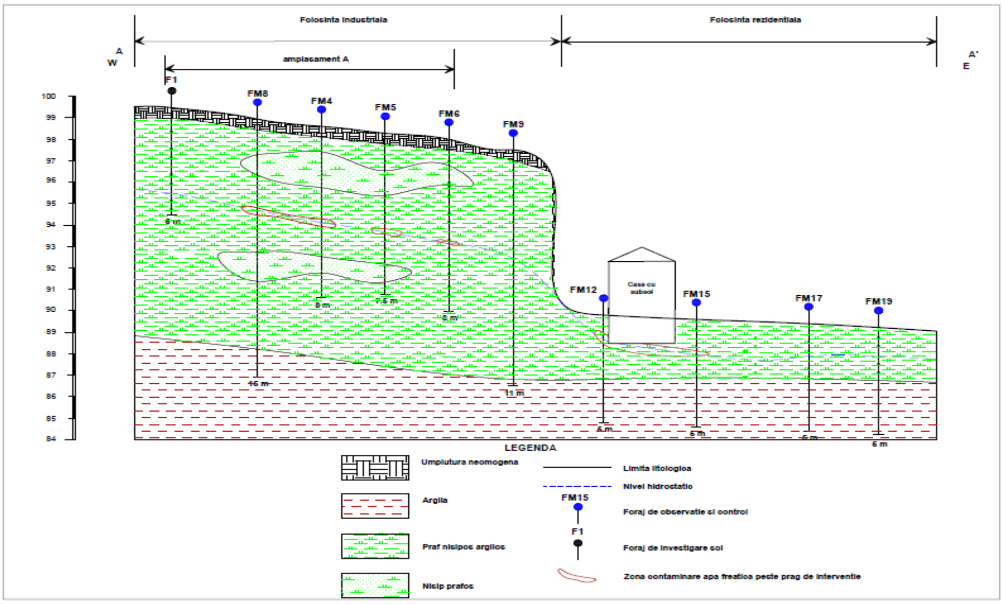

Figure 5 Hydrogeological profile of site A

Following the analysis of the existing data and the methodology of location of the investigation works, it resulted the need to execute a number of 34 investigation boreholes from which 20 boreholes will be transformed into observation and control boreholes (piezometers), from which samples will be taken. of soil and water, in situ tests will be performed in piezometers to determine hydrogeological parameters.

In order to determine these parameters in which the groundwater aquifer is located, in four observation and control boreholes, experimental pumping was performed, in 3 increasing flow stages, measuring the hydrostatic level, flow, hydrodynamic level and time. Based on the results of the experimental pumping, the hydraulic conductivity was determined (table 3.1):

Table 3.1 Values of hydraulic conductivity

Indicative monitoring well FM	**hydraulic conductivity k (cm/s)**
FM4	3.2×10^{-3}
FM6	5.1×10^{-3}
FM12	1.1×10^{-3}
FM15	7.9×10^{-2}

The flow rate of the aquifer varies with the hydraulic conductivity and in the risk quantification process, the value of the flow rate calculated with Darcy's formula is 1.1E-4 cm / s.

The predominant flow direction is west-east, but there are also local variations given by the presence of buildings in the residential area, by the physical characteristics of the soil that drains water on randomly oriented secondary directions (figure 6)

