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PhD THESIS SUMMARY

ASSESSMENT OF THE PRESENCE OF INORGANIC POLLUTANTS IN THE ENVIRONMENT FROM AREAS AFFECTED BY ANTHROPOGENIC POLLUTION

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CONTENTS *

I. BIBLIOGRAPHY RESEARCH

CHAPTER 1
ASSESSMENT OF THE PRESENCE OF INORGANIC POLLUTANTS IN THE ENVIRONMENT

CHAPTER 2
METHODS USED TO ASSESS THE PRESENCE OF INORGANIC POLLUTANTS IN THE ENVIRONMENT

II. ORIGINAL CONTRIBUTIONS

CHAPTER 3

EXPERIMENTAL STUDY ON CHARACTERIZATION OF MINING WASTE

CHAPTER 4

SOIL CHARACTERISTICS IN AREAS AFFECTED BY THE PRESENCE OF MINING WASTE DUMPS IN VALEA CĂLUGĂREASCĂ

CHAPTER 5
GROUNDWATER QUALITY IN VALEA CĂLUGĂREASCA

CHAPTER 6
MODELS FOR PREDICTION OF ARSENIC AND CADMIUM CONCENTRATIONS IN PLANTS DETERMINED BY METAL MOBILITY IN THE SOIL SYSTEM - SOLUTION

CHAPTER 7

HUMAN HEALTH RISK ASSESSMENT DUE TO EXPOSURE TO CONSUMPTION OF CONTAMINATED WATER

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KEYWORDS

Anthropogenic pollution, inorganic pollutants, soil quality assessment, groundwater quality assessment, degree of pollution, modeling of metal concentrations in plants, pollution risk assessment

INTRODUCTION

The research in this PhD thesis focused on ***assessing the presence of inorganic pollutants in the environment in areas affected by anthropogenic pollution***. This research addresses the pressure aspects of anthropogenic activities that generate groundwater and soil pollution in the area of these abandoned mining waste sites. The present study can contribute to the awareness of the environmental impact as well as to the assessment of the toxicological effects of the presence of toxic compounds in water on human health. Environmental impact assessment is an environmental policy tool that is part of sustainable development as it addresses the effects of anthropogenic pollution pressure on natural systems. Current approaches and tools for reporting and data collection create significant gaps in when data become available to inform the public and do not optimise opportunities for capturing good quality data. Factors causing this problem include non-automated, outdated reporting systems and manual processing, hence the time lag in reporting by plant operators, processing, aggregation, verification and submission of data by competent authorities. The assessment of the impact of the location of abandoned mine waste dumps on soil and groundwater in nearby rural areas is the first step in proposing the necessary changes to significantly reduce the concentrations of these hazardous compounds continuously released into the environment. It is also the environmental specialists who can propose to the governmental/parliamentary authorities, on the basis of the studies carried out, urgent measures to regulate the maximum permissible concentrations of inorganic contaminants in groundwater, soils and to establish the level of pressure exerted by the presence of mining ash dumps on human habitat.

The main objectives of this doctoral thesis were as follows:

1. Obtaining new knowledge related to the presence of inorganic pollutants in an environment affected by the existence of some mining waste in the Valea Călugărească, through research carried out to characterize the waste, soils and groundwater in the area of these abandoned ashes. To this objective, methods such as:

- Chemometric analysis methods used for characterization of mining ash waste.
- Combined methods of multivariate analysis for establishing the extraction capacity of some solutions and the study of these complex processes.
- Hydrogeochemical methods of assessment of pollutant sources in groundwater in Călugărească Valley.
- Models of prediction of the concentrations of As and Cd in the plant Sinapis alba determined by their mobility in the soil system – solution and establishment of the accumulator potential of the plant for these metals from contaminated soils.

2. Assessment of the risk to human health of groundwater in the industrial area of Râmnicu Vâlcea.

The originality of the results obtained in the doctoral thesis is highlighted by the update of the database on the impact of the presence of some mining ash waste on the Valea Călugărească region. Chemometric analysis methods have been used to characterize mining ash waste. Also for the establishment of the extraction capacity of some solutions and the study of these complex processes, combined methods of multivariate analysis have been developed. Hydrogeochemical methods were used to evaluate sources of pollutants in groundwater in Călugărească Valley. Models of prediction of the concentrations of As and Cd in the plant Sinapis alba determined by their mobility in the soil – solution system have been generated to establish the accumulating potential of the plant from soils contaminated with toxic metals. The risk to human health due to exposure to drinking contaminated water was assessed for groundwater in the Râmnicu Vâlcea industrial area.

The complexity of the presented paper results from the following aspects: - Application of combined multivariate analysis methods in assessing the impact of toxic metals and other inorganic pollutants on contaminated soils and underground aquatic environment. - Obtaining numerous experimental data in the decision-making process for establishing the strategy for remediation of the terrestrial environment and underground aquifer affected by the location of chemical waste landfills in Valea Călugăreasca and Ramnicu Valcea industrial area.

The doctoral thesis addresses ***important issues of environmental chemistry and quality of life***, providing solutions and valuable technical-scientific information related to the evaluation of the composition of some mining ash waste and the application of their characterization methods.. The paper also highlights the need to use machine learning in developing studies to assess the pressure of active or abandoned anthropogenic activities on environmental factors. At the same time, the methods developed in the thesis provide an advanced analytical control tool on soil contamination and provide useful information in establishing the remedy strategy.

The doctoral thesis was conducted through an interdisciplinary approach, the studies carried out combining concepts and methodologies from several scientific branches: analytical chemistry, environmental science, hygrogeochemistry and statistics. Moreover, the work contributes to the understanding of the processes that anorganic pollutants undergo under the influence of anthropogenic phenomena and the impact on various environmental factors.

Structure of the work

The paper entitled ***"Assessment of the presence in the environment of inorganic pollutants in areas affected by anthropogenic pollution"*** is structured in seven chapters, systematized in two parts:

Part I entitled BIBLIOGRAPHICAL RESEARCH, consists of two chapters that synthesize the current state of knowledge in the field of assessment of the impact of the main sources of anthropogenic inorganic pollution on the environment and health. The sub-chapters included here present data on monitoring of water and soil quality, sources of pollution and the behavior of inorganic pollutants in water and ground. Methods for determining and evaluating the presence of inorganic pollutants in the environment are also presented, used in determining the level of pollution of areas affected by chemical waste.

Part II of the thesis entitled ORIGINAL CONTRIBUTIONS, includes the original research carried out during the doctoral period. Each chapter is structured in sub-chapters that highlight the objectives pursued, the materials and tools used, the process of developing and optimizing the methods of assessment for each environmental factor and for contaminants, the interpretation of the results obtained and the conclusions obtaining from the conduct of the study.

Chapter 3, entitled *"Caracterization of some mining wastes in the Valea Călugărească",* sought to develop a new method of characterizing the composition of the ashes from abandoned haldes.

For this purpose, an analysis of the compositions of some samples of mining waste from abandoned huts located in the Valea Călugărească and a PCA analysis of oxide composition on the process of generating these ashes was carried out. Also included in this chapter were a characterization of the ashtray process, the influence of the contact time on pH and the oxide-reduction potential in ashtra samples, as well as a mineralogical analysis of ashes.

Interpretation of the results of the analysis of the chemical composition of the ash samples from the Valea Călugărească indicated the presence of potentially dangerous elements Pb, Zn, Cu, Fe and Al. The presence of pyrite was confirmed by the high Fe content of ash. PCA analysis of oxide composition identified the presence of titanium dioxide and calcium oxide elements used as stabilizers in mining ash burning processes. Saturation indices for different minerals calculated on the basis of the concentrations of component elements of the ashes, indicated the presence of calcium sulfate formed as a result of unsaturated dissolving processes in the molten samples and precipitation tendency determined by the process of over-saturation of this mineral.

Chapter 4, entitled *"Caracterization of soils in areas affected by the presence of some mining waste halls in the Valea Călugărească"*, followed the evaluation of inorganic pollutants in soils taken from the chemical waste hall area present in the Valley Călugărească.

The aim of this study was to know the fertility level of these soils in the area adjacent to some abandoned ashes and to assess the risk of pollution caused by the presence of these ashes. Achieving this goal included a presentation of the physical and geographical peculiarities of the area studied, the physico-chemical and agrochemical characterization of soil samples and a PCA analysis of factors affecting soil fertility. The level of soil metal pollution and environmental risk for contamination with potentially hazardous elements was also determined. The analysis of spatial distribution assessed the impact of soil pollution in the region studied. The geo-accumulation index and the ecological risk index were used to assess the degree of toxic metal pollution of the soils studied. A repair scenario of soils contaminated with toxic metals has generated solutions to repair polluted soils.

Interpretation of the results obtained in the study of the characterization of soils in the Valea Călugărească affected by the presence of chemical waste indicated a poor availability of nutrients to plants and the significantly negative influence of the soluble components of pyrite ash reflected by the values of conductivity and sulphate content.

The spatial distribution of toxic metals analyzed in the area studied shows an extension of contamination with a high content of these metals to an area of about 100m of abandoned deposits, the level of pollution being reduced considerably with the increase of distance. The results obtained in the study of the assessment of the ecological risk index for contamination with toxic metals in soils located near chemical waste indicated a very high environmental risk for soils taken at 50m and 100m of ash deposits by contamination by As, Cd and Pb. The soil taken from the site located 200m from the pyrite ashes presented a considerable ecological risk of contamination with Ace.

The scenario generated by the SQAPP application developed under the HORIZON 2020 Project, using partial data based on the information obtained in this study, recommended remedial procedures such as phytoremediation using plants with deep root system and minimizing irrigation with salinated water.

Chapter 5, entitled *"Quality of groundwater in Călugărească Valley"* presents a part of the investigations aimed at the long-term effects of some pyrite ash sites on the groundwater of rural areas located near these hales.

The objective of the study was to identify sources of anthropogenic pollution of groundwater in the region of Calugareasca Valley using multivariate analysis and identify natural sources of pollutants of ground water by combining hydrochemical and geochemical analysis as well as the evaluation of water quality for irrigation and consumption.

The results obtained in the research carried out for the study of the quality of groundwater in the area investigated indicated a content of sulfates and nitrates as anthropogenic sources of pollution of the waters in the Valea Călugărească, pyrite and gips being the two main anthrogene sources of sulphate in water samples located in locations near the chemical waste sites. natural sources of ions, influenced by the dissolving processes of minerals in the aquifer, such as dolomite and gypsum. Evaporation and ion exchange processes characterized the geochemistry of groundwater for the entire area studied, this type of processes determining their salinity level. The groundwater in the area under investigation is suitable for use in agricultural practices. A 3% percentage was established with good water quality, 87% being classified with acceptable quality. Three samples of water from the Points located in the area of 50m around the pyritic ash halls showed poor quality and therefore cannot be recommended for consumption.

Chapter 6, entitled *"Models of prediction of arsenic and cadmium concentrations in plants determined by the mobility of metals in the soil system - solution"*, aimed to evaluate the potential of accumulation of Ace and Cd of the plant Sinapis alba from soils contaminated with these metals, this plant being selected due to its ability to retain different metals with potentially toxic.

To this objective, a complex method of assessing the extraction capacity of solutions that included values of soil characteristics and representative values for moving metal fractions and a study of the factors influencing these processes, combining PCA and RSM analysis, has been developed. The witness soil from the Călugărească Valley was used as material for this study. Models for prediction of concentrations of Ace and Cd accumulated in the plant Sinapis alba (White Mustard) have been developed.

The results obtained in this study confirmed the potential for accumulation of the Sinapis alba plant in contaminated soils with high concentrations of As and Cd using the values of the Kd distribution coefficient of these metals in the established solutions with the highest extraction capacity from contaminate soils. Multiple regression models developed presented performance parameters values that confirm the use as variables of representative values of moving metal fraction, respectively Kd.

Chapter 7, entitled *"Evaluation of the risk to human health due to exposure to drinking contaminated water"*, represents a systematic approach to the risk assessment of the harmful impact of pollutants in groundwater intended for consumption on human health.

To this end, we conducted a study on the quality of groundwater in the Râureni chemical platform region and the area comprising the Stoiceni and Răureni towns, located in the industrial area of Râmnicu Vâlcea. Analysis of the composition of groundwater in the area carried out to establish the presence of pollutants in the underground aquifer. Spatial distribution analysis was used to assess the impact of the pollutants identified on the region studied. A model developed by the United States Environmental Protection Agency (USEPA) was used to assess the risk to human health due to exposure to drinking contaminated water**.**

Interpretation of the results obtained indicated that, 25% of the groundwater analyzed present a high content of nitrates, nitrites and ammonium in the rural area of the locality Stoiceni. The risk to the health of age groups (men, women and children), evaluated in this study, identified five wells from which samples of groundwater were collected that show values of nitrate and ammonium concentrations exceeding the limits permitted by the National Standard and WHO, and therefore may lead to an increased risk to human health caused by long-term consumption of these waters.

The doctoral thesis concludes with a chapter of **general conclusions** in which are synthesized the main conclusions resulting from the research carried out for the study of the assessment of the inorganic pollution of the soil and groundwater in the Valea Călugărească and Râmnicu Vâlcea and prospects of expanding the research activity in the field of the evaluation of the impact of anorganic contamination on the environment with other possibilities of remediation of soils in this area.

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LIST OF NOTATIONS

Symbol	**Meaning**	**Unit of measurement**
DOC	Organic carbon dissolved in leachate	mg/kg
Ntot	Concentration of total nitrogen in soil	mg/kg
Ptot	Concentration of total phosphorus in soil	mg/kg
TDS	Total solids dissolved in water/leachate	mg/L / mg/kg
EC	Electrical conductivity	µS/cm /
RSC	Residual sodium carbonate index	mg/L
L/S	Liquid/solid ratio	L/kg
TOC	Total organic carbon in soil	mg/kg
SOC	Soil organic carbon	%
CBE	Ion equilibrium error	%
CEC	Cation exchange capacity in soil	%
TH	Total hardness	mg $CaCO_3$/L

Abbreviation	**Meaning**
PCA	Analysis of the main components
GIS	Geographic information system
DAS	Groundwater Directive
XRF	Method of analysis based on emission of fluorescent radiation
ICP-OES	Inductively coupled plasma optical emission spectrometry
UV-Vis	UV-Vis spetroscopy
SI	Groundwater saturation index
PI	Groundwater permeability index
SAR	Absorption ratio of sodium in groundwater
%Na	Percentage of Na in groundwater
USEPA	Environmental Protection Agency (USEPA)
Rfd	Reference dose of a contaminant
CDI	Chronic daily consumption
ABW	Average body weight
DU	Duration of exposure
FE	Frequency of exposure
RA	Absorption rate
DV	Life expectancy
HI	Health hazard risk index
EF	Enrichment factor
EDTA	Ethylenediaminetetraacetic acid
IDW	Weighted interpolation with distance reversal
RMS	Response surface methodology
ROP	Oxido potential - reduction
Igeo	Geo-accumulation index
Ei	Ecological risk index
Tr	Reference toxicity coefficient of metal
Ri	Ecological risk index
GPS	Spatial geographical coordinates

Soluri cu folosință	Agricultural soils according to Order 756/97
SQAPP	Mobile application for soil quality assessment
KMO	Kaiser – Meyer – Olkin report, performance parameter in factor analysis
AF	Factor analysis
CAI	Chloro-alkali index
Kd	Distribution coefficient
BAC	Bioaccumulation coefficient
RMSE	The average square root of the error
SW	Shapiro-Wilk performance parameter for checking normality in multiple regression
DI	Ultrapure water
DW	Durbin Watson performance parameter for serial autocorrelation analysis in multiple regression model
aR^2	Adjusted regression correlation coefficient
OMS	World Health Organization (eng. WHO)

I. BIBLIOGRAPHIC RESEARCH

CHAPTER 1

ASSESSMENT OF THE PRESENCE OF INORGANIC POLLUTANTS IN THE ENVIRONMENT

1.1. ASSESSMENT OF THE IMPACT OF ANTHROPOGENIC POLLUTION ON ENVIRONMENTAL QUALITY

Anthropogenic environmental impacts include changes in ecosystems, biodiversity and natural resources caused by humans, directly or indirectly. Modifying the environment to meet societal needs has serious consequences such as global warming, ecological degradation, biodiversity loss or ecological crises [1.1].

1.1.1. Impact of agriculture on environmental quality

Causes of environmental pollution from agriculture are burning of waste materials from agricultural activities, clearing of land, application of fertilisers in excess of plant requirements and use of pest control agents that are not biodegradable [1.4]. The consequences of these activities include the entry of specific chemicals into the food chain, the creation of smoke and PM, and the destabilisation of habitats.

1.1.2. Impactul irigațiilor asupra calității mediului

The impact of irrigation on natural processes upstream and downstream of the irrigation system is included in the environmental impact of irrigation due to changes in hydrological conditions caused by the installation and operation of these systems [1.8].

1.1.3. Impact of mining and exploitation of mining resources on environmental quality Mining activity and exploitation of mining resources generate varying degrees of pollution, affecting air, water and soil quality. Although mineral exploration can bring small amounts of pollution, the few stages of large-scale exploration can lead to more intense soil, water, and air contamination. Pollution is significantly worse when it occurs as a result of large-scale extraction of rocks, oil and limestone used in various construction operations [1.13].

1.1.4. Impact of anthropogenic pollution on human health

Adverse health impacts due to water pollution continue to be a leading cause of morbidity and mortality in developing countries. Recent studies have addressed this issue by looking at the impact of water pollution on human health according to heterogeneity of diseases. The significantly negative and increasing impact of water and soil pollution on food safety exposes more and more people to the risk of carcinogenic diseases, and this appears to be strongly associated with the majority regions of food production [1.25].

1.2. GROUNDWATER POLLUTION

1.2.1. Legislative regulations on water quality

At national level, the quality of water intended for human consumption is regulated in harmonization with European directives, by Ordinance nr. 7 of 18 January 2023 which replaced Law 458/2002 and Water Law 107/1996 updated 2023 which provides that groundwater use is based on reserves determined by hydrogeological studies. The Water Framework Directive was implemented in Romanian legislation by Water Law 107/1996, with subsequent amendments from 2020.

1.2.2. State of play of groundwater quality

Groundwater provides a continuous base flow for rivers and wetlands and is of great importance to these natural ecosystems and is an important source of water for human consumption, agriculture, industry and tourism. Accidental pollution is an important source of release of chemicals or waste into the environment. Groundwater quality monitoring showed that approximately 16% of groundwater bodies were outside the chemical parameters required by the standards in 2016, with 47 accidental contaminations reported.