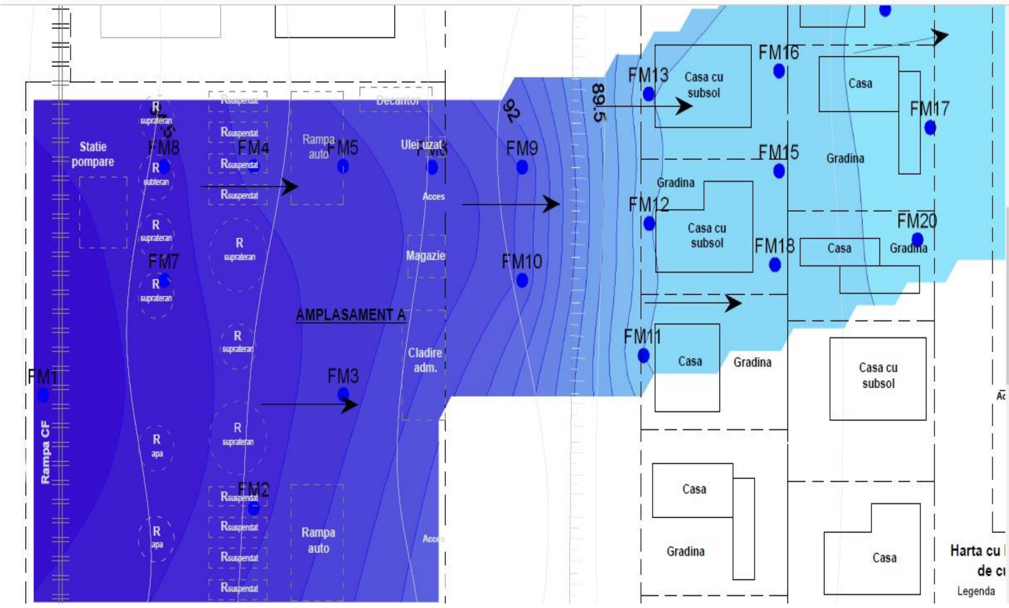

Figure 6 Direction of groundwater flow in the site area

The results of the laboratory analyzes on the soil samples and for the detailed investigation stage were related to the provisions of Order no. 756 of November 3, 1997 on the assessment of environmental pollution issued by the Ministry of Waters, Forests and Environmental Protection. It was used as a limit the concentration of intervention thresholds for soils "with less sensitive use" taking into account the future development of the site (in accordance with the industrial area of the warehouse). In the case of the results of the laboratory analyzes on the groundwater samples, the comparison with the threshold values from Decision no. 449/2013 on amending and supplementing the annex to Government Decision no. 53/2009 for the approval of the National Plan for the protection of groundwater against pollution and damage.

Soil and water samples were transported to the environmental laboratory, analyzing the concentrations of pollutants in soil and groundwater for total aliphatic hydrocarbons (THP), volatile aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene), polycyclic aromatic hydrocarbons (PAH).), phenols, lead, bio-ethers such as MTBE (methyl-tert-butyl-ether), ETBE (ethyl-tert-butyl-ether) and TAME (tert-amyl-methyl-ether).

3.6 Results of the field investigation

Figure 7 shows the values of THP 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.

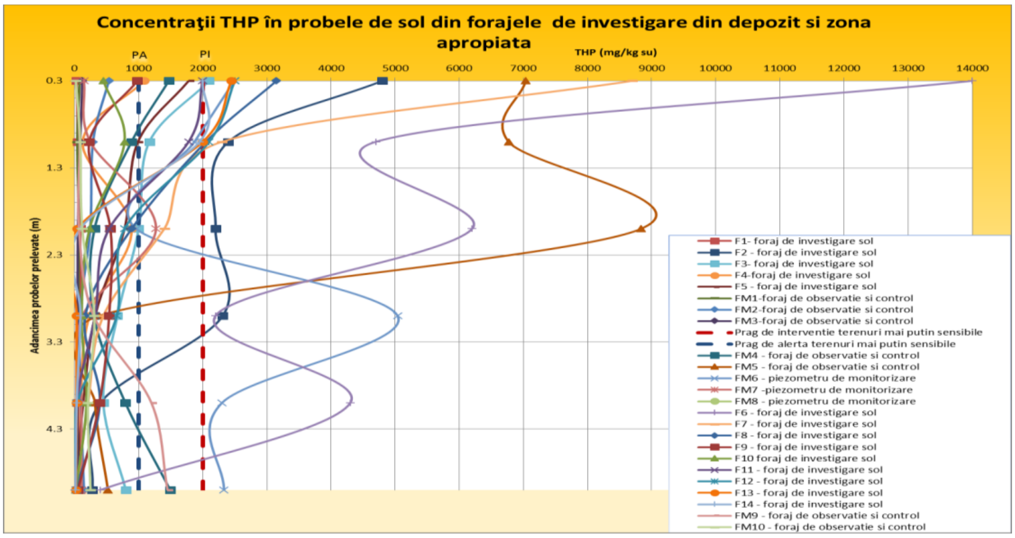

Figure 7 THP concentrations in soil samples from investigation wells in the warehouse / site and nearby area

The results of the laboratory analyzes were introduced in the Surfer specialized program, which modeled the distribution of soil contamination with petroleum products at various depths, highlighting the following aspects:

at the depth of 0,30 m (figure 8)

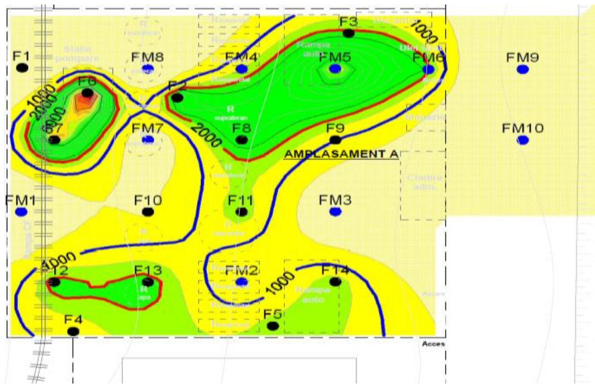

Figure 8 Contaminant isolines for the depth of 0.3 m

The following observations can be made for the area inside the site:

- THP contamination above the intervention threshold (2000 mg / kg su) for less sensitive uses in the area of former constructions: pumping station (F6), CF ramp (F7), tanks (F2, F8) and car ramp (F3, FM5) from the northern area of the site, the waste oil storage area (FM6) and on a small area in the area of a tank (F12, F13) from the south;

- THP contamination above the alert threshold (1000 mg / kg su) for less sensitive use in the area of former constructions: pumping station (F6), CF ramp (F7), tanks and car ramp both in the southern area (F4, F12, F13, F5, F14) central (F11) and northern (F2, FM4, F8, F9, FM5, F3) of the site, decanter, waste oil storage area (FM6).

For the area outside the site, the following observation can be made:

- in this residential area the THP values showed their inclusion in the normal values.

at the depth of 1,00 m (figure 9)

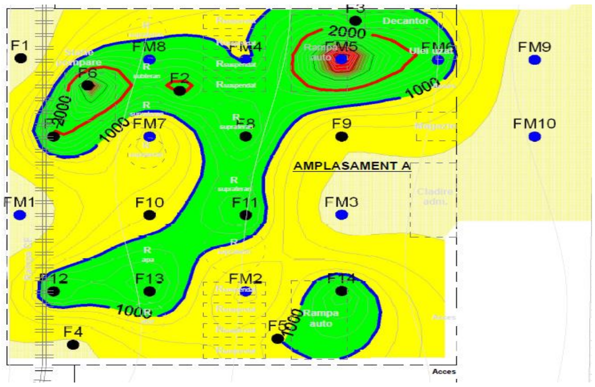

Figure 9 Contaminant isolines for the depth of 1.0 m

The following observations can be made for the area inside the site:

- THP contamination above the intervention threshold (2000 mg / kg s.u.) for less sensitive use in the area of former constructions: pumping station (F6) and car ramp (FM5) in the northern part of the site;

- THP contamination above the alert threshold (1000 mg / kg su) for less sensitive use in the area of the former facilities: pumping station (F6), punctual CF ramp (F7), tanks and car ramp both in the southern area (F12, F13 , F14), central (F11) and northern (F2, FM8, F8, FM4, FM5) of the site, decanter (F3) and waste oil storage area (FM6).

For the area outside the site, the following observation can be made:

- in this area the THP values determined in the laboratory analyzes showed their inclusion in the normal values.

at the depth of 2,00 m (figure 10)

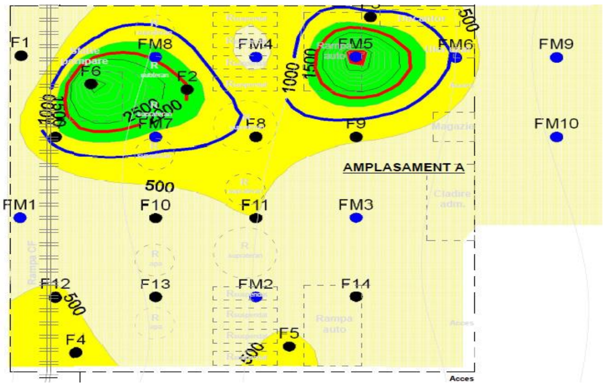

Figure 10 Contaminant isolines for the depth of 2.0 m

The following observations can be made for the area inside the site:

- THP contamination above the intervention threshold (2000 mg / kg s.u.) for less sensitive use in the area of former constructions: pumping station (F6), tanks (F2) and car ramp (FM5) in the northern part of the site;

- THP contamination above the alert threshold (1000 mg / kg su) for less sensitive use in the area of former constructions: pumping station (F6), punctual CF ramp (F7), tanks (FM7, F2, FM8) and car ramp (FM5) from the northern area of the site, part of the decanter (F3) and the used oil storage area (FM6).