1.2.3. Inorganic pollutants in water

Many of the fundamental concerns facing mankind in the 21st century are related to water availability and water quality problems [1.32]. Water pollution sources may contain natural minerals rich in harmful metals, which dissolve in water bodies, thus creating water contamination.

Since these major dissolved constituents are naturally found in water, they are not generally considered pollutants, however, the presence of unusual concentrations of major disolved constituent may be an important indicator of contamination, and knowledge of their behavior and patterns may be useful in interpreting the formation and dispersion of pollutant. The main sources of ions in groundwater and riverwater are the alteration and dissolution of rocks and rainwater. Some minerals, such as carbonates (crete, limestone, and dolomite), and evaporative minerals (gem salt, halite, and gypsum) are water-soluble, others such as silicates (quartz, feldspate, and clay minerals) are less soluble. Therefore, the composition of the water reflects both the geological environment of the drainage basin and the time of residence.

1.3. SOIL POLLUTION.

The soil is the result of the activity of different processes determined by different environmental factors, through a constant adaptation to natural and/or man-induced changes in the environment, recording and accumulating through certain phenomena and processes of key evolutionary moments different characteristics [1.37].

1.3.1. Legislative regulations on soil quality

In accordance with the aforementioned national legislation, the warning threshold is defined as a concentration of a pollutant that warns the competent authority of a possible adverse impact on the environment, a declaration that determines additional monitoring of the concentrations of the existing contaminant in emissions. The action threshold is defined as the concentration of a pollutant at which the competent authority has ordered a risk assessment study or a reduction in the contaminant's concentration in emissions.

1.3.2. Current state of soil quality

The main sources of soil pollution and degradation are active or inactive mining activities, the existence of decanting ponds, waste deposited inappropriately or abandoned, residues or waste with a high content of minerals, inorganic materials, metals, salts, acids or bases, of salt names from the extractive or petroleum industry, solid particles or substances carried by air (hydrocarbons, fluors, nitrogen oxides, sulphur dioxide, chlorides, ammonia, lead compounds, etc.).

1.3.3. Inorganic pollutants in soils

The integration of different parameters of soil, such as physical activity, chemical, biological and enzymatic composition, can contribute to an effective and accurate assessment of its quality. [1.47]. Factors contributing to physical soil pollution are agricultural activities, excess pasture, deforestation, industrial activities and excessive pasture. Desertification and excessive humidity intensify the soil erosion process, being a type of physical soil contamination that is present globally and in Romania.

1.3.4. Soil fertility

Fertility is the property of the soil to provide sufficient water and nutrients for the growth and development of plants. Maintaining and improving soil fertility is necessary to stable, long-term and high-quality yields. There is a limit to the amount of nutrients that can naturally accumulate in the soil. If the nutrients extracted from the soil by applying mineral and organic fertilizers are not recovered, soil nutrient reserves will decrease, and yields will fall accordingly. Therefore,ining and increasing soil fertility under certain conditions is of fundamental importance.

Nitrogen and phosphorus are considered among the most important indicators of soil productivity and fertility [1.55]. Therefore, sustainable soil development requires a better understanding of SOC, Ntot and Ptot and their stoichiometric variability, as well as an assessment of the state of nutrients in soil ecosystems.

1.3.5. Automated assessment of recommendations on soil quality management

In order to assess the quality of the soil in its natural state and in the context of various situations involving anthropogenic activities, indicators are needed that can estimate the actual quality of soils in quantifiable categories.

In pursuit of these goals, the iSQAPER Project [1.62], within the Horizon 2020 programme, has created an app (Figure 1.8) for all stakeholders involved in agriculture who want to preserve soils for future generations.

CHAPTER 2
METHODS USED TO ASSESS THE PRESENCE OF INORGANIC POLLUTANTS IN THE ENVIRONMENT

2.1. METHODS USED FOR THE DETERMINATION OF INORGANIC POLLUTANTS IN WATER, SOIL, WASTE AND PLANTS

The analysis methods used to determine inorganic pollutants in environmental samples are procedures that establish rules and responsibilities for determining the physico-chemical indicators of groundwater and soil, in accordance with the national regulations in force. Those for determining toxic metals in plants are not regulated by national standards.

Below are briefly presented the main methods used for determining inorganic pollutants in environmental samples.

Volumetric methods

- Determination of chlorides in water and soil;
- Determination of bicarbonate ions in water;
- Determination of total nitrogen in the soil;
- Determination of water hardness;
- Determination of organic carbon of the soil;

Gravimetric methods

- Determination of soluble sulfate in soil;
- Determination of total solids dissolved, TDS in water;

Electrochemical Methods

- Determination of pH in water and soil samples;
- Determination of the conductivity of water samples;
- Determination of fluoride ions.

Spectrometric methods

- Determination of nitrate in drinking water;
- Determination of nitrite in water;
- Determination of ammonium ion in water;
- Determination of sulfate in water;
- Determination of total phosphorus in the soil.

Determination of metals in samples of water, soil and waste

Determine of metal oxides in chemical waste by XRF analysis

Detection of dissolved organic carbon

2.2. METHODS FOR ASSESSING POLLUTION OF GROUNDWATER AND SOILS IN VALEA CĂLUGĂREASCĂ USED IN THE STUDY

2.2.1. Hydrogeochemical methods used to assess the geochemical composition of groundwater and chemical wastes

Groundwater-rock interactions

Gibbs dispersion graph

Chloroalkaline indices (CAIs) Saturation index (SI)

2.2.2. Evaluarea calității apelor subterane pentru irigații și potabilizare

2.2.3. Modelul de evaluare a riscurilor pentru sănătatea umană

2.2.4. Metode pentru evaluarea gradului de poluare si a riscului ecologic

Indicele de poluare (Pi)

Indicele de geo-acumulare (Igeo)

Indicele de risc ecologic de mediu, Ri

2.3. METODE CHEMOMETRICE UTILIZATE PENTRU EVALUAREA CALITATII APELOR SUBTERANE SI SOLULUI

Cele mai utilizate metode chemometrice, precum analiza spațială GIS, analiza componentelor principale PCA, analiza factorilor, regresia multiplă și mai puțin utilizate, ca metoda suprafeței răspunsului RSM sunt prezentate în această lucrare.

2.3.1. Analiza spațială GIS (Geographical Information System)

GIS include mai multe metode de interpolare si geostatistice. Cele mai frecvent utilizate metode de interpolare sunt IDW, OK, SK și EBK. Interpolarea inversă cu ponderarea distanței (IDW) și krigingul. sunt utilizate în condiții diferite. Panhalakr și Jarag în 2016 au susținut că metoda IDW este chiar mai bună și mai precisă decât kriging [2.49].

2.3.2. Analiza multivariată

În ultimii ani, dezvoltarea de noi tehnici analitice a făcut posibilă folosirea intensa a chemometriei, iar analiza multivariată, care permite utilizarea simultană a tuturor variabilelor, a făcut posibilă rezolvarea unor sisteme analitice complexe. Dintre metodele de analiza statistica utilizate în evaluarea mediului se prezinta în continuare patru dintre cele mai practicate.

2.3.2.1. Analiza componentelor principale PCA este una dintre cele mai importante tehnici de reducere a datelor pentru seturile de date multivariate [2.51].

2.3.2.2. Analiza factorilor (AF) este o tehnică statistică multivariată utilizată pe scară largă pentru a descrie relațiile generale dintre mai multe variabile observate cu un număr potențial mai mic de variabile neobservate, numite factori, cu o pierdere minimă de informații de fond.

2.3.2.3. Modelul de regresia multiplă

2.3.2.4. Metodologia suprafeței de răspuns RMS

2.4. BIODISPONIBILITATEA METALELOR ÎN SOLURI CONTAMINATE ȘI FACTORII CARE INFLUENȚEAZĂ MOBILITATEA ACESTOR ELEMENTE

2.5. MĂSURI DE REMEDIERE A SOLURILOR CONTAMINATE CU METALE

Fitoremedierea solurilor contaminate cu metale grele se bazează pe utilizarea unor plante cultivate in-situ pentru decontaminarea solurilor poluate. Această tehnică utilizează plante care sunt tolerante la elemente metalice și metaloizi, *Sinapis alba* fiind o plantă cu cerințe sale reduse de îngrășăminte pe bază de N (în comparație cu alte culturi), productivității ridicate și longevității sale chiar și în condiții temperate și reci.

II. ORIGINAL CONTRIBUTIONS

CHAPTER 3
CHARACTERIZATION OF MINING WASTE FROM VALEA CĂLUGĂREASCĂ

Mining waste can have a significant negative impact on the environment depending on one or more intrinsic criteria, such as chemical and mineralogical composition, physical properties, volume and surface area, and disposal methods. Understanding pollutant leaching behaviour and mechanisms controlling this process in relation to the main components is important for assessing environmental impact [3.1]. In view of the above, the objective of the study presented in this chapter was to evaluate the chemical and mineralogical composition of ash samples from abandoned mine ash deposits in Valea Călugărească.

3.1. LOCATION OF ASHES DUMPS

A number of 12 samples of iron pyrite ash were taken from chemical waste dumps located in the abandoned area of Romfosfochim Fertilizer Chemical Plant - Valea Călugăreasca locality. The soil area covered by ash heaps is 1.57 km^2, the area is characterized by reduced vegetation and areas of land affected by soluble compounds solidified due to climate change.

The location of the mining ash heaps is geographically bounded by an area between 26°11'00" and 26°12'30" north longitude and between 44°56'00" and 44°56'42" east latitude.

3.2. CHARACTERISATION OF SAMPLES OF MINING ASH

3.2.1. Determination of chemical composition

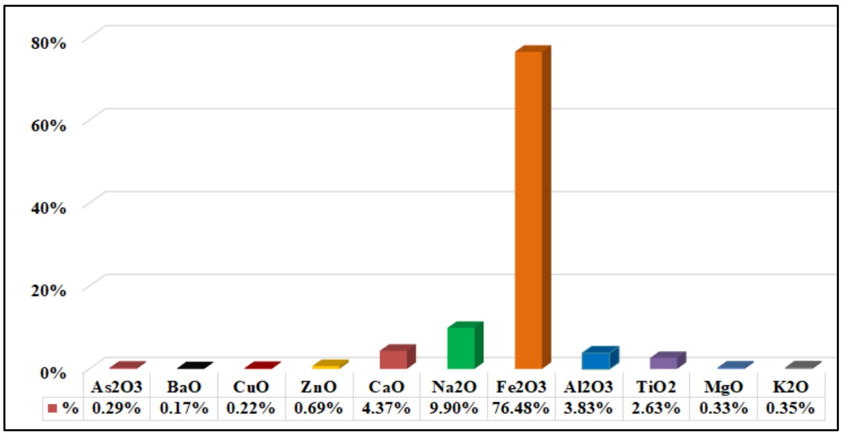

Fig. 3.2. Chemical composition in oxides of mining ash samples from Valea Călugărească shown as a percentage

The interpretation of the results obtained from the analysis of the composition of ash samples from Valea Călugărească shows that the main constituent of ash is Fe, with concentrations up to 158 g/kg, equivalent to Fe_2O_3 concentrations of 76.48%. These values indicate the presence of a significant amount of pyrite in the mining ash samples from Valea Călugărească.

The major constituents of the ash samples were sulphate content up to 47.5 g/kg and sodium concentration with an average value of 25.6 g/kg equivalent to 9.90%. Sulphur (S) being a major soluble element of ash present in the form of sulfates, has a close relationship with the presence of highly soluble elements such as Ca. The mean value of soluble sulphur calculated from the percentage of sulphate content was 4,75 %.

Data obtained from the analysis of oxide composition indicated the presence of TiO2 at a percentage value of 2.63%. Silicon was not determined in chemical analysis, due to volatilization and loss of silica during digestion. The pH value determined in the ash samples analysed showed values between 2,1 and 2,7 indicating a high leaching potential due to the soluble element content, also confirmed by the results obtained from the conductivity analysis of 32,1 mS/cm. Reduced concentrations of nitrogen at 0.4% and organic carbon at 0.45% were also observed.

3.3. PCA ANALYSIS OF ASH GENERATION PROCESS

Mining residues are recognised as an important potential source of reusable raw materials. In addition to the potential risk to the environment, mining residues are recognised as an important source of reusable raw materials taking into account some key aspects that need to be accurately characterised before these mining residues can be treated and used effectively. For this purpose, the results obtained from the PCA analysis applied to the concentration values of the determined elements in the oxide composition were used, which can give information on the generation process of these ashes.

3.3.1. Determination of variable values obtained from PCA analysis

The PCA analysis was applied to the oxide content values determined by the XRF method, which can give information on ash type depending on correlations between different oxide compounds of ash samples. The results obtained showed two main components, PC1 and PC2 generated by PCA analysis. The first main component, PC1, indicated a sustained contamination potential by oxide compounds such as CuO, PbO, Sb2O3, ZnO, Na2O, MnO, Fe2O3, Al2O3, MgO, and K2O, explaining a variance value of 64.56% of total variance. The second main component, FP2, comprised the data values of TiO2 and CaO, elements used in the process of stabilizing burnt ash in the mining industry, which constituted 28.15% of the total variance [3.5].

3.3.2. Characterization of the leaching process of ash samples

Pyritic ash samples from abandoned ash dumps in Valea Călugăreasca were first subjected to morphological analysis to verify that they met the basic condition for applying leaching tests (particle sizes ≤ 1mm). The values obtained from specific surface area analysis and particle size distribution determination performed with a Malvern Mastersizer 2000 analyzer ranged from 10.8 to 11.7 m2/g and the particle size distribution for 10% of the sample was 0.356 μm, for 50% of the sample – 0.658 μm and for 90% of the sample 0.929 μm. These values concluded the presence of an amorphous structure (particle size ≤ 1), a necessary condition for leaching tests.

The analysis of the chemical composition of leachates was carried out in accordance with national standards applicable to granular non-hazardous waste and stable and non-reactive hazardous waste obtained for a liquid/solid ratio L/S = 2/1 L/kg (L 1:2) and L/S = 10/1 L/kg. (L 1:10).

Interpretation of results obtained

Of the analysed elements As, Cd, Co, Cr, Ba, Ni, Sb, Mn, Pb, Zn, Cu, Mm, Al, Fe, K, Na, Ca and Mg, arsenic, cadmium and nickel indicated potentially hazardous according to the permissible limit values of the national standard.

Interpretation of the results obtained from the analysis of the levelling tests indicated exceeded values in the elements with potentially hazardous for the environment such as As, Cd and Ni. The analysis of the composition of levigates indicated mean values of **Arsenic** of 2.66 mg/kg in levigate L 1:2 (levigate prepared in solid ratio:liquid = 1:2) and 2.22 mg/ kg in levigat L 1:10 (levigat prepared and in solid:liqueid ratio = 1:10), compared to the national standard limit values 0.4 mg / kg (L/S = 2/1, L/kg) and 2 mg /kg (L/S = 10/1, L / kg) respectively. **Cadmium** showed average concentration values of 4,07 mg/kg in L 1:2 and 3,99 mg/ kg in L 1:10, compared to the national standard limit values at 0.6 mg/kg (L/S = 2/1, L/kg) and 1 mg/Kg (L / S = 10/1, L / kg), respectively. The median values of nickel were 8.4 mg/kg in L 1:2 and 10.9 mg/ kg in L 1:10, compared to the national standard limit values for 5mg/kg (L/S = 2/1, L/kg) and 10 mg/ Kg (L / S = 10/1, L / kg), respectively. Although high **sulphate** concentrations were observed in levitate samples of 8250 mg/kg in L 1:2 and 16408 mg/kg in L 1:10, no exceeding values were in relation to the national standard limit values of 10000 mg/ Kg (L/S = 2/1, L/kg) and 20000 mg/Kg (L / S = 10/1, L/kg), respectively.

The oxidation of pyrite, when exposed to air and water produces increased acidity of levitation samples showing up to mean values of 3.6 in levitate L 1:2 and 3.9 in levidate L 1:10 and containing containing SO_4^{2-}, Mn, Al, Na, Cl-, metals and metaloids such as As, Ni and Cd. This process is complex because it involves chemical, biological and electrochemical reactions and varies depending on environmental conditions.

For the purpose of evaluating the behavior of the main major elements of the composition of the ashes samples and the levitating samples, a comparative analysis using their percentage values was carried out. The comparative analysis of the values of the component elements evaluated in the ashes samples and levy samples (L 1:2 and L 1:10), calculated as percentages are presented in Table 3.3.

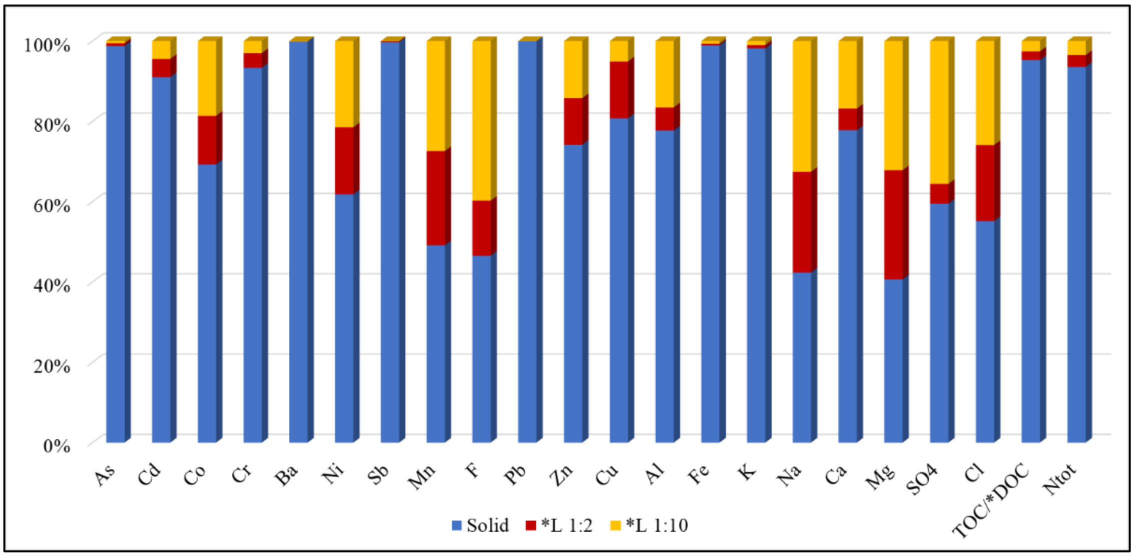

Fig. 3.3. Comparative analysis of assessed component concentration values in ash and leachate samples, calculated as a percentage

The comparative graphical representation of the values of the component elements evaluated in the ash and leachate samples, calculated as a percentage, gives indications of elements with high mobility in aqueous solutions. The interpretation of the obtained results showed that the metallic and semimetallic elements As, Cd, Cr, Sb, Pb, Fe are in the form of compounds that do not have leaching properties being retained by particles of solid material. Organic carbon and nitrogen, which are indicators of fertility and nutrition, showed low values in leachate samples.