For the area outside the site, the following observation can be made:

- in this area the THP values showed their inclusion in the normal values.

at the depth of 3,00 m (figure 11)

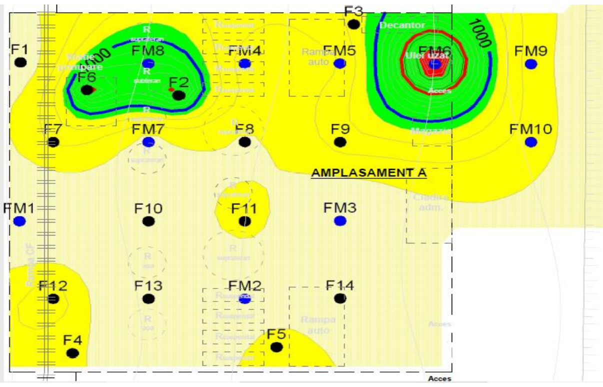

Figure 11 Contaminant isolines for the depth of 3.0 m

The following observations can be made for the area inside the site:

- THP contamination above the intervention threshold (2000 mg / kg s.u.) for less sensitive use in the used oil storage area (FM6);

- THP contamination above the alert threshold (1000 mg / kg s.u.) for less sensitive use in the pumping station area (F6), tanks in the northern area (FM8, F2) of the site and the used oil storage area (FM6).

For the area outside the site, the following observation can be made:

- in this area the THP values showed their inclusion in the normal values.

at the depth of 4,00 m (figure 12)

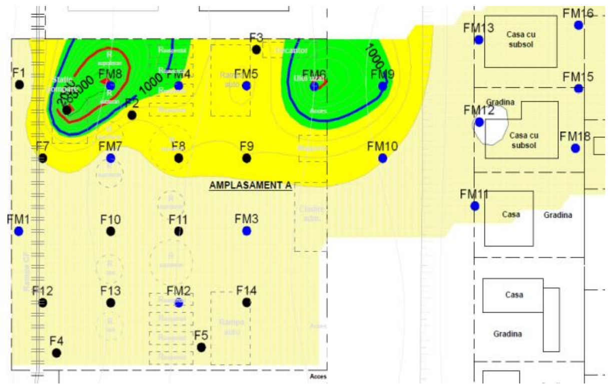

Figure 12 Contaminant isolines for the depth of 4.0 m

The following observations can be made for the area inside the site:

- THP contamination above the intervention threshold (2000 mg / kg su) for less sensitive use in the area of former constructions: pumping station (F6), tanks (FM8) in the northern part of the site and the used oil storage area (FM6) ;

- THP contamination above the alert threshold (1000 mg / kg s.u.) for less sensitive use in the area of former constructions: pumping station (F6), tanks in the northern area of the site (FM8), decanter point and used oil storage area.

For the area outside the site, the following observation can be made:

- in this area the THP values showed their inclusion in the normal values.

at the depth of 5,00 m (figure 13)

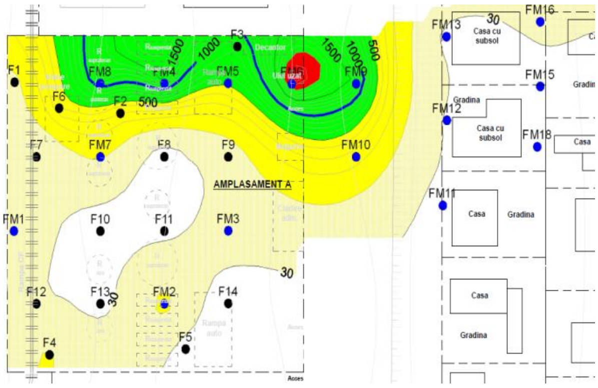

Figure 13 Contaminant isolines for the depth of 5.0 m

The following observations can be made for the area inside the site:

- THP contamination above the intervention threshold (2000 mg / kg s.u.) for less sensitive use in the used oil storage area (FM6);

- THP contamination above the alert threshold (1000 mg / kg su) for less sensitive use in the area of former constructions with pollution potential: tanks in the northern area of the site (FM8, FM4), decanter and used oil storage area (FM6);

For the area outside the site, the following observation can be made:

- in this area the THP values determined in the laboratory analyzes showed their inclusion in the normal values.

The potentially generating causes of pollution at site A are:

• for soil:
- tightness of the walls of oil storage tanks;
- leaks of the technological pipes and in the area of the pumping station fittings;
- accidental spills during the operation of technological objects;
- the action of handling and transporting the products within the site;

• for groundwater:
- percolation of products from the soil surface or from the subsoil (cracks, leaks from the buried pipes).

From the observation and control boreholes (piezometers) of the groundwater were taken water samples by pumping which were transported to the environmental laboratory analyzing the concentrations of THP and benzene.

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. THP 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. THP 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.

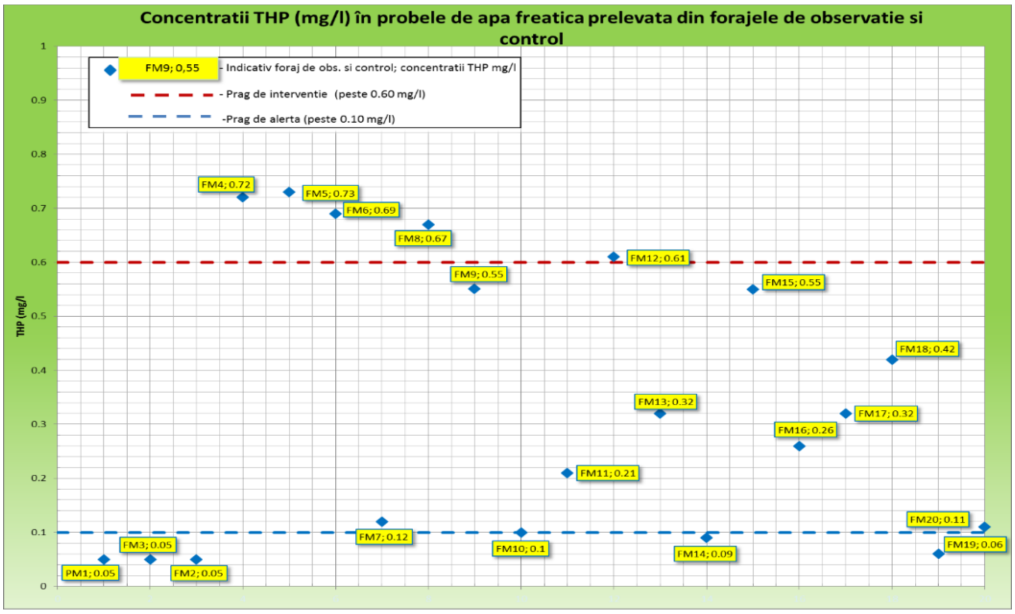

Figure 14 THP concentrations in groundwater samples taken from monitoring wells

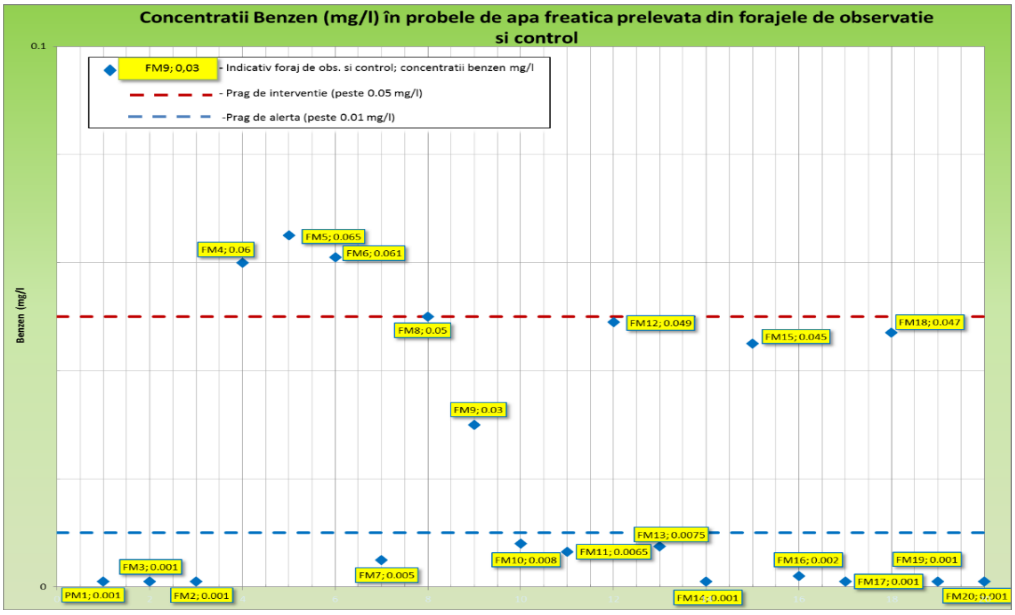

Figure 15 Benzene concentrations in groundwater samples taken from monitoring wells

The form of THP 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 16).