3.3.3. Assessment of the factors influencing the mobility of organic carbon and nitrogen in pollutant samples

For the purpose of assessing the factors that influence the process of mobility in water-based solutions, a correlation analysis of the values of the major elements determining their mobility has been carried out. Figure 3.4 shows the matrix of Pearson correlation coefficients between the values of the concentrations of DOC, Ntot, SO42-, Cl-, Na and Mn in the Levigat samples L 1:10, the red color representing a positive correlations and the blue color a negative correlates.

The Pearson correlation coefficient matrix between the concentrations of DOC, Ntot, SO4, Cl, Na and Mn in the Levigat samples L 1:10 indicates a strongly negative influence of salinity on Ntot nitrogen, determined by the sulfate and sodium chloride concentrations, compounds formed in the levigation process, with a correlation coeficient r (Ntot-SO4) = -905. The concentration values of dissolved organic carbon are influenced poorly positively by the salinity determined by the soluble compounds and the presence of soluble elements of Mn in the levigate samples, with values for r (DOC-Cl) = 0, 374, respectively r (COC-Mn) = 0.324.

The interpretation of the results obtained indicates a potential for increasing the salinity of the levigat samples, salinities caused by high concentrations of dissolved sulphates. This phenomenon can also cause a decrease in nitrogen concentrations in these pollutants. The results presented above may be useful in assessing the impact on the soil on which these mining waste deposits are located as well as on the arable areas in this area.

3.4. INFLUENCE OF CONTACT TIME ON PH AND OXIDATION-REDUCTION POTENTIAL IN ASH SAMPLE LEACHATES

Evaluation of the influence of contact time on pH and ROP for leachates ash samples were analysed in prepared leachates at L/S ratio = 10/1 L/kg. The pH and ROP values were measured in leachates with a Hach HQ440D Multiprameter at different contact times of ash samples. The influence of contact time on pH and ROP was evaluated at time t = 0 minutes, 30 minutes, 2h, 8h, 24h and 48h in leachate samples. The equilibrium pH value of ash in contact with deionised water was 2,8 (t = 0), indicating the acidic character of the raw material. The evolution of pH values compared to contact time values of 30 minutes, 2h, 8h, 24h and 48h indicated an increase in pH and stabilization at 3.6 in the range 24h-48h. ROP characterizes the evolution of a system as oxidizing (positive values) or reducing (negative values). The ROP values measured during the mentioned time interval showed positive values at 30 minutes of 484mV, at 2h of 486mV, at 8h of 135mV and negative values at 24h of -327mV and at 48h of -332mV. Under acidic conditions, the ROP value is high, indicating an oxidation state, decreasing in proportion to the increase in pH. The measured ROP values indicate a stabilized oxidising medium of the leachate samples at a contact time of 24h, this result being obtained according to the leaching test procedure.

In order to evaluate the factors influencing the variation of ROP in the analyzed leachate samples, an analysis of the correlation coefficients between the elements with high soluble potential in the leachate samples evaluated at a time of 24h was performed. The interpretation of the results of the analysis of the correlation coefficients applied between the ROP values and the values of SO_4^{2-}, Ca, Na, K, Mn and Cl- concentrations in leachate samples at a time t = 24h indicated the strongest positive correlation between soluble Ca and ROP, r = 0.976, for a value p value < 0.05, which shows that the variation of the values of this element can favor reduction processes and increase of soluble species concentrations in the analyzed leachate samples. Similar studies confirm the efficacy of Ca ions in suppressing metal leaching [3.8].

3.5. MINERALOGICAL ANALYSIS OF PYRITE ASH

In this study, compounds with the highest dissolution potential in aqueous extracts of ashes were selected for geochemical modeling. The mineral phases obtained from geochemical modelling and the values of the SI saturation indices were calculated for two types of leachate L 1:2 and L 1:10.

Interpretation of the results obtained from the mineralogical analysis presented Table 3.6 indicated the probability of precipitation of calcium sulphate in the form of anhydrites determined by the SI value = 0.44 or gypsum, determined by the SI value = 0.69 in leachate L 1:10, the positive values being explained by a process of supersaturation of calcium sulfate [3.7]. During the leaching process, the subsaturated dissolution process prevailed in the aqueous extract L 1:2, as evidenced by the negative SI value.

The highest SI values are present in mineral types whose composition includes F-containing minerals, such as:

- $CuF2·2H2O(s)$ with a value of SI = -15.8 in leachate L 1:2 and SI = -12.1 in leachate L 1:10;
- $CaF2$ (Fluorite), with a value of SI = -9,09 in leachate L 1:2 and SI = -4,37 in leachate L 1:10;
- sulfate-containing minerals such as Chalcanthite;
- $CuSO4·5H2O(s)$ with a value of SI = -3.66 in leachate L 1:2 and SI = -3.05 in leachate L 1:10.

Minerals formed by associating sulfate with metals such as Cd, Cu, Zn or Mn have also been identified, whose mobile fractions showed a high degree of solubility in both types of leachate.

3.6. PARTIAL CONCLUSIONS

In this chapter, an analysis of the compositions of samples of mining waste from abandoned dumps located in Valea Călugăreasca and a PCA analysis of the composition of oxides regarding the process of generating these ashes was performed. Also included in this chapter were a characterization of the leaching process of ash samples, the influence of contact time on pH and oxidation-reduction potential in leachate samples and a mineralogical analysis of ashes.

Interpretation of the results of the analysis of the chemical composition of the ash samples from the Valea Călugărească indicated the presence of potentially dangerous elements such as Pb, Zn, Cu, Fe and Al. The high content of Fe indicated the presence of pyrite in the composition of the ashes samples analyzed. PCA analysis of oxide composition identified the presence of titanium dioxide and calcium oxide elements used as stabilizers in mining ash burning processes.

Interpretation of the results of the pollution sample analysis carried out in accordance with national standards applicable to non-dangerous granular waste and non-hazardous stable non-active waste, showed insignificant excesses for the As, Cd, and Ni metals that form compounds with low polluting properties. Organic carbon and nitrogen showed low mobility due to the presence of high concentrations of sulfates and fluorides that may cause increased salinity in the levigat samples.

The results obtained from the study of the influence of the contact time on the pH and oxide-reduction potential in the levigate samples indicated the presence of an oxidizing medium and a strong acidic pH stabilized at a 24h contact time, the process being positively influenced by the increase in the concentration of soluble Ca in the Levigates samples.

The saturation indices for various minerals, calculated on the basis of the concentrations of component elements of the ashes, indicate the presence of calcium sulfate formed as a result of unsaturated dissolving processes in the molten samples and the precipitation tendency determined by the process of over-saturation of this mineral.

The results obtained are useful for assessing soils affected by the presence of mine ash deposits.

CHAPTER 4

CHARACTERIZATION OF SOILS IN AREAS AFFECTED BY THE PRESENCE OF MINING WASTE DUMPS IN VALEA CĂLUGĂREASCĂ

The study of the characterization of some soils in Valea Călugărească presented in this chapter aimed to know the fertility level of these soils in the area bordering abandoned ash dumps and to assess the risk of pollution caused by the presence of these ashes. Updating the database on the impact of ash on soils near abandoned dumps is important for the protection and sustainable use of that agricultural land, preventing degradation and preserving its functions.

4.1. CHARACTERIZATION OF THE AGRICULTURAL AREA OF VALEA CĂLUGĂREASCĂ

4.1.2. Soil pollution in Valea Călugărească

Pe teritoriul comunei Valea Călugărească există încă surse de poluare a solului si/sau a pânzei freatice, cum ar fi bataluri, halde și decantoare, deși în prezent activitățile desfășurate de combinatul chimic "ROMFOSFOCHIM", principalul poluator al zonei, au încetat. Singura sursă activă de contaminare a solului si apei provine din aplicarea îngrășămintelor chimice sau a ierbicidelor pentru creșterea producției agricole. Acest lucru are un impact local și de scurtă durată. În plus, sunt prezente zone cu exces de umiditate în care există băltiri, situate de obicei lângă cursurile de apă, unde vor fi utile măsuri de drenaj pentru ape. Apele superficiale se acumulează în straturile subterane deschise din cauza substratului argilos impermeabil.

Datorită prezenței fenomenului de eroziune hidrică a solului din zona amintită, fertilitatea acestor soluri este redusă, fiind necesară aplicarea regulată de îngrășăminte organice și minerale. Aceasta întrebuințare, pe lângă efectele benefice, ar putea avea un impact negativ asupra producției de biomasă a culturilor agricole din regiunea afectată.

4.1.4. Soil sampling and preparation for analysis

In order to determine the degree of contamination of soils with metallic and semimetallic pollutants (Zn, Cd, Pb and As) and to assess their quality, soil samples were taken from eleven sites located within the perimeter of pyrite ash heaps.

The location of the study area included the Valea Călugăreasca commune area and arable areas located in the area bordering chemical waste dumps made of pyrite ash. The sites were located on an area of about 2km around abandoned chemical landfills.

4.2. PHYSICO-CHEMICAL CHARACTERIZATION OF SOIL SAMPLES FROM VALEA CĂLUGĂREASCA AREA

In order to establish the quality state of soils taken from the region of abandoned haldees in the Valea Călugărească area, a number of physical and chemical studies were carried out, their purpose being, mainly, the evaluation of some significant physico-chemical indicators in soil pollution, and in this case this evaluation is associated with the presence of pyritic ash.

The parameters analyzed for the physical and chemical characterization of soils were as follows: humidity, pH, electrical conductivity, assimilable nitrogen (NO3), content of soluble salts (sulfates, chlorides), cations of solute compounds (Ca, Na, Mg, K), organic carbon content of the soil, total nitrogen content, total phosphorus, metals and metaloids (As).

4.2.2. Interpretation of the results obtained from the analysis of the physical and chemical parameters of soil samples in the Valea Călugărească area

Interpreting the results of the analyses of metals and soil metaloids in the area of pyritic ash halids of the Valley Călugârească region showed increased values of the concentration of Fe with averages of 85.1 g/kg, especially for soils near the halids (S3 – 512.8 g /kg, S4 – 181.4 g / kg and S5 – 43.5 g/ kg).

Increased concentration values were obtained for the following potentially hazardous elements:

- *Arsenic*: values of concentration of 33.5 mg/kg with increased values in soils S3 – 151 mg/ kg, S4 – 69.4 mg/ Kg and S5 – 86.4 Mg/kg;
- *Copper*: increased concentration values in soils S3 – 1091mg/kg, S4 – 735 mg/kg and S5 – 211mg/ kg with an average of 238.4 mg/ kg;
- *Cadmium*: increased concentration values in soils S3 – 15.79 mg/kg, S4 – 9.44 mg/ kg and S5 – 2.59 mg/ Kg with an average of 3.3 mg/Kg;
- *Manganese*: concentration values of 370,8 mg/kg with maximum values in soil S4 – 572 mg/ kg;
- *Nickel*: concentration values of 27.8 mg/kg with maximum values in soil S11 – 43.9 mg/ kg;
- *Lead*: increased concentration values in soils S3 – 2916 mg/kg, S4 – 1224 mg/ kg and S5 – 130 mg/ Kg with an average of 406.7 mg/Kg;
- *Stibium*: increased concentration values in soils S3 – 2869 mg/kg, S4 – 2232 mg/ kg and S5 – 552mg/kg with an average of 597.1 mg/ Kg.

The concentrations of the indicators presented below were in normal values of the soil as follows:

- *Chromium* was identified in soil samples with an average concentration of 17.2 mg/kg, titanium - 134.8 mg/ kg, thalium - 9.5 mg/ Kg, vanadium - 24, mg/ кг and barium with a concentration value of 185.3 mg/Kg. *Calcium* was the majority of the soluble cations with concentration values ranging from 125 mg/kg to 377 mg/ kg, the order of mean values being as follows: Ca – 306 mg/kg > Mg – 18.7 mg/ Kg > K – 17.2 mg/ kg > Na – 15.8 mg/Kg.

The pH of the soils was between 5.30 and 6.71, the soil located 50m away from the ashes showing acid character (S3).

Conductivity indicated increased values in soils S3 – 1940 μS/cm, S4 – 1214 μS /cm and S5 – 765 μS-/cm due to increased sulphate concentrations with values of 1054 mg/kg in S3, 968 mg/ kg in S4 and 566 mg/ Kg in S5. The analyzed soils showed an average humidity value of 18.5%.

Low values of nitrate concentrations (6.25 mg/kg in S3, 8.16 mg/kg in S4, 15.3 mg/kg in S5), Ntot (0.10% in S3, 0.10% in S4, 0.20% in S5) and TOC (1% in S3, 0.88% in S4, 1.12% in S5) were recorded in soil samples from the pyritic ash area. Ammonium in the analyzed soils had low concentrations ranging from 3.02 mg/kg to 45.6 mg/kg. Ptot showed concentration values of 0,50 % with minimum values in S4 soil of 0,12 %. Chlorides ranged from 10.2 mg/kg to 17.3 mg/kg.

4.3. AGROCHEMICAL CHARACTERIZATION OF SOIL SAMPLES FROM VALEA CĂLUGĂREASCA AREA

In order to assess the quality status of soils taken from the area of pyritic ash dumps, agrochemical investigations were also carried out, their purpose being, mainly, to establish the degree of soil fertility by evaluating significant indicators resulting from the assessment of soil pollution. For this purpose, the cation exchange capacity CEC, humus content, nitrogen index, C:N ratio and N:P ratio in soil were calculated using experimental values of these parameters.

4.3.2. Interpretation of results obtained from the analysis of soil fertility indicators

CEC cation exchange capacity dynamics are inversely proportional to the dynamics of exchange acidity and directly proportional with the value of the exchange base cation concentration. Therefore, a significant increase in CEC of 20.4% was observed in the soil located at 50m (S3) and 11.4% in soil at 100m(S4) distance from the ashes, compared with the control soil samples (S6 - solul martor). This suggests that it is possible that the soil salts have been solubilized by increasing the degree of salinity in soil samples affecting the osmotic pressure of soil solution. The CEC value indicates the presence of clay minerals in the mineral composition of soils.

The degree of saturation in compounds with basal pH of the soil had values ranging from 74.2% to 83% in soil samples located at a distance greater than 200m from abandoned hills. Basic pH compounds (SB) decreased in soil samples S3 – 31.8% and S4 – 60.4% due to their acidity associated with the presence of pyrite ash.

Low values of Humus and assimilable Nitrogen content in soils S3, S4 and S5 of 1.72%, 1.52% and 2.65% and 1.9 mg/kg, 2.4mg/kg and 4.0 mg/ kg respectively indicate a low degree of nutrients in soil structure.

The C:N ratio of soils showed elevated values in the area adjacent to the ash halves of 10.0 in S3, 8.8 in S4 and 7.7 in S5, with the remaining samples having values ranging from 1.30 to 3.74. These differences indicate a change in soil structure in the area close to the ashes and an increase in the rate of decomposition of organic matter proportional to the reduction in the availability of nutrients for plants, in this case soils having a low fertility. The map of the spatial distribution of the values of the C:N ratio in soil samples in the area of the deposits of pyrite ash in the Valea Călugărească area is shown in Figure 4.5, the red color indicating maximum values, and the blue color the minimum values. This shows a low level of fertility in soils occupying an area of up to approximately 500m around ash deposits [4.3].

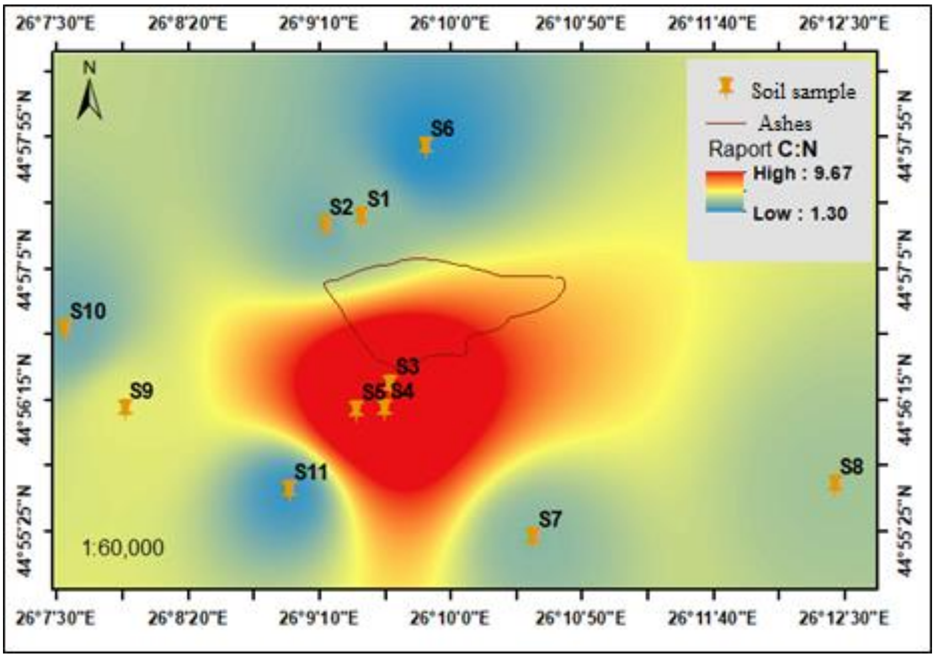

Fig. 4.5. Spatial distribution of C:N ratio values in soil samples from the area of pyritic ash deposits in the Valea Călugărească area

The N:P ratio ranged from 0.29 to 1.61. Low values present in soils close to pyritic waste landfills show poor availability of nutrients to plants under the influence of combined climate effects associated with the presence of ash. The spatial distribution map of N:P ratio values in soil samples from the pyritic ash heap area shown in figure 4.6 showed significantly negative changes in soil fertility over a large area affecting arable areas outside the study area. The meaning of the colours indicates the existence of soils with low fertility (green) and soils with normal fertility (red).

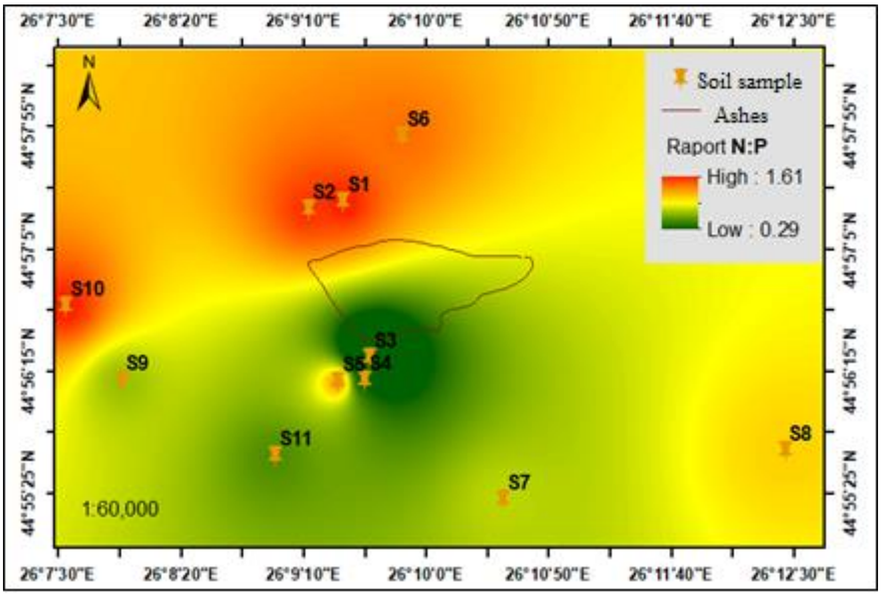

Fig. 4.6. Spatial distribution of N:P ratio values in soil samples from the area of pyritic ash dumps in the Valea Călugăreasca area

4.4. PCA ANALYSIS ON FACTORS IMPACTING SOIL FERTILITY IN VALEA CALUGAREASCA AREA

In order to evaluate the factors affecting the fertility of soils affected by the presence of abandoned pyrite ashes, the analysis of the main components of PCA was carried out using the statistical software NCSS 2021, the method being presented in Chapter 2. The Kaiser-Meyer-Olkin test (KMO) was used to assess the adequacy of the values of all included variables, with a value of KMO > 0.6 considered acceptable in terms of analysis efficiency. The PCA analysis of the factors affecting soil fertility affected by the presence of pyrite ash is presented in Figure 4.6 which included the values of Ntot, TOC, Ptot, N-asim, pH, conductivity and C:N, respectively N:P ratios. Two main components PC1 and PC2 were generated, KMO = 0.721 for (N=12) (four replicates of three samples from each soil sample) confirming the applicability of the method. The first main component PC1 showed 84.2% of the total variance and grouped the components that influence the C:N ratio, respectively, the soluble sulphate concentration and the content of soluble soluble components indicated by the conductivity value. The second main component had 12.3% of the total variance, grouping the elements that support plant nutrition (Ntot, TOC, Ptot, N-asim).

This PCA analysis showed that the fertility of soils in the area of abandoned haldees located near the municipality of Valea Călugărească is affected by the increased salinity of these soils, saltiness caused by the high concentrations of dissolved salts, especially of sulfates derived from the cleaning of the soluble components of the ashes.

4.5. EVALUATION OF METAL POLLUTION OF SOILS IN THE AREA OF A PIRITIC AESE HALDE

It is well known that metals with potentially dangerous are among the most important environmental pollutants, due to their toxicity, bioaccumulation properties, they are also non-biodegradable. The soils in the chemical waste storage area in the Valea Călugărească are affected by the presence of these mining wastes, it is important to evaluate the pollution with metals in order to make decisions on the planning of the use of the respective land. There is no specialized literature on heavy metal pollution in soils in the Valea Călugărească area.

The main objective of this study was to evaluate the concentrations of Pb, As, Cd, Cr, Co, Mn, Zn and Sb in soils located dinn the area of these abandoned halde.

The values of the concentrations of metals and metaloids in the soil samples presented in Table 4.2 were compared with the limit values allowed in accordance with the National Standard - Order 278/2011 and with the values for the concentration of these elements in the ashes samples shown in Chapter 3. For the purpose of assessing the level of contamination with potentially hazardous elements of the study region, spatial distribution maps were generated using the methodology described in sub-chapter 4.3.

Comparison of arsenic content in soil samples with arsenic content values in ash samples and permissible limit values

Figure 4.8a. represents the comparison of the concentration values of As in soil samples with the limit values of the national standard and with the values obtained in ash samples. According to the permissible limit value of the national standard of 5 mg/kg, the arsenic content in the soil samples analysed exceeds this limit in 73 % of soil samples. The highest values were determined in arable soils at a distance between 50 – 200 m from ash heaps (maximum value of 197 mg/kg). The high level of As concentration in this area could be due to arsenic intake from pyrite ash (384 mg/kg) but also to atmospheric deposition during periods of climate change (wind and rain). Also an important source of increased arsenic concentrations are Fe(III) oxides, which show an increased affinity for As(III) and As(V) species at low pH values.

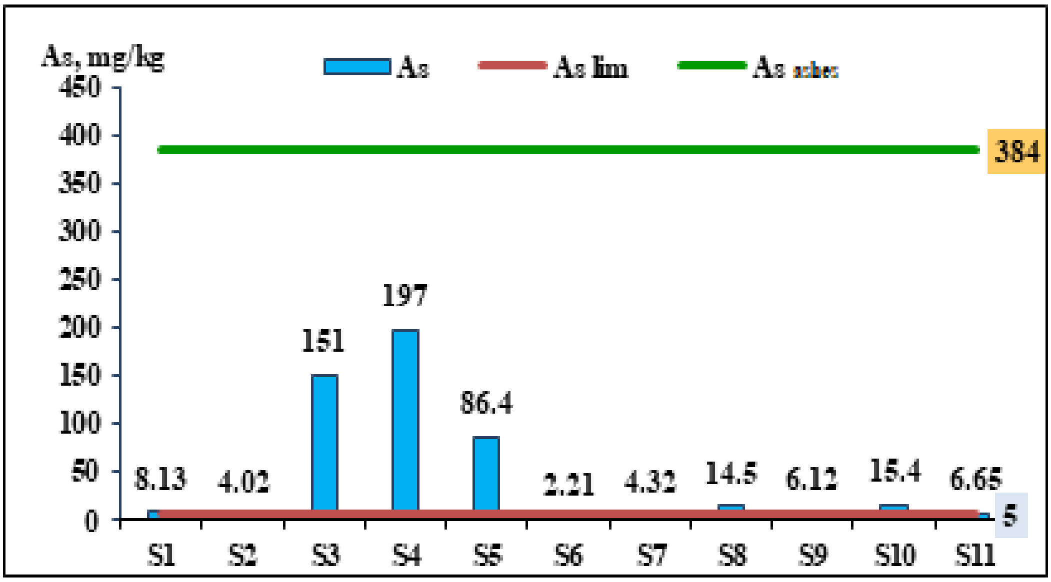

Fig. 4.8a. Comparison of the As concentration values in soil samples with the limit values of the national standard and with the values obtained from ash samples from Valea Călugărească area

The spatial distribution map of arsenic concentration values in soils in the pyrite ash heap region shown in Figure 4.8b shows contamination with this chemical element throughout the study area. It is observed that the distribution level is extended about 2 km from the warehouse area, this extension being explained by the influence of the wind whose direction is usually E → W (source: accuweather/wind-flow) [4.4]. In the remaining areas of the study area, As concentrations ranged from 2.21 mg/kg in S6 (control soil) to 14.5 mg/kg in S8.

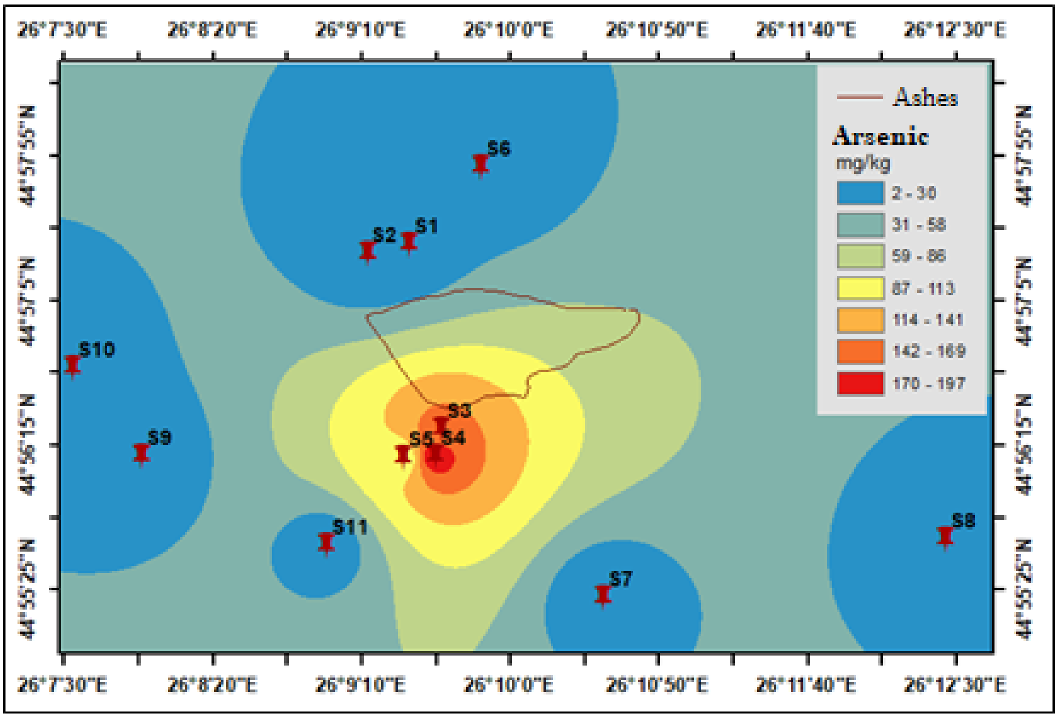

Fig. 4.8b. Map of spatial distribution of Arsenic concentration values in soils in the region of pyrite ash heaps in the Valea Călugărească area

Comparison of the cadmium content in soil samples with the values of cadmio content in ash samples and with permissible limit values

In accordance with the national standard's allowed limit value of 1 mg/kg, the cadmion content in the analysed soil sample exceeds this limit in 64% of soils samples.

Maximum values of 15.7 mg/kg were observed in two of the arable soils at a distance of between 50 – 100m of chemical ashes. The map of the spatial distribution of the values of cadmium concentrations in the soils in the pyrite ash halls region indicates a contamination that is not due to the presence of pyrite ashes (Cd concentration = 80 mg/kg), the distribution is reduced to a distance of approximately 200m. Atmospheric deposits can be considered a source of the increased content of this element in soils in this area. In other soil samples the concentration values of Cd ranged from 0.73 mg/kg (S6 - observing soil) to 1.36 mg/kg (S2).

Comparison of copper content in soil samples with copper contents in ashes samples and with permissible limit values

In accordance with the national standard's permitted limit value of 20 mg/kg, the arsenic content in the soil sample analysed exceeds this limit in all soils samples.

The spatial distribution of the values of copper concentrations in soils in the pyrite ash region indicates a contamination of the affected area by the presence of high concentrations of this chemical element in pyrite ashes (1018 mg/kg). With strong complexes at a pH = 5.5 the solubility of this element is inversely proportional to the pH.

Comparison of manganese content in soil samples with manganese levels in ash samples and with permissible limit values

In accordance with the national standard limit of 900 mg/kg, there were no exceeded manganese values in analysed soils samples.

The map of the spatial distribution of the manganese concentration values in soils in the pyrite ash halls region, indicates a slight increase in the concentrations in the area away from the chemical ash Halls.

Comparison of the nickel content in soil samples with the nikel content values in ash samples and the permissible limit values

In accordance with the national standard limit of 20 mg/kg, only one soil sample (S3) showed exceeded values of this chemical element.

The spatial distribution of the values of nickel concentrations in soils in the pyrite ash halls region indicates a uniform distribution in this element in the study area. The increase in Ni concentrations close to permissible limit values may be of a geogenic nature due to the imbalance of the C:N cycle.

Comparison of lead content in soil samples with lead content values in ash samples and with permissible limit values

In accordance with the national standard's permitted limit value of 20 mg/kg, the lead content of the analysed soil sample exceeds this limit in 64% of soils samples.

The highest value was determined in soil S3 at a distance of 50m from the pyrite ashtray. The soil at a distance of 100m had a concentration of 1224 mg/kg, and that at 200m showed a value of 130 mg/ kg. The results obtained indicate a high level of Pb concentration in this area affected by the presence of pyrite ash with a high content of this element (4356 mg/kg) and provide useful data on its behavior over time. Soil particles being over-saturated with a high Pb content, precipitation is favoured. In this way, it can be explained that a very high level of contamination is limited to a distance of approximately 100m from the mining ashtray.

The map of the spatial distribution of the values of lead concentrations in soils in the pyrite ashtray region shows the limitation of contamination with this element in soil samples near ashes (soils S3 and S4).

Comparison of the stivium content in soil samples with the stibium content values in ash samples and with the permissible limit values

In accordance with the national standard's permitted limit value of 5 mg/kg, the stibiu content in the soil sample analysed exceeds this limit in 36% of soils samples.

The spatial distribution of the values of stivium concentrations in soils in the pyrite ash halls region indicates lead-like behavior.

Comparison of zinc content in soil samples with zinc contents in ash samples and with permissible limit values

In accordance with the national standard's permitted limit value of 100 mg/kg, the arsenic content in analysed soils samples exceeds this limit in 54% of soils. The map of the spatial distribution of the zinc concentration values in soils in the pyrite ashtray region, indicates the contamination of the land limited to an area of approximately 200m. The increase in concentration values in areas further away from chemical ash deposits could be caused by processes of atmospheric deposition of ash particles that have flattened in the soil solution.

4.6. ESTABLISHING THE DEGREE OF METAL POLLUTION OF SOILS AND THE ECOLOGICAL RISK TO THE ENVIRONMENT

In this study, it was established the degree of pollution with potentially hazardous metals of the soils in the Valea Calugareasca area affected by the presence of pyrite ash dumps and the ecological risk for the environment. For this, various geochemical indices such as the PI Pollution Index, the Igo Geoaccumulation Index and the Ecological Environmental Risk Index Ri were used. PI, Igo indices were used to assess soil pollution levels against a single potentially hazardous chemical element. The integrated ecological risk index Ri is oriented towards the entire group of pollutants, providing a comprehensive assessment of the pollution level of these soils. The formulas for calculating the geochemical indices used and their classification were presented in Chapter 2.

4.6.1. Single pollution index (PI)

The determination of soil pollution by arsenic, cadmium, copper, lead, antimony and zinc based on the values of the IP Pollution Index is presented in Table 4.6. The interpretation of the results obtained from the evaluation of the Single Pollution Index (PI), calculated for each of the six analyzed elements As, Cd, Cu, Pb, Sb, Zn from soil samples, showed increased values of the PI for Pb with a PI = 286 and for Zn with a PI = 65.5 in soil S3 sampled at 50m from pyritic ash dumps. The lowest PI values were observed for Sb and Cu, with PIs of 0.2 and 0.4. Soils in the area near chemical landfills showed an increased degree of pollution with potentially hazardous elements in the following order: Pb > Zn > Cd > As > Cu > Sb for soils S3 and S4 (Figure 4.1). The S5 soil at the location located 200m from the ash heaps showed an increased degree of pollution with Pb, Zn, As and Cd.

4.6.2. Geochemical pollution index (Igeo)

The determination of the degree of geochemical pollution of soils with arsenic, cadmium, copper, lead, antimony and zinc based on the values of the Igo Geoaccumulation Index is presented in Table 4.7. The interpretation of the results obtained from the assessment of the geochemical polarization degree of soils with potentially hazardous elements for the environment based on the geoaccumulation index (Igeo) showed that soils S3, S4, according to the classification scale presented in Chapter 2, revealed a very high degree of contamination with toxic metals following the order: Pb > Zn > As > Sb > Cd. The values obtained for soil sample S5 indicated a very high degree of lead pollution, zinc, arsenic and cadmium. The calculated Igeo values for these elements were characterized by increased variability.

4.6.3. Integrated environmental risk index (IR)

The determination of the degree of ecological risk to the environment of soils polluted by arsenic, cadmium, copper, lead, antimony and zinc on the basis of values of Ri is presented in Table 4.8. Interpretation of these data indicated a very high environmental risk in soil samples S3 and S4 from contamination with arsenic, cadmium and lead. The S5 soil sample posed a considerable ecological risk due to the arsenic polluter.

From the data obtained in this chapter, the assessment of the degree of pollution of soils in the Valea Călugărească rural area affected by the presence of pyrite ash dumps was carried out, which indicated an increased level of arsenic, cadmium and lead pollution of a land area of about 200m around these abandoned deposits. The ecological risk to the environment of these soils caused by arsenic pollution has been established.

4.7. REMEDIATION OF SOILS CONTAMINATED WITH TOXIC METALS

The soils in the Valea Călugărească rural area affected by the presence of pyrite ash dumps have a low fertility and a relatively high level of pollution, requiring the implementation of remedial measures. In this study, it was chosen to choose a solution for remediation of contaminated soils, which included the use of the SQAPP application developed within the HORIZON 2020 project. This application generated a scenario regarding the choice of various techniques for remediation of soils polluted with arsenic (in this study – soil S5). The benchmarks introduced in that application included the results from Table 4.2 for S5 soil, arable soil with a considerable ecological risk to the environment from arsenic contamination. The existing database in the application, resulting from all studies carried out to assess the quality of soils in soil zone S5, located at a distance of 200m from abandoned ash dumps.

The steps taken to choose S5 soil remediation techniques polluted with arsenic, cadmium and lead using the SQAPP app were as follows:

- Establishing the location, the location can be located manually or automatically; - Introduction of soil characteristic values obtained in this study. The data obtained in this study have a blue font;
- Establishing types of threats to soil quality;
- Assessment of threat and potential for improvement of soil characteristics;
- Recommendations on remediation techniques.

The main recommendations for remediation of soil contaminated with arsenic, cadmium and lead generated by the SQAPP application were:

- phytoremediation;
- application of raised germination beds to crush and improve soil structure;
- the use of techniques specific to conservative agriculture for the purpose of regenerating arable land;
- minimization of irrigation with salinized water;
- cultivation of plants with radicle system.

4.8. PARTIAL CONCLUSIONS

In chapter 4 of this doctoral thesis, the characterization of soils in areas affected by the presence of pyritic ash hales in the rural Valley Călugărească region was carried out.

Achieving this objective included the physical-geographic characterization of the area studied, the physico-chemical and agrochemical characterisation of soil samples and a PCA analysis of factors affecting soil fertility. The assessment of soil pollution by metals in the area of pyritic ash halls and the establishment of the degree of soils pollutation with metals and the environmental risk for the environment regarding contamination with potentially dangerous elements was also carried out.

The interpretation of the results obtained in the study presented in this chapter showed an extension of contamination on an area of approximately 200m around the abandoned deposits, the degree of pollution being significantly reduced by the increased distance to the pyritic ash halls.