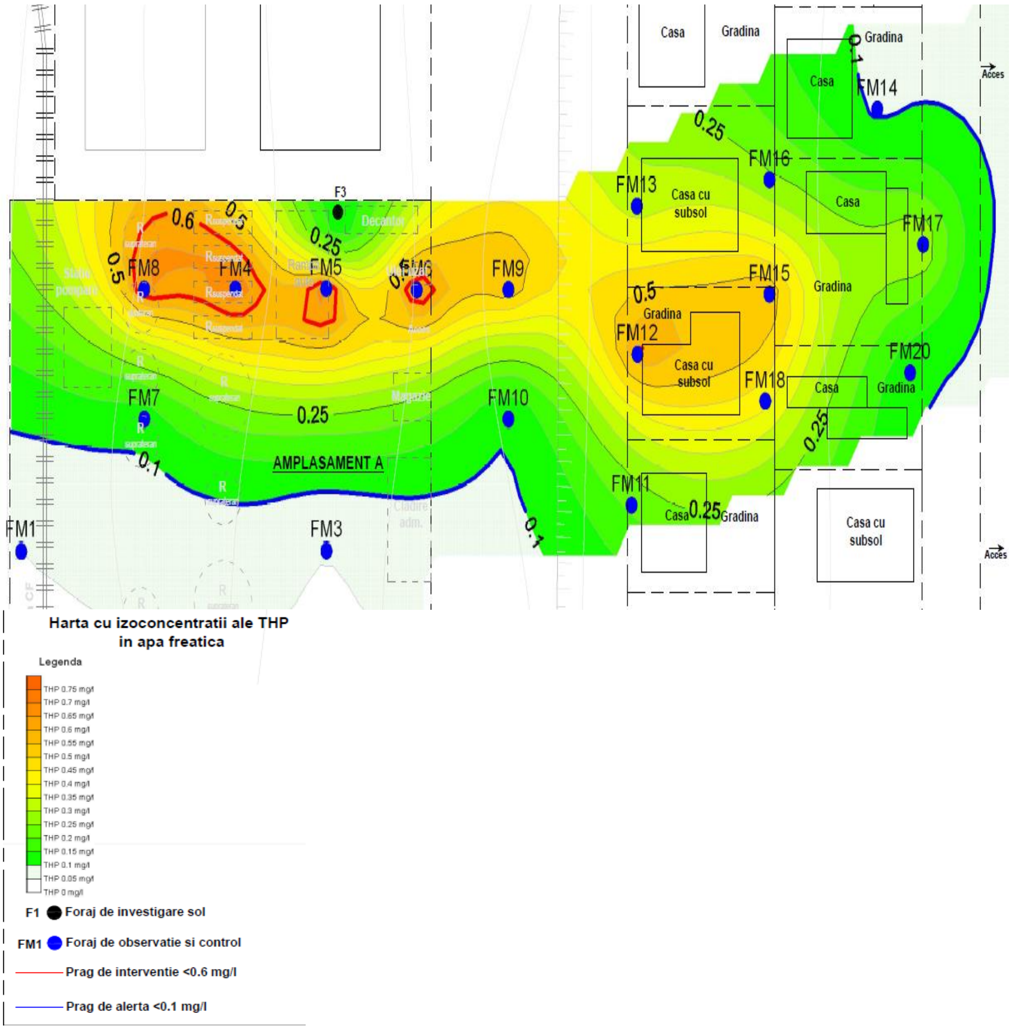

Figure 16 Distribution of THP contamination in groundwater

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 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. Benzene values in groundwater above the alert threshold (above 0.01 mg / l) were identified in several observation and control boreholes except those located in the central and southern part of the site (FM1, FM2, FM3 and FM7), F3 as well as those in the residential area FM10, FM11, FM13, FM14, FM16, FM17, FM20 and FM19.

In conclusion, it can be observed that at the level of the geological environment, the organic pollutants are of the type of compounds BTEX (aromatic hydrocarbons), respectively benzene and THP (aliphatic hydrocarbons).

Conclusions

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 THP 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 revealed a significant pollution with petroleum products (THP, 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).

In conclusion, the most contaminated areas by the presence of THP and BTEX (benzene) compounds are the reservoir area, the car ramp, the former CF ramp area and the used oil storage area, both for the soil environment factor and for groundwater.

Taking into account that a significant pollution at the site level has been identified, a soil and groundwater risk assessment study will be carried out on the population's health with the help of the specialized software RBCA Toolkit in order to ensure the management and remediation of the site.

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