The SQAPP application developed under the HORIZON 2020 Project, using as a partial database the information obtained in this study, recommended the most effective soil remediation procedures.

CHAPTER 5
GROUNDWATER QUALITY IN VALEA CĂLUGĂREASCĂ

5.1. CHARACTERIZATION OF THE VALEA CĂLUGĂREASCĂ AQUIVER

5.1.2. Groundwater pollution

The study on the quality of soils affected by the presence of abandoned pyritic ash waste in the Valea Călugăreasca area presented in Chapter 4 identified a number of sources of chemicals potentially hazardous to the environment such as arsenic, cadmium, lead and an increased degree of salinity caused by the presence of leached sulfates in pyritic ash samples.

În this context, a comparative study of groundwater quality in this region was carried out, both in terms of anthropogenic pollution and pollution from natural sources. The indicators used to assess the quality of water for irrigation and consumption were determined.

5.3. CHEMICAL COMPOSITION OF THE GROUNDWATER IN VALEA CĂLUGĂREASCA

In order to study the chemical composition of groundwater, thirty samples were taken from wells located in the households of Valea Călugăreasca commune inhabitants or from street wells in accordance with groundwater sampling procedures. In order to take a representative sample of water, water from a well was removed three times by means of a bucket and discharged to specially designated areas. In the case of pumps, groundwater was discharged continuously for about 10 minutes. The samples were collected in plastic containers and stored at 4oC to be analysed in the laboratory.

5.3.1. Materials and methods used

The analytical methods used to determine the above indicators have been in accordance with international standards, the laboratory applying all requirements imposed by EN ISO/IEC 17025.

5.3.2. Chemical composition of groundwater in Valea Călugărească

In order to determine the chemical composition of groundwater, the most significant indicators of drinking water quality were determined. The values of the parameters determined in the 30 analyzed water samples varied between maximum and minimum values, being calculated the averages of these values.

Following the interpretation of the results obtained when analyzing the chemical composition of groundwater samples, the following observations were made:

- the pH of the groundwater samples showed an average value of 7.5 at a temperature of 20.5oC, the water being slightly alkaline due to the influences of climatic conditions and the character of the aquifer;
- conductivity values were in the range of 758 ÷ 1308 µS/cm,
- the concentration of TDS averaged 732 mg/L. Conductivity and TDS are key factors in assessing the long-term viability of a water source.

Exceeded values were recorded for the following parameters:

- sulphates, whose maximum value of 321 mg/L was determined in the sample in Section 4 and elevated values close to the maximum permitted limits were found in samples taken from Sections 5 to 19),

- chlorides, the maximum value of which was found in the sample in Section 4 and increased values close to the maximum permitted limits, in samples in Sections 5 to 10)

- nitrates, the increased concentration of which was determined in samples in Sections 20 to 23 in the range 208 ÷ 220 mg//L and in samples in Sections 24 (166 mg/L) and 25 (121 mg/L) respectively.

As regards the determination of elements As, Fe, Cu, Zn and Al, they were below the limit of quantification of the method, being in the form of ultra traces in the groundwater samples analysed, thus making the water quality fit for human consumption according to national legislation. Concentrations of Cd, Cr, Ni, Pb, Hg, Mn, Se and Sb were also below the limit of quantification of applied methods (ICP-EOS). The CBE error ranged from -3.89 ÷ 3.47 confirming the accuracy of ionic equilibrium results in groundwater samples.

5.4. IDENTIFICATION OF Sources OF ANTHROPIC POLLUTION OF SUBTERNAL WATERS IN THE VALEA CĂLUGĂREASCĂ USING MULTIVARIATED ANALYSIS

Identification of sources of anthropic pollution of groundwater in Valea Călugărească can be achieved through a multivariate statistical approach using factor analysis (AF). This is a method widely used to describe the relationship between groundwater quality, implicit pollution and land use. The method is applied by combining the measured concentrations for groundwater quality parameters with values exceeded according to the National Standard for Drinking Water concerning the content of sulfates, nitrates and chlorides and other parameters whose presence influences the composition of water (bicarbonates, fluors, conductivity). Before performing the factor analysis, the KMO and Bartlett sphericity test must be performed to determine whether the data are suitable for factor analysis as presented in Chapter 2 of this paper. The XLSTAT 2014 calculation software was used to perform AF. A KMO value of 0.643 and a calculated probability p value less than 0.001 indicated that the data were suitable for factor analysis. Table 5.2 shows the values of the components in the Varimax rotation factor matrix for a two-factor D1 and D2 model.

Table 5.2. The values of components in the Varimax rotation factor matrix for a two-factor model D1 and D2.

Variable	D1	D2
EC	0.430	**0.915**
NO_3^-	**0.677**	0.058
SO_4^{2-}	**0.913**	-0.133
HCO_3^-	-0.220	**0.594**
Cl^-	**0.690**	0.557
F^-	0.399	0.066

Factor D1 explains 31,62 % of total variance and shows a significantly positive value of 0,913 for sulfates, moderately positive values of 0,690 for chlorides and 0,677 for nitrates. The values of correlations of this factor establish the relationship between these variables whose presence in the composition of groundwater indicates a source of anthropogenic pollution associated with the presence of pyrite ash and other polluters from agriculture. The factor D2 explains 25.28% of the total variation, with a moderately positive component value for bicarbonates of 0.594. The conductivity factor value was 0.915, indicating the presence of other sources of compounds from natural sources.

The spatial analysis was used in order to geographically visualize the distribution of chemical compounds sulfates, nitrates and chlorides established following the AF analysis as sources of anthropogenic pollution of groundwater samples from Valea Călugărească. Figure 5.3a shows the distribution of sulphate concentration values.

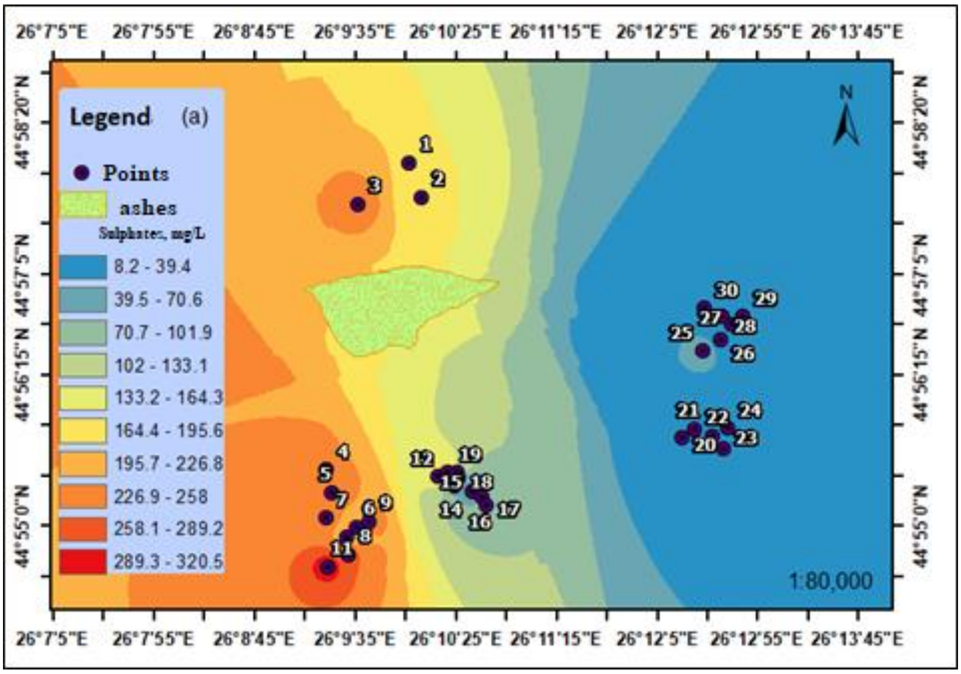

Fig. 5.3a. Distribution of sulfate concentration values in groundwater samples from Valea Călugărească

The geographical visualization of the sources of anthropogenic pollution with impact on the quality of groundwater in Valea Călugăreasca indicated an increase in the values of sulfates and chlorides concentrations in the aquifer affected by the presence of pyrite ashes in the direction of water flow but also in the direction of winds. Nitrate pollution is punctual due to excessive use of fertilizers on the soils of the studied region.

5.5. IDENTIFICATION OF NATURAL SOURCES OF POLLUTANTS IN GROUNDWATER IN VALEA CĂLUGĂREASCA REGION USING HYDROCHEMICAL AND GEOCHEMICAL ANALYSIS

Geochemical analysis provided information on the origin of major ions in groundwater samples according to the methodology presented in Chapter 2. Knowing the dominance of hydrochemical components of groundwater can identify the origin of the water, including a possible natural source of pollution. Piper's trilinear diagram, shown in Figure 5.4, was used to identify hydrochemical components established by the values of major ion concentrations obtained in groundwater samples from Valea Călugărească.

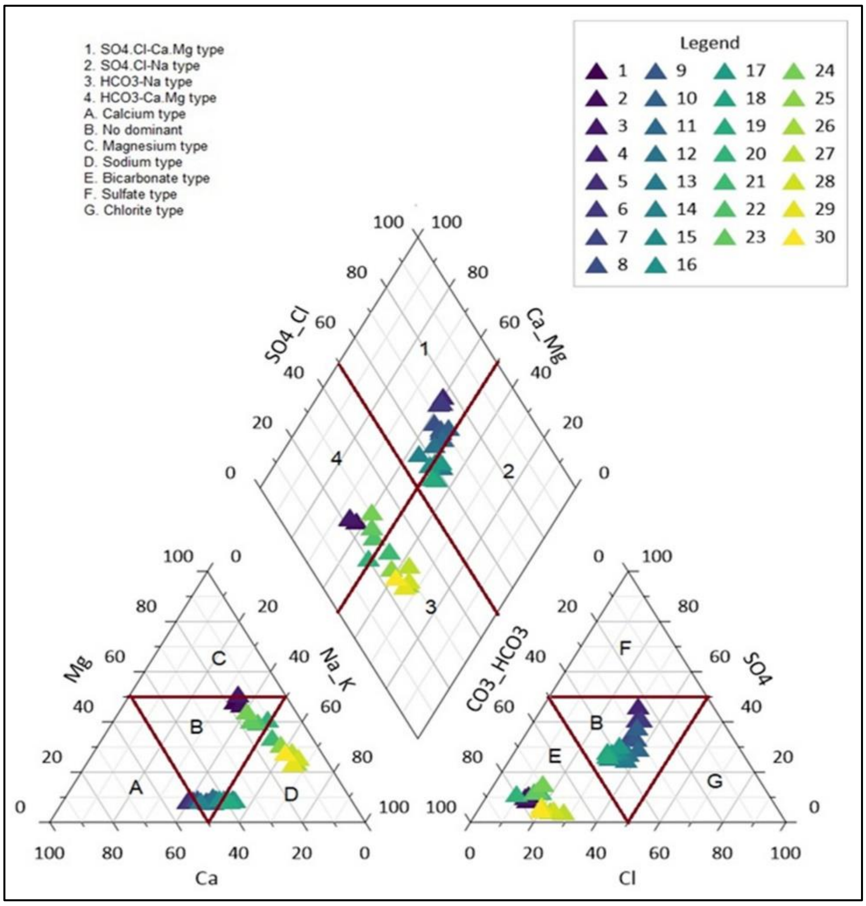

Fig. 5.4. Identification of hydrochemical components established by major ion concentration values in groundwater samples from Valea Călugărească using the Piper diagram.

The interpretation of the Piper diagram showed that 47% of the groundwater samples analyzed fell into the water type with a mixed composition, 20% presented the water type with a dominant composition HCO_3^- - $Ca^{2+}.Mg^{2+}$, 23% of the analyzed water samples were of type HCO_3^- - Na^+, compounds of type $SO_4^{2-}.Cl$ - Na^+ being present in only 10% of the analyzed waters. Of the water samples analyzed, 43% had Na+ as the majority ion. Bicarbonates had a major presence in 47% of water samples, and 53% of groundwater samples showed a mixed type. Analysis of the Piper diagram indicated the existence of increased bicarbonate concentrations. The dominance of these ions can be explained in groundwater following the natural processes of evaporation and precipitation present in the alkaline-earth alluvial nature of soils in the studied region. Gibbs diagrams were generated using values of ionic concentrations in the composition of the analyzed groundwater to identify existing natural processes that can cause changes in the composition of the aquifer.

The interpretation of the Gibbs diagrams indicated the influence of evaporation processes on the ionic composition of groundwater in the Călugărească Valley region which causes increased salinity by the concentration of soluble chemical constituents. The phenomenon of evaporating groundwater through soil pores results in the loss of a certain amount of this water, thereby affecting the chemical composition of groundwater.

For the identification of potentially polluting natural sources of the soil-ground water system that may cause a change in the quality of groundwater in the analyzed region, graphs of the relations between ions present in the composition of water have been drawn up. The natural processes generated by the reactions existing in the soil – groundwater system that can be considered a potential source of pollution are presented in Figure 5.6.

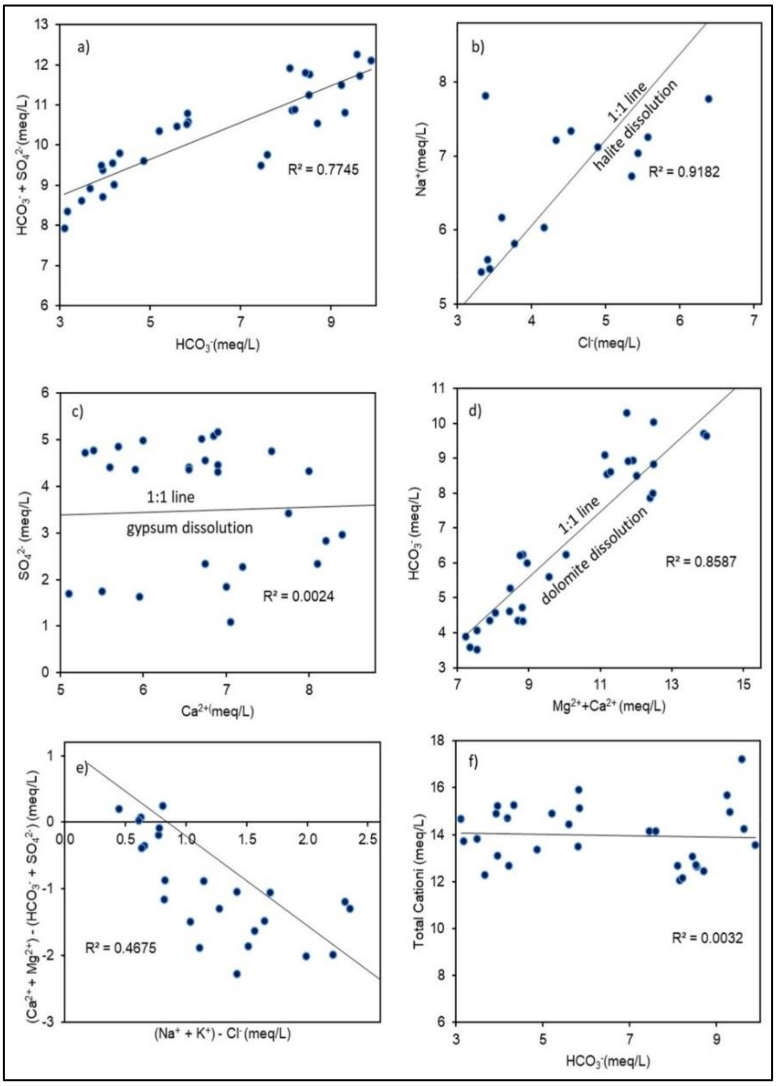

Fig. 5.6. Natural processes generated by reactions existing in the soil-groundwater system indicated by relationships between ionic compounds: a) (HCO_3^- + SO_4^{2-}) - HCO_3^-; b) Cl^-- Na^+; c) Ca^{2+} - SO_4^{2-}; d) (Mg^{2+} + Ca^{2+})- HCO3-; e) (Ca^{2+} + Mg^{2+}) – (HCO_3^- + SO_4^{2-}) versus (Na^+ + K^+) – Cl^-,
f) Cationi totali - HCO_3^-

From the interpretation of the graphs of ionic relationships between the concentrations of major ions in the composition of the analyzed groundwater, the following considerations emerged:

- ionic relation (HCO_3^- + SO_4^{2-})/ HCO_3^- shown in Figure 5.6a had a strong correlation coefficient with an $R^2 = 0.7745$, indicating the presence of an important source of bicarbonate ions in the aquifer;

- ionic relationship graph Na^+/Cl^- shown in Figure 5.6.b showed a strong correlation with an $R^2 = 0.9182$. The strong correlation between Na^+ and Cl^- ions may provide indications of the hallite dissolution process (NaCl);

- ionic relation SO_4^{2-}/Ca (Figure 5.6c), was characterized by a value of R2 close to zero. Pyrite, FeS2 and gypsum, $CaSO_4$x2H2O, are the two main sources of sulfate in groundwater in the region affected by the presence of pyrite ash. The relationship between SO_4^{2-} and Ca^{2+} ions indicated that the main source of SO_4^{2-} ions in groundwater was leaching of this chemical compound from mining ash samples;

- ionic relation HCO_3^-/(Mg^{2+} + Ca^{2+}) of Figure 5.6d showed a strong correlation R2 = 0.8587, indicating as the source of ion concentrations of Mg^{2+} the existence of a dolomite dissolution process;

- diagram representing the ion relation (Ca^{2+} + Mg^{2+}) + (HCO_3^- + SO_4^{2-})/(Na^+ + K^+)-Cl^-, was shown in Figure 5.6.e. Thus (Na^+ + K^+) - Cl^- represented the concentration of Na^+ and K^+ replaced by dissolved sodium chloride, while (Ca^{2+} + Mg^{2+}) - (HCO_3^-+ SO_4^{2-}) meant the amount of Ca^{2+} and Mg^{2+} accumulated as a result of dissolution of dolomite or gypsum. The ion exchange process is an important process that determines groundwater chemistry and constitutes a moderate source of ions in groundwater;

-The graph of the ionic relationship between total cations and bicarbonate anions (Figure 5.6.f) showed an R^2 value close to zero, suggesting that the geochemical processes influencing groundwater chemistry were dolomite dissolution and hallite precipitation. Cation exchange processes influence the hydrogeochemical evolution of groundwater.

5.6. GEOCHEMICAL ANALYSIS OF GROUNDWATER IN THE AREA USING VALEA CĂLUGĂREASCA SATURATION INDEX

The study of SI indices indicated the presence of processes of supersaturation with carbonate and sulfate anions, determined mainly by the dissolution of aragonite, calcite, dolomite and gypsum rocks. Negative values of the SI index for halites, ranging from -5.26 to -3.4, indicated that salt accumulation can occur from NaCl dissolution processes, a process also confirmed from ionic relationship graphs. The dissolution of gypsum plays a considerable role in the saturation state for calcite and dolomite, where the saturation state indicates the direction of the precipitation process of calcite and dolomite minerals, as well as the dissolution of gypsum.

5.7. EVALUAREA CALITĂȚII APELOR SUBTERANE DIN VALEA CĂLUGĂREASCĂ PENTRU IRIGAȚII ȘI CONSUM

The evaluation of groundwater quality in Valea Călugăreasca for human consumption was performed using TDS concentration values. The groundwater quality indicators %Na, SAR and CSR were used to assess the analysed water for irrigation, the calculation formulas being presented in Chapter 2. The values of groundwater quality indicators in Valea Călugăreasca are presented in Table 5.4.

Table 5.4. Values of quality indicators TDS, %Na, SAR și RSC groundwater from Valea Călugărească

Groundwater quality indicators	Classification	Domaine of indicators	%, from 30 groundwater samples analyzed	Sampling point
TDS, mg/L (drinking water)	Good	300 - 600	3	14
	Acceptable	600 - 900	87	1-13,15-19, 23-30
	Poor	900 - 1200	10	20,21,22
%Na (water for irrigation)	Excellent	0 – 20	100	1-30
	Good	20 – 40	-	-
	Permissible	40 - 60	-	-
	Acceptable	60 - 80	-	-
SAR, meq/L (water for irrigation)	Excellent	0 – 10	100	1-30
RSC, meq/L (water for irrigation)	Good	< 1.25	3	26
	Acceptable	1.25 – 2.5	97	1-25, 27-30

The interpretation of the results of this study indicated that out of the total 30 groundwater samples analyzed between 97% - 100% were suitable for use in agriculture for irrigation, the Evaluation of groundwater quality for human consumption indicated that only 3% of all analyzed water samples have a good quality of groundwater samples and 87% of all water samples have an acceptable quality and can be recommended for consumption. The samples taken under points 20, 21 and 22 were of poor quality and not recommended for human consumption.

5.8. PARTIAL CONCLUSIONS

In this chapter of the doctoral thesis, an evaluation of the groundwater quality in Valea Călugărească was carried out. This study included characterization of the composition of the aquifer as well as identification of sources of anthropogenic and natural pollution impacting groundwater quality in this region. The mineralogy of these groundwaters and their classification for use for human consumption or irrigation was assessed.

The results obtained indicated the existence of anthropogenic pollution on groundwater caused by the presence of pyrite ash dumps in the Valea Călugăreasca region. In groundwater samples analyzed from the area of these abandoned dumps, increased concentrations of sulfates and chlorides were found. In groundwater in agricultural areas treated with an excess of fertilisers, nitrate concentrations exceeded the permissible limits. Natural sources with potential for groundwater pollution included evaporation processes in the soil-groundwater system, their mineralogy being determined by the dissolution of gypsum and the precipitation of calcite and dolomite minerals.

CHAPTER 6

MODELS FOR PREDICTION OF ARSENIC AND CADMIUM CONCENTRATIONS IN PLANTS DETERMINED BY METAL MOBILITY IN THE SOIL SYSTEM - SOLUTION

The mobility of a pollutant in the soil corresponds to its ability to dissolve in soil pores' water and to be transported through processes of advection and diffusion through soil environment. Metals can be transported into the soil under various chemical species, including as free metal ions (hydrated ions), in the form of inorganic and organic complexes that can be absorbed. Metal concentrations are generally expressed in the scientific literature and in national legislation as total values. Therefore, it is necessary to develop simple statistical methods to predict the concentrations of “biodisponible” metal for plants.

For this purpose, we conducted a detailed study on the mobility of arsenic and cadmium in the soil system – extraction solution using Kd distribution coefficients of these metals, taking into account soil properties. The extraction capacity of these elements was established in contaminated soil samples using the laboratory batch method. Models for prediction of the concentrations of Ace and Cd accumulated in the plant Sinapis alba (White Mustard) were developed which included values of soil characteristics and representative values for moving metal fractions [6.1].

6.1. MATERIALS AND METHODS USED

6.1.1. Preparation of soil samples and extraction solutions

In order to understand the mobility and biodisponibility of metals, an experimental study was conducted on the extractibility of solutions in soil samples contaminated with As and Cd by the laboratory batch method.

A larger amount (about 2 kg) of uncontaminated vegetable soil from 2 different areas were collected at a depth of 0-30 cm, dried at room temperature and passed through a 2 mm sieve. To provide the plants with the necessary nutrients for rapid growth, the soil was mixed in a quantitative ratio of 1: 3, with a universal soil type amendment provided by the manufacturer Bănățene Services SRL. Its composition included a mixture of peat from medium to intense decomposing mud, wood fibers, green compost, tree bark humus, NPK fertilizer and marsh. The universal soil was mixed with soil1 (identified as the S6 witness soil in Table 4.2) taken from the established as uncontaminated area of the Valea Călugărească area and with agricultural soil from the Giulești area, soil2 which was harvested from a depth of 0-50 cm from a garden area with grass type vegetation.

The soil's characteristic physico-chemical parameters were analyzed before contamination with Ace and Cd. The method of contamination of soil samples consisted of spraying with solutions of different concentrations and combined metal in a repetitive thin layer, calculated to the required amount of ground. Soil contamination was performed with six different concentrations of metals resulting in six soils:

- soil contaminated with a concentration of Cd - 2 mg/kg, S1;
- soil contaminated with a concentration of Cd - 5 mg/kg, S2;
- soil contaminated with a concentration of As - 10 mg/kg, S3;

- soil contaminated with a concentration of As - 25 mg/kg, S4;
- soil contaminated with a concentration of As - 15 mg/kg and with a concentration of Cd - 3 mg/kg, S5;
- soil contaminated with a concentration of As - 15 mg/kg and with a concentration of Cd - 3 mg/kg, S5 and a concentration of Ni – 10 mg/kg, S6.

The concentration of Ni was added in to simulate a combined contamination process and the influence of another pollutant element presence on AS and Cd mobility. The mobility of nickel in soil was not analyzed in the present study.

For the production of metal-enriched mixtures, the amount of metal required for addition was calculated based on the values of the initial metal concentrations in the soil, soil mass and the value of the final metal concentration. Metal solutions/metal mix are sprayed on the thin layer of soil. Similarly, other layers sprayed with solutions of contaminants were added until the soil and solution were exhausted. After a stabilization period of 10 days, the concentrations of As and Cd were determined. The cationic exchange capacity (CEC) was empirically estimated on the basis of the cation content in the extraction solutions and the Kd distribution coefficient was calculated based on the ratio between the amount of metal ion adsorbed on the soil mass and the quantity of metallic ion left in the solution at balance. The bioaccumulation coefficient (BAC) was calculated on the basis of the ratio between the concentration of Ace and Cd in plant parts (roots, stems, leaves, flowers and leaves) and the total concentrations of these elements in contaminated soils. The calculation formulas for CEC, Kd and BAC can be found in Chapter 2.

Four samples taken from each soil were used to assess the extraction capacity of four solutions (DI – deionized water, $CaCl_2$, DTPA și EDTA). Four other samples were used to germinate *Sinapis alba* plant.

6.2. CHARACTERISATION OF SOILS BEFORE AND AFTER CONTAMINATION

The most significant indicators were determined for determining the chemical composition of soils with amendment. The values of the parameters determined in the two soil samples Sol1 and Sol2 analysed before contamination varied between maximum and minimum values being calculated the averages of these values.

Soils Sol1 and Sol2 showed similar characteristics, except for SOC and conductivity values. The SOC had in Sol1 averages of 0.92% and in Sol2 an average of 6.93%. The conductivity showed an average value of 80,7 µS/cm measured at 25oC in Sol1 and 115 µs/cm in Sol2. The pH averages were 7.12 in Sol1 and 6.93 in Sol2. Concentrations of Ace and Cd showed mean values of 0.35 mgAs/kg in Sol1 and 0.56 mgAs / kg in Sol2, respectively 0.02 mgCd/kg for Sol1 as well as 0.07 mg Cd / Kg in Sol2.

The values of the concentrations of Ace and Cd determined by the analysis of the samples S1-S6, contaminated according to the procedure previously presented after the stage of artificial contamination of soils Sol1 and Sol2 reflect the correct execution of the procedure for enriching an uncontaminated soil with different concentration of these two elements.

Table 6.2. As and Cd concentration values in S1-S6 contaminated soils

Soil samples	As Mean value (n=12) ± SD	Cd Mean value (n=12) ± SD
S1 (Sol1 cu Cd 2 mg/kg)	0.28 ± 0.02	2.32 ± 0.13
S2 (Sol1 cu Cd 5 mg/kg)	0.51 ± 0.04	4.47 ± 0.52
S3 (Sol1 cu As 10 mg/kg)	10.6 ± 1.21	0.12 ± 0.06
S4 (Sol1 cu As 25 mg/kg)	26.1 ± 1.85	0.09 ± 0.04
S5 (Sol1 cu As 15 mg/kg and Cd 2 mg/kg)	15.1± 1.65	2.12 ± 0.07
S6 (Sol2 cu As 15 mg/kg, Cd 3 mg/kg, Ni 10 mg/kg)	16.9 ± 1.37	2.97 ± 0.32

6.3. ESTABLISHMENT OF EXTRACTION CAPACITY OF SOLUTIONS USED FOR THE DETERMINATION OF MOBILE As AND Cd FRACTIONS FROM ARTIFICIALLY CONTAMINATED SOILS

For the purpose of determining mobile fractions of As and Cd from contaminated soils, the extraction capacity of four solutions was established. The extraction solutions of As and Cd from contaminated soil samples S1-S6 (Table 6.2) were as follows:

- Solution M-DI (distilled water) - ratio 1:10 soil: extraction solution (M);
- Solution M1-$CaCl_2$ - 0,002 mol/L Diethylenetriaminepentacetic acid DTPA, 0,01 mol/L calcium chloride; soil ratio: extraction solution = 1:5 (M1);
- Solution M2-DTPA - 0,01 mol/L calcium chloride, 0,1 mol/L triethanolamine, 0,005 mol/L DTPA, in sol ratio: extraction solution = 1:10 (M2);
- Solution M3-EDTA - 1 mol/L acetic acid, 0,01 mol/L tetrametric ethylenediamine disodium salt; soil ratio: extraction solution = 1:10 (M3).

From these solutions were determined the mobile fractions of As and Cd. Values of mobile fractions of Cd and As in extraction solutions M, M1,M2 and M3 for the five contaminated soils S1 to S5 are presented in Table 6.3.

Table 6.3. Values of mobile fractions of Cd and As in extraction solutions M, M1,M2 and M3 for contaminated soils S1 to S6

Mobile fractions	S1	S2	S3	S4	S5	S6
CdM	0.07 ± 0.003	0.16 ± 0.005	-	-	0.05 ± 0.002	0.79 ± 0.06
CdM1	0.38 ± 0.01	0.64 ± 0.02	-	-	**0.25 ± 0.02**	**0.30 ± 0.03**
CdM2	0.21 ± 0.01	0.45 ± 0.02	-	-	0.19 ± 0.01	0.28 ± 0.02
CdM3	**2.23 ± 0.07**	**3.88 ± 0.12**	-	-	0.14 ± 0.12	0.79 ± 0.06
AsM	-	-	0.15 ± 0.02	0.42 ± 0.04	0.20 ± 0.01	0.50 ± 0.05
AsM1	-	-	1.20 ± 0.24	1.24 ± 0.01	**0.99 ± 0.04**	**0.18 ± 0.02**
AsM2	-	-	0.36 ± 0.03	0.47 ± 0.02	0.33 ± 0.02	0.20 ± 0.02
AsM3	-	-	**2.43 ± 0.14**	**3.56 ± 0.13**	0.23 ± 0.02	0.50 ± 0.05

The highest values of mobile fractions were obtained for Cd in solution M3 for soils contaminated with a concentration of Cd 2 mg/kg (S1) and Cd 5 mg/kg (S2) and in solution M1 were found the highest values of mobile fractions for soils S5 and S6.

For As, mobile fractions showed the highest values in solution M3 for contaminated soil with a concentration of As 10 mg/kg (S3) and As 25 mg/kg (S4), with solution M1 having the highest mobile fractions in soils S5 and S6.

The mobile metal fractions were also evaluated by the distribution coefficient (Kd), which shows the ability of the soil to retain the metal in the solid phase or release it into the extraction solution. Table 6.4 presents values of the distribution coefficients KdCd and KdAs in extraction solutions M, M1,M2 and M3 for the five contaminated soils S1 to S56.

Table 6.4. Values of distribution coefficients KdCd and KdAs in extraction solutions M, M1,M2 and M3 for contaminated soils S1 to S6

Values of Kd	S1	S2	S3	S4	S5	S6
KdCd-M	32.2 ± 3.28	28.7 ± 1.20	-	-	42.8 ± 1.66	29.5 ± 1.61
KdCd-M1	6.67 ± 0.49	7.06 ± 0.34	-	-	8.65 ± 0.59	3.77 ± 0.24
KdCd-M2	11.3 ± 1.15	10.1 ± 0.42	-	-	11.0 ± 0.47	10.0 ± 0.52
KdCd-M3	1.04 ± 0.07	1.16 ± 0.07	-	-	15.0 ± 0.58	10.3 ± 0.56
KdAs-M	-	-	68.9 ± 5.22	62.0 ± 4.70	77.6 ± 4.73	101 ± 5.92
KdAs-M1	-	-	12.8 ± 2.01	21.1 ± 0.81	15.5 ± 0.54	21.3 ± 0.67
KdAs-M2	-	-	41.3 ± 3.13	55.4 ± 1.70	46.5 ± 2.84	60.7 ± 3.55
KdAs-M3	-	-	6.15 ± 0.41	7.32 ± 0.39	65.6 ± 5.09	52.4 ± 1.26

Four types of extractive solutions (M1, M2 and M3) and deionised water (M-DI) were used to determine the concentrations of As and Cd extracted from soils contaminated with different concentrations of As, Cd and Ni. The distribution coefficient of arsenic KdAs, calculated for soils contaminated with different concentrations of As, showed the highest values in distilled water of 68,9 L/kg (S3), 62,0 L/kg(S4), 77,6 L/kg(S5) and 101 L/kg(S6). KdCd calculated for soils contaminated with different concentrations of Cd had the highest values in distilled water of 32.2 L/kg (S1), 28.7 L/kg(S2), 42.8 L/kg(S5) and 29.5 L/kg(S6).

The interpretation of the results obtained showed the following decreasing order of extraction capacity of As and Cd in the analysed extraction solutions from artificially contaminated soils:

For arsenic extraction the order was:

- soil S3: M3-EDTA > M1-$CaCl_2$ > M2-DTPA > M-DI;
- soil S4: M3-EDTA > M1-$CaCl_2$ > M2-DTPA > M-DI;
- soil S5: M1-$CaCl_2$ > M2-DTPA > M3-EDTA > M-DI.
- soil S6: M1-$CaCl_2$ > M2-DTPA > M3-EDTA > M-DI.

For cadmium extraction the order was:

- soil S1: M3-EDTA > M1-$CaCl_2$ > M2-DTPA > M-DI;
- soil S2: M3-EDTA > M1-$CaCl_2$ > M2-DTPA > M-DI;
- soil S5: M1-$CaCl_2$ > M2-DTPA > M3-EDTA > M-DI.
- soil S6: M1-CaCl2 > M2-DTPA > M3-EDTA > M-DI.

The experimental results established that solution M1-CaCl2 has the highest extraction capacity of Cd and As from soils contaminated singularly with these elements (S1,S2,S3 and S4). The M3-EDTA solution showed the highest extraction capacity of Cd and As from combined contaminated soils (S5 and S6). The method of extracting As and Cd in DI deionised water was not suitable for determining extractable metal quantities from soils with high contamination levels. The results obtained in the analysis of As and Cd concentrations in solutions using water as extractant from contaminated soils were eliminated from this study due to the very low water extraction capacity indicated by Kd values.

6.4. ASSESSMENT OF THE INFLUENCE OF FACTORS ON MOBILITY As AND Cd FROM CONTAMINATED SOILS USING PCA AND RSM ANALYSIS

Due to complex relationships regarding metal distribution in soil and extraction solutions, arsenic and cadmium mobility can be influenced by various factors such as pH, cation exchange capacity and soil organic carbon.

In the three extraction solutions (M1, M2 and M3) the pH values were determined. Solution M1 (CaCl2) showed a very low pH value of 2,6 due to the extraction procedure requiring adjustment of the pH of the solution to this value, the mean pH values of solution M2 being 7,32 and of solution M3 7,1.

CEC has been used as an indicator of nutrient retention capacity in the soil. Soil organic carbon SOC is a natural or anthropogenic dynamic component, due to the decomposition of soil organic matter, the impact it has on it being significantly positive or negative. Table 6.6. show estimated cation-exchange capacity values for extraction solutions and organic carbon values in contaminated soil samples. The estimation of cation exchange capacity was made as described in Chapter 2.

Table 6.6. Estimated values of cation exchange capacity (CEC) and soil organic carbon (SOC) in studied soils S1 to S6

Soil samples	CEC_M1, meq/100g	CEC_M2, meq/100g	CEC_M3, meq/100g
S1	27.9 ± 1.52	21.7 ± 1.98	38.2 ± 2.36
S2	34.7 ± 2.09	22.0 ± 0.85	35.9 ± 3.52
S3	29.0 ± 2.56	22.4 ± 1.66	38.5 ± 2.38
S4	27.7 ± 1.62	22.4 ± 0.99	37.7 ± 1.26
S5	30.9 ± 2.21	31.7 ± 2.12	39.8 ± 2.29
S6	33.5 ± 1.62	28.1 ± 1.32	41.2 ± 3.06

Mean SOC values for the two soils s1(Sol1) and s2(Sol2) were used to assess the influence of this factor on the mobility of As and Cd in metal-contaminated soils, which can be found in Table 6.1 Due to its stability over time, SOC can be an important factor influencing the effective sorption/desorption processes of different toxic metals in the soil. Mean CEC values ranging from 27,7 to 34,7 meq/100g in extraction solution M1, between 21,7 and 31,7 meq/100g in extraction solution M2 and between 35,9 and 41,2 meq/100g in extraction solution M3 indicated the presence of clay minerals in the soils studied.

The assessment of the influence of factors on As and Cd mobility in metal-contaminated soils was carried out using the PCA statistical method and the RSM surface response method, presented in Chapter 2.

In order to understand the complex relationship between the characteristic parameters of the analyzed soils and the distribution of As and Cd concentrations evaluated using Kd in the 3 extraction solutions, the RSM response surface method and the analysis of the main PCA components were used. RSM is a chemometric technique that reflects how much each variable (pH, SOC, CEC, total metal concentration in soil, Kd) contributes to the evolution of the mobility process of As and Cd from contaminated soils and helps interpret the relationship between these variables. The RSM method was used to evaluate how the variables pH, SOC, CEC and total metal concentration in soil affect Kd,. The response surface of KdAs and KdCd as well as contour diagrams were generated based on experimental results.

Since the RSM method uses only 3 variables and the experiment included 5 variables, a PCA analysis was required to determine two of the components with the greatest influence on the distribution of As and Cd concentrations in the analysed extraction solutions, represented by KdAs and KdCd values.

The values of the main components PC1 and PC2 generated by PCA analysis after Varimax rotation for the solution with the highest extraction capacity of As, M3 - EDTA from soil S3 are given in Table 6.7. The highest values (positive or negative) of the coefficients of the variables included in the analysis (pH, CEC, AsS3) were selected to establish the factor with the greatest influence on the mobility of this soil contaminant, respectively on the KdAs values. In solution M3, the Ace mobility in S3 soil was negatively influenced by variations in CEC (PC1_M1: -0.539) and SOC (PC2_M3: -0.720).

Figure 6.1 shows the 3D diagram and contour diagram of the surface response of the KdAs distribution coefficient in the previously established M3 extraction solution with the highest extraction capacity of the Ace from the soil contaminated with 10 mg/kg As (S3). Contour diagrams are useful for exploring potential relationships between only three variables, showing a three-dimensional relationship in two dimensions, the values of the response being represented by contour lines. For example, in Figure 6.1, the darker red regions identify the highest Kd values, and the dark blue regions the lowest KD values. The contour levels reveal a red area between the CEC values: 36.5 ÷ 41 meq/100g and the SOC value: 1.1 ÷ 1.3% in which Kd As shows increased values, representing a decrease in Ax mobility in the S3 soil.

The 3D surface graph of the KdAs response shows in this red area a maximum KdAS peak of 6.7 L/kg indicating the retention of arsenic by soil particles and, by default, a decrease in mobility in the M3 extraction solution. Also, the blue color area determined by CEC values lower than 36,5 meq/100g and SOC values: 1.2 ÷ 1.3% where Kd As shows low values, represents the range of values of the two factors in which the mobility of the As in the soil contaminated with a concentration of this pollutant of 10mg/kg (S3) is positively influenced. 3D surface graphs can provide a clearer concept of the response surface than contour graphs, the maximum and minimum peaks representing the interactions between the variables that influence the efficiency of the Axis mobility in the M3 - EDTA solution determined by the complexity of this process.

Table 6.7. PC1 and PC2 values for As extraction solution (M3 - EDTA) in soil S3

Soil	Extraction solution	PC1 and PC2 values after Varimax rotation
S3	M3	PC1 = 0.572 pH_M3 - 0.309 SOC_s1 **– 0.539 CEC_M3S3** – 0.102 AsS3 – 0.525 Kd_M3S3
		PC2 = 0.087 pH_M3 **- 0.720 SOC_s1** + 0.069 CEC_M3S3 – 0.432 AsS3 **+ 0.531 Kd_M3S3**

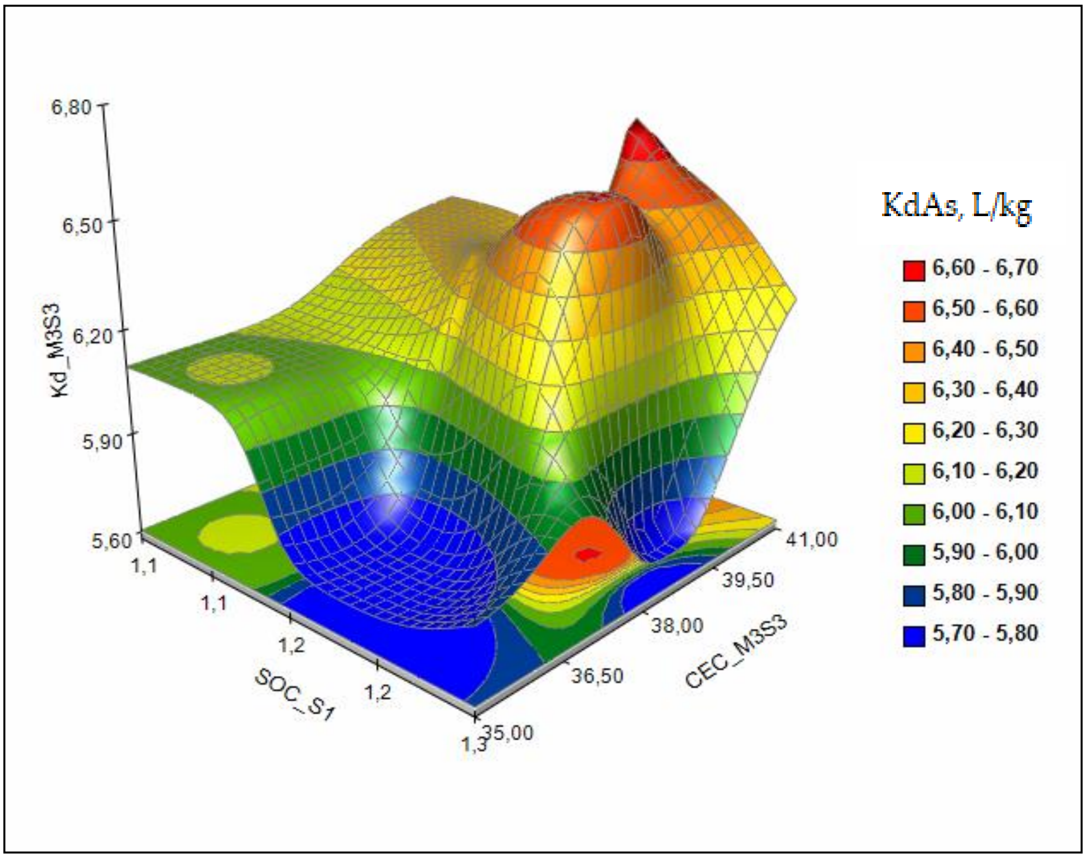

Fig. 6.1. KdAs response surface area and contour diagrams generated by RSM analysis of the evolution of As mobility in M3-EDTA extraction solution from soil contaminated with 10 mg/kg As (S3).

Similarly, the influence of pH, CEC and SOC factors on the KdAs values determined in solutions with the highest extraction capacity of Ace from soils contaminated with different single or mixed concentrations of this toxic element can be assessed.

The values of the main components generated by the PCA analysis after Varimax rotation for the solution with the highest extraction capacity of Ace, M3 - EDTA from soil S4 are presented in Table 6.8. In solution M3, the mobility of the Axis in soil S4 was negatively influenced by the variation of the total Axis concentration in the soil (PC1_M1: – 0.618) and the CEC value determined in the M3 extraction solution of the Ace from the Soil S4, CEC_M3S4 (PC2_M3: – 0.733).

The increase in the level of contamination in soil S4 slightly stabilizes the course of the desorption process, but at concentrations of Ace greater than 26.25 mg/kg in the soil, the metal is retained in the solid fraction.

Increasing the axis concentration in the soil decreases the efficiency of the metal desorption process in the M1 extraction solution, the Axis mobility in the contaminated soil S5. The process is favoured by the low pH value in the solutions M1, pH_M1 (PC1_M1:+0,598) and the value of the total concentration of Ace in the soil, AsS5 (PC2_ M1: - 0,662).

The presence of a mixed contamination with As and Cd reduces the mobility of arsenic in the M1 solution, a process indicated by the increased values of KdAs determined in this extraction solution.

The presence of a mixed concentration of metals in the soil S6 has a negative influence on the extraction of As in the solution M1. SOC was the factor that negatively influenced the extraction of Ace from soil S6, SOC_S6 (PC1_M1: -0,581), the low values of pH favouring the mobility of Ace in solution M1, pH_M1(PC2_M 1:+0,634).

The study of the extraction of As from contaminated soils with different concentrations of As, Cd and Ni, indicated the influence of pH factors CEC on the mobility of this toxic element in the solutions identified as the best extractors of Ace, M3-EDTA from soils S3 and S4 and Cd, and M1-CaCl2 from soil S5 and S6, respectively.

Similarly, the influence of the factors indicated above on Cd mobility in solutions with the highest extraction capacity from soils contaminated with different concentrations of As, Cd and Ni was assessed.

The results obtained in the case of soil samples S1 contaminated with Cd, show that the mobility of this element in the soil solution M3 was negatively influenced by the value of the metal concentration in soil S1, CdS1 (PC1_M2: -0,513) and the CEC value in solution M3, CEC_M3S1(PC2_M3: -0,892).

The contour chart shows a blue area between CEC_M3S4 values: 38÷ 42 meq/100g and CdS1: 2.1 ÷ 2,23 mg/kg in which KdCd shows low values, and represents the range of values of the two factors in which the mobility of Cd in soil S1 is positively influenced similarly to that of the Axis in soils contaminated with single metal concentrations.

The process of extraction of Cd from S2 soil into M1 solution is positively influenced by the pH value of the M3 extraction solution of this metal from soil S2, CdS2 (PC1_M3: +0,577) and the SOC value in soil, SOC_s1 (PC2_M3: +0,766).

The increase of the concentration of Cd to 5 mg/kg in the soil S2 had the effect of stabilizing over time the mobility process of the metal in the solution M3-EDTA in S2 soil to a SOC value of 1.2% and pH of 7.2, their changes may cause the metal to be retained by the particles of S2.

The results obtained in the case of soil samples S5 contaminated with Cd, the results show that the mobility of this element in the soil solution M1-CaCl2 was negatively influenced by the value of the metal concentration in soil S5, CdS5 (PC2_M1: -0,544) and the pH value in the solution M1, pH_M1 (PC2/M1:-0,633).

The data obtained from the PCA analysis show a strong influence of pH in solution M1, pH_M1 (PC1_M1: -0,972) and empirically determined CEC in soil extraction solution Cd S6, CEC_ M1S6 (PC2_M2: -0,958).

The mobility of Cd in the M1-CaCl2 extraction solution from S5 soil indicated a slowdown of this process due to complex interactions between factors that influenced the extraction of this element from the soil contaminated with a mixed concentration of toxic metals.

The RSM analysis, supplemented with PCA applied for the purpose of assessing the influence of pH, SOC and CEC of the two solutions of extraction M1-CaCl2 and M3-EDTA of As and Cd from contaminated soils with single or mixed concentrations of As, Cd and Ni, indicated a decrease in the mobility of these two metals proportional to the increase in contaminant concentrations in the soils analysed. The process of extraction of Cd with M1-$CaCl_2$ solution from soils contaminated with mixed concentrations of metals showed a reduction in the evolution over time of the mobility of this element from these analysed soils.

6.5. EVALUATION OF ARSENIC AND CADMIUM ACCUMULATION POTENTIAL IN *SINAPIS ALBA* PLANT FROM ARTIFICIALLY CONTAMINATED SOILS

To assess the potential for arsenic and cadmium accumulation in *Sinapis alba*, the bioaccumulation coefficient (BAC) was calculated using concentration values of these chemical elements in parts of Sinapis alba. The values of As and Cd concentrations determined in parts of Sinapis alba cultivated in metal-contaminated soil (As, Cd and Ni) are presented in Table 6.15.

Table 6.15. Valorile concentrațiilor de As și Cd determinate în organele plantei Sinapis alba crescute în soluri contaminate cu metale (As, Cd și Ni)

Plant (*Sinapis alba*)	**AsS5 mg/kg**	**AsS6 mg/kg**	**CdS5 mg/kg**	**CdS6 mg/kg**
Root	**2.56 ± 0.12**	**9.02 ± 0.12**	0.44 ± 0.02	0.41 ± 0.05
Stem	0.75 ± 0.04	0.75 ± 0.04	0.29 ± 0.01	0.36 ± 0.04
Leaves	0.76 ± 0.05	2.18 ± 0.09	**1.46 ± 0.10**	**2.52 ± 0.10**
Flowers	0.75 ± 0.10	0.73 ± 0.09	0.11 ± 0.01	0.15 ± 0.02
Pods	2.32 ± 0.11	0.74 ± 0.02	0.18 ± 0.01	0.12 ± 0.01
Seeds	0.75 ± 0.06	0.74 ± 0.03	0.12 ± 0.02	0.10 ± 0.01
Plant	7.85 ± 0.25	14.2 ± 0.21	2.60 ± 0.14	3.66 ± 0.26

The interpretation of the results obtained from the analyzed concentrations of As and Cd in the root, stem, leaves, flowers, pods and seeds of plants grown in soils S5 and S6, contaminated with concentrations of As, Cd and Ni indicated the accumulation of As in the root (2.56 ± 0.12 mg/kg in S5 and 9.02 ± 0.12 mg/kg in S6) and the accumulation of Cd in leaves (1.46 ± 0.10 mg/kg in S5 and 2.52 ± 0.10 in S6). The total concentration of metal in the plant was obtained by summing the concentrations in the plant organs.

BAC shows the ability of plants to retain toxic metals. The results obtained from the analysis of As and Cd concentrations in parts of Sinapis alba grown under glass on soils contaminated with different metal concentrations (As, Cd and Ni), as well as the concentration of metals accumulated in the plant, are presented in Table 6.15.

The bioaccumulation coefficient (BAC) was determined as the ratio of the concentration of metal in plant organs to the concentration of metal in soil, the calculation formula being presented in Chapter 2.

The values of the bioaccumulation coefficient of As, BAC-As and the bioaccumulation coefficient of Cd, BAC-Cd determined in the root (R), stem (St), leaves (L), flowers (F), pods (P) and seeds (Se) of Sinapis alba grown on soils contaminated with mixed concentrations of As, Cd and Ni (S5 and S6), as well as the pattern of metal accumulation in the plant are shown in Table 6.16.

Table 6.16. BAC-As and BAC-Cd values determined in parts of *Sinapis alba* plant grown in soils contaminated with As, Cd and Ni and pattern of accumulation of As and Cd in this plant

Plant (*Sinapis alba)*	BAC-AsS5	BAC-AsS6	BAC-CdS5	BAC-CdS6
Root (R)	0.166 ± 0.006	0.532 ± 0.015	0.174 ± 0.003	0.132 ± 0.006
Stem (St)	0.048 ± 0.003	0.045 ± 0.003	0.126 ± 0.001	0.116 ± 0.005
Leaves (L)	0.049 ± 0.002	0.130 ± 0.001	0.671 ± 0.032	0.813 ± 0.024
Flowers(F)	0.047 ± 0.001	0.045 ± 0.003	0.048 ± 0.003	0.048 ± 0.003
Pods (P)	0.151 ± 0.006	0.044 ± 0.001	0.081 ± 0.005	0.039 ± 0.004
Seeds (Se)	0.048 ± 0.002	0.044 ± 0.002	0.052 ± 0.004	0.032 ± 0.002
Accumulation pattern	R > P > L > St, Se > F	R > L > St, F > P, Se	L > R > St > P > Se > F	L > R > St > F > P > Se

The results obtained from the evaluation of bioaccumulation coefficients BAC-As and Cd (Table 6.16) showed values between 0.1 and 1 in the two soils S5 and S6. The highest average values of BAC-As (0.166 for soil S5 and 0.851 for S6) showed a moderate potential for accumulation of Ace in the root of Sinapis alba. The highest average BAC-Cd values obtained (0,567 for soil S5 and 0,813 for S6 indicated a moderate potential for phytoaccumulation of Cd in the leaves of Sinapis alba).

The accumulation pattern of the Ace and Cd metals in the plant parts followed the following descending order:

- for AsS5 - root > pods > leaves > stem, seeds > flowers;
- for ASS6 - root > leaves, stem > flower, pods, seed;
- for CdS5 - leaves, root > stem > pods > seeds > flowers;
- for CDS6 – leaves > root > stem > flower > pods > seeds.

The results obtained in this study indicate the ability of the Sinapis alba plant to survive high concentrations of Ace and Cd as well as the potential to be used in a phytoremediation strategy.

6.6. USEFUL PREDICTIVE MODELS FOR EVALUATING ARSENIC AND CADMIUM CONCENTRATION IN *SINAPIS ALBA* USING Kd DISTRIBUTION COEFFICIENTS

The accumulation of metals in plants is related to chemical concentrations and fractions of metals in the soil. Understanding dissolved chemical elements and the availability of metals in soil is essential for soil management and choosing remediation methods. In this dispute, extractable fractions may be more cost-effective than total metal content as an indicator of metal bioconcentrations in plants. In this study, the mobile metal fraction, represented by the KdAs and KdCd values determined in solutions with the highest extraction capacity previously established, was used to predict As and Cd concentrations in the *Sinapis alba* plant.

6.6.1. Evaluation of the interdependence between variables used in the elaboration of multiple regression models for evaluation of As and Cd concentrations in the plant Sinapis alba using PCA analysis

The PCA analysis was applied to assess the interdependence of the variables used in the development of multiple regression models generated for the purpose of obtaining predictive values of the concentrations of As and Cd in the plant Sinapis alba. The purpose of this analysis was to statistically validate the linear correlation between KdAs and KdCd values, the values of the concentrations of As and Cd in parts of the plant Sinapis alba and the total metal content in the plant, which is the basis for the calculation of the multiple regression models used in this study.

PCA analysis was used for the values of the concentrations of As and Cd determined in soil contaminated with mixed concentration of these metals (solul S5).

Interpretation The results obtained from the PCA analysis, on the evaluation of the correlation of axis concentration values, showed that the first main component, PC1, included six variables (Kd_M1S5, Asplant_S5, Răd_ S5, Tulp_S 5, Fr_S5 and Pass_S5) that vary together. This shows the increase in the concentration of Ace (variable value of 0.933) in the whole plant proportional to the increase of the metal concentration in the stem (0,920), leaves (0,886), root (0,680), influenced by the small values of KdAs in the moving fraction (-0,715). PC2 correlated the variables Flo_S5 and Sem_S5. The results of the PCA analysis, applied for the purpose of evaluating the correlation of Cd concentration values, showed that the first main component, PC1, correlated six variables (Rad _S5, Tulp_S5, Flo_S, Pass_S5) that vary together. The second main component PC2 correlated three variables (Kd_M1S5, Asplant_S5, Răd_S5 and Leaves_S5). The PC2 component is strongly correlated with Asplant_S5 (correlation 0.931), the increase of this variable resulting in an increase in the concentration of Ace in the leaf (0.812) and increased values of KdCd in solution M1, Kd_M1S5 (0.763). The results obtained confirmed the interdependence relationship determined by the linear correlation between the variables proposed to be used in the development of predictive models of the concentrations of As and Cd in the plant *Sinapis alba*.

6.6.2. Models for prediction of concentrations of As and Cd in the plant Sinapis alba using values of the distribution coefficients KdAs and KdCd

Following statistical validation showing the linear correlation between KdAs/KdCd values and total As and Cd concentration values in Sinapis alba, multiple linear regression models were developed to predict the concentration of As and Cd accumulated from soil S5 in parts of this plant. The model was extended under the same conditions of statistical correlation for soil S6. The prediction model equations, the experimental and predictive mean values of the metal in the plant organelles as well as the values of the statistical parameters used in the validation process of the multiple linear regression model (aR2, DW, SW, RMSE) are presented in Table 6.18. for As (soil S5 and S6) and Table 6.19. for Cd where N is the number of observations (four plant samples/part of plant determined in three replicates) and k is the number of variables.

Table 6.18. Multiple regression model equations, experimental and predictive mean values of accumulated As concentration in Sinapis alba plant parts of soils S5 and S6 and values of model validation parameters (aR^2, DW, SW andRMSE)

Soil	Plant (*Sinapis alba*)	Predictive model equation*	aR^2	As_{exp}	As_{pred} ± SE	DW**	SW*	RMSE
S5	Root_S5	= 0.37 *Asplant_S5 - 0.003 *Kd_M1S5*Asplant_S5	0.9985	2.56	2.54 ± 0.031	2.77	0.77	0.072
	Stem_S5	= 0.0007*Asplant_S5*Kd_M1S5*Asplant_S5	0.9974	0.78	0.766 ± 0.062	2.27	0.80	0.039
	Leaves_S5	= -0.071 * Asplant_S5 + 0.012 *Asplant_S5*Kd_M1S5	0.9967	0.75	0.761 ± 0.051	2.40	0.82	0.051
	Pods_S5	= -0.039* Kd_M1S5 + 0.479* Asplant_S5 - 0.0129 *(Asplant_S5)2	0.9912	2.32	2.317 ± 0.023	2.50	0.81	0.136
S6	Root_S6	= - 0.039* Kd_M1S6*Kd_M1S6 +0.088* Asplant_S6*Kd_M1S6	0.9989	9.03	9.06 ± 0.052	2.80	0.81	0.075
	Stem_S6	= 0.00012*Kd_M1S6*Asplant_S6*Kd_M1S6	0.9976	0.75	0.754 ± 0.005	2.37	0.86	0.099
	Leaves_S6	= -0.053 * Kd_M1S5 + 0.21 *Asplant_S6	0.9966	2.76	2.79 ± 0.084	2.49	0.88	0.051
	Pods_S6	= 0.0002*(Kd_M1S5*Asplant_S6*Asplant_S6)	0.9862	0.74	0.736 ± 0.006	2.88	0.88	0.028

*p-value < 0.05; **(N = 12; k = 2); SE – standard error.

Table 6.19. Equations of multiple regression model, experimental and predictive values of concentrations of Cd accumulated in leaves of Sinapis alba plant in soils S5 and S6 and values of model validation parameters (aR2, DW, SW and RMSE)

Sol	Plant (*Sinapis alba*)	**Ecuația modelului predictiv***	aR^2	Cd_{exp}	Cd_{pred} ± SE	DW**	SW*	RMSE
S5	Leaves_S5	= 0.16 * Kd_M1S5 + 0.21 *Cdplant_S5 - 0.014* Kd_M1S5* Cdplant_S5	0.9986	2.46	2.461 ± 0.012	2.29	0.86	0.093
S6	Leaves_S6	= 1.25 * Kd_M1S6 + 0.025* (Cdplant_S6)2 - 0.19 *Cdplant_S6 *Kd_M1S6	0.9987	2.72	2.685 ± 0.055	2.36	0.87	0.102

*p-value < 0.05; **(N = 12; k = 2); SE – standard error.

The aR^2 values obtained in the As concentration prediction models in Sinapis alba organs cultivated in S5 soil showed values ranging from 0.9912 to 0.9974, and in the Ace concentration forecasting models in S6 soil cultivated organs showed value ranging between 0.9862 and 0.9989. For the forecasting models of the Cd concentration in the leaves of the Sinapis alba plant cultivated in soil S5, the aR^2 values obtained showed values ranging from 0.9986 to 0.9987 and for the Forecasting model of the concentration of Cd in the foliage of the cultivated plant in soils S6.

Values of the Durbin Watson and Durbin-Watson tests were used as performance parameters for statistically validating multiple regression models generated from experimental data, the theoretical method applied being found in Chapter 2.

The Durbin Watson test values for a 5% significance level used for the analysis of serial autocorrelation in the multiple regression models generated for the KdAs and KdCd prediction (N = 12; k = 4) were between 1.85 and 2.66 and for the prediction of the concentration of Ace and Cd in the parts of Sinapis alba (N=12; k=2) were between 2.27 and 2.80. The results of the Durbin-Watson test indicate values greater than dU (critical d-values Durbin - Watson - 95%, dL-the lower limit value, dU-the upper limit value), so there is no autocorrelation between the residual values. Critical values for models generated without interception were dL = 0.397 and dU = 1.682 (N=12, k=4) and dL=0.674 and du = 2.268 (N = 12, k=2). The SW test results for verifying the normality of the data did not indicate non-normality values for the independent variables KdAs, KdCd, the concentration of As and Cd in the parts of *Sinapis alba* for a significance level of 5% (value $p < 0.05$). The square average error values, RMSE obtained in the prediction models indicated values between 0.152 and 0.524 for KdAs and between 0.148 and 0.643 for Kcd, values from 0.037 to 0.331 for the Axis concentration and values ranging from 0.092 to 0.103 for the Cd concentration in the parts of Sinapis alba. Low RMSE values indicated a good matching of the models to the original experimental data sets.

6.7. PARTIAL CONCLUSIONS

Chapter 6 of this thesis developed models for predicting the concentrations of arsenic and cadmium in the plant Sinapis alba determined by the mobility of these metals in the soil. The study presented in this chapter included a soil characterization before and after contamination, the establishment of the extraction capacity of the solutions used to determine the movable fractions of As and Cd in artificially polluted soils, and an assessment of factor influence on the mobility of these metals from contaminated soil samples using PCA and RSM analysis. Useful predictive models for assessing the concentration of As and Cd in the plant Sinapis alba have been developed using values of soil characteristics and values for the coefficient of distribution of these metals in the established solutions with the highest extraction capacity from contaminated soils.

According to the conclusions of the study, the plant Sinapis alba, has the potential of accumulation of increased concentrations of As and Cd from contaminated soils, and can be used in phytoremediation techniques of soils contaminated with these metals. Multiple regression models developed presented performance parameters values that confirm the use as variables of representative values of moving fraction of metal determined in the established solutions with the highest extraction capacity.

CHAPTER 7

HUMAN HEALTH RISK ASSESSMENT DUE TO EXPOSURE TO CONSUMPTION OF CONTAMINATED WATER

A systematic approach to risk assessment of pollutants in drinking water can be used to determine adverse impacts on human health. This assessment can help identify these risks and make decisions on measures to reduce exposure levels while maintaining acceptable levels of risk. The purpose of this study was to establish the composition of groundwater in the Ramnicu Valcea industrial area and to assess the risk to human health due to exposure to contaminated water consumption, for different ages and sex groups (men, women and children) in the studied region [7.1].

7.2. MATERIALS AND METHODS USED

In order to determine the chemical composition of groundwater, groundwater samples have been taken in accordance with the procedures establishing the rules and responsibilities for carrying out the activities of taking, preserving and transporting ground water samples. Of the total of 20 groundwater samples, 13 samples were taken from drilling sites located in the area of the Râureni chemical platform (sample code: H1-H12), 4 samples of groundwater were collected from fountains of some households located in Râureeni (F2-F4, H13) and 4 water samples have been taken from the rural area of Stoiceni municipality. (P4 – P7).

The analytical methods used to determine the above indicators were in accordance with international standards, the laboratory applying all the requirements imposed by the standard EN ISO/IEC 17025.

The GIS-based analysis was used to identify the spatial-temporal behavior of groundwater samples taken from the study area for nitrate, nitrite and ammonium parameters and the risk index for human health. The space distribution maps were generated using ArcGIS 10.5 software. The analysis of the spatial distribution of the values of the characteristics of groundwater taken from in the area of the city of Râmnicu Vâlcea and the non-canceric health risk indices associated with the consumption of water polluted with nitrate compounds (nitrate, nitrite and ammonium) used the IDW interpolation technique presented in Chapter 2.

7.3. ANALYSIS OF THE CHEMICAL COMPOSITION OF GROUNDWATER IN RAMNICU VALCEA INDUSTRIAL AREA

There were exceeded values at the following parameters in relation to the permissible limit values of the National Standard on Drinking Water and of the WHO: - concentrations of NO3 nitrates3- in the analysed waters show values ranging from 5.12 to 98.3 mg/L;

- nitrite NO2-, recorded minimum concentration values of 0,001 mg/L and maximum concentration of 1,12 mg/ L;

- ammonium NH4+, showed concentration values in the range of 0.008 mg/L and 85.2mg/L). The conductivity values analyzed in groundwater samples exceeded in samples P5 (2672 μS/cm), P6 (2694 μS /cm) and P7 (2550 μs/cm) at a temperature of 21.9oC, with the TDS concentration showing a maximum value of 1864 mg/L in the P6 sample.

%CBE results were within the acceptable range of ±5%, indicating that measurement accuracy in the study area was significantly good (minimum = -2.69; maximum = 3.81).

In conclusion, the analysis of the chemical composition of groundwater in the industrial area Râmnicu Vâlcea established that the water samples show contamination with nitrogen compounds (ammonium, nitrates and nitrites).

7.4. ANALYSIS OF THE SPATIAL DISTRIBUTION OF NITROGEN COMPOUNDS IN THE AQUIFER OF THE RAMNICU VALCEA INDUSTRIAL AREA

In order to identify the impact of pollution by nitrogen compounds (nitrate, nitrite and ammonium) of groundwater samples taken from the rural area of the village of Stoiceni on the region studied, the spatial distribution of the values of concentrations of these compound in this area was analyzed.

The analysis of the spatial distribution of ammonium concentration values in the groundwater analysed shows a region where high concentrations of this chemical compound are present similar in extension to the region where nitrate water pollution was identified. This blue region includes points from which P4 (1,22 mg/L), P5 (3.3 mg/ L), P6 (85.2 mg/ l) and P7 (71 mg/l) samples were taken. There is a possibility that the increased concentrations of nitrates and ammonium in the underground water samples analysed may result from anthropogenic sources, irrigation, septic wells, degradation of organic waste or nitrogen-based fertilizers used for soil adjustment or from animal production activities. Ammonia (NH4+) can be present in groundwater naturally, due to anaerobic degradation of organic matter, or artificially, because of the disposal of the organic waste, being one of the main dissolved components in some types of aquifers.

The analysis of the spatial distribution of the values of nitrate concentrations in groundwater samples in the industrial area of Râmnicu Vâlcea municipality, indicated a red area in which contamination of the low depth aquifer with values in the concentrations of nitrates exceeding the permissible legal limits was identified. This region includes points P4 (68.6 mg/L) and P5 (98.3mg/L). Being a rural and implicitly agricultural area, the contamination may be due to the excessive application of fertilizers on the land in this area.

The spatial distribution of the values of nitrite concentrations in the underground water samples analysed showed a white area that includes points P4 (1,12 mg/L), P5 (0,62 mg/ L), P6 (0,98 mg/ l) and P7 (71 mg/l). Increased values of nitrites in these water samples can be due to an oxidizing environment that can cause the nitrification reaction by turning ammonia into nitrate and then into nitrite, thereby increasing the concentration of these two pollutants in the underground aquifer in the region where these points are located.

7.5. HUMAN HEALTH RISK ASSESSMENT DUE TO EXPOSURE TO CONSUMPTION OF WATER CONTAMINATED WITH NITRATES, NITRITES AND AMMONIUM

In the risk assessment process, the health consequences of the various sensitive (vulnerable) groups of the population associated with environmental conditions are characterized. Risk assessment results are mainly used to develop and implement strategies that lead to a reduction in exposure and risks associated with environmental pollution and involve the selection of parameters (risk exposure factors):

- frequency of exposure to consuming contaminated water (days/year), EF;
- duration of exposure to water consumption (in one year), ED;
- daily intake of groundwater consumed as drinking water, IR;
- average human body weight (kg) for men, women and children, ABW;
- average exposure time (days) to contaminated water consumption, AET, the calculation formulas and the methodology applied are presented in Chapter 2.

In this study, the values of the parameters selected for assessing the risk to human health due to exposure to drinking water contaminated with nitrates, nitrites and ammonium were taken from the risk assessment model for human health developed by USEPA, and presented in Table 7.2.

Table 7.2. Parameters selected for health exposure assessment in groundwater samples

Risk exposure factors	Men	Women	Children	U.M.
IR	2.5	2.5	1	L/zi
ED	76.89	82.82	12	years
EF	365	365	365	days/year
ABW	78	65	14.5	kg
AET	28065	30229	4380	days
C	Contaminant concentration			mg/L

In order to assess the overall potential of the effects associated with the consumption of water contaminated with nitrates, nitrites and ammonium, the risk index for each contaminant HQ nitrate/nitrites/ammonium and risk index (HItotal) for all nitrogen compounds was calculated, the recommended limit being 1. In this study, according to the WHO-indicated Toxicological Profile, the RfD reference dose was 1.6 mgN-NO3-/L for nitrates, 0.1 mgS-NO2-/L to nitrites and 0.9 mgS -NH4+/L in ammonium. The risk assessment model for human health and the toxicological profile data for nitrogen compounds included in the calculation mode of the HItotal risk index were presented in Chapter 2.

HItotal values were obtained from the risk assessment on human health for men, women and children due to exposure to drinking water contaminated with nitrates, nitrites and ammonia in the Râmnicu Vâlcea industrial area.

Interpretation of the results obtained from the risk assessment on human health due to exposure to drinking water contaminated with nitrates, nitrites and ammonium from the Râmnicu Vâlcea industrial area for men, women and children by ingestion of contaminated water with these compounds concluded the following:

- HQnitrate index values were in the range of 0,0371 to 0,7117 for men, between 0,0445 and 0,8540 for women, and values in the area of 0,0798 and 1,531 for children;
- HQnitrit risk index values for the three age groups showed very low minimum values (near to zero) for all groups, with maximum values of 0,0109 (men), 0,0131 (women) and 0,0235 (children);
- HQamoniu showed peak values of 2,133 in the male group, 2,560 in the female group and 4,5905 in the children's group.

- HItotal values in the range 1 and 2 indicating an average risk to human health associated with the consumption of water contaminated with nitrogen compounds were identified in points P4 (1,432) and P5 (1,298) for the male age group and in points F4 (1,131), P4 (1.718), P5 (1,558) for women.

- HItotal values greater than 2 showing an increased risk to human health due to the consumption of water contaminated with nitrogen compounds, in particular nitrates and ammonium, were identified in points P6 (2,682), P7 (2,237) for men and P6 (3,218), P7 (2.684) for women. The consumption of water from the points F4 – P7 by children causes an increased risk for the health of this age group, HItotal values being in the range between 2,028 and 5,770.

The analysis of the spatial distribution of the HItotal total risk index values carried out in order to identify the area affected by the risk to human health due to the use of groundwater hazard to health is shown in Figure 7.5a for men where the red color indicates the area with elevated HITotal values, in Fig. 7.5b for women where the blue color shows the region with the highest HITOTAL values. Figure 7.5c shows the spatial distribution of the HItotal values for the group of children, in which the blue color reflects the presence of increased values of this risk index.

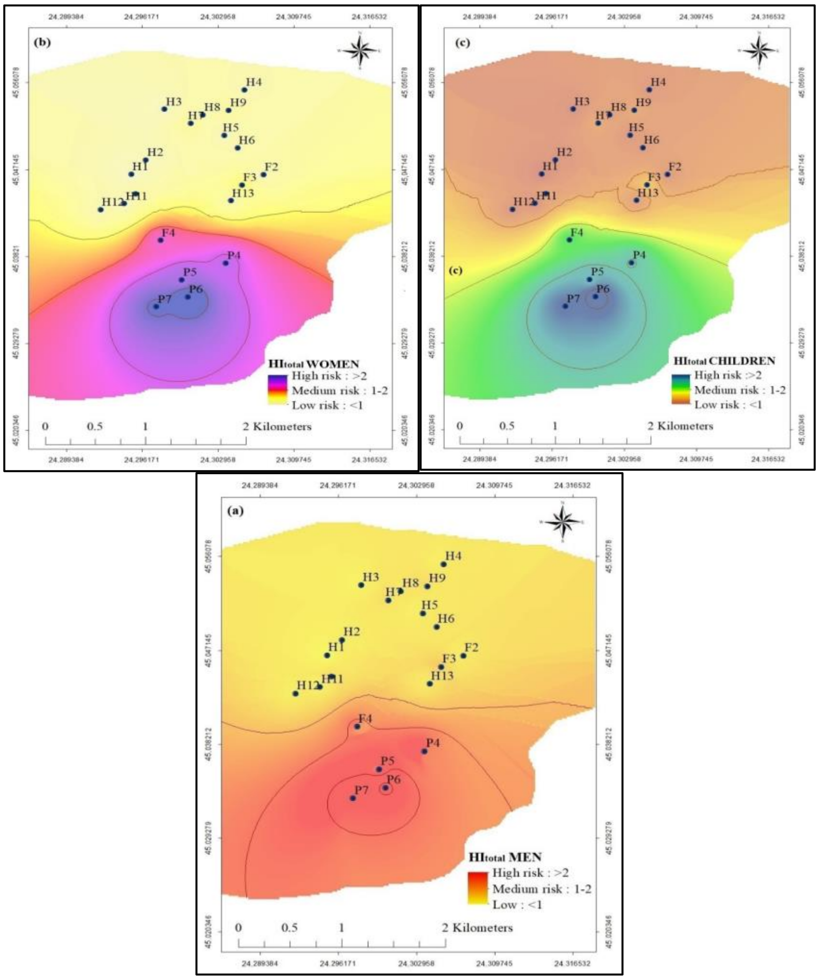

Fig.7.5. Spatial distribution of **HItotal** values for men (a), women (b) and children (c) in the groundwater aquifer of Ramnicu Valcea industrial area

As mentioned above, a HItotal value greater than 1 indicates the likelihood of a negative risk to human health due to exposure to contaminated water consumption. The results obtained indicate that, out of twenty sampling points, five boreholes from which groundwater samples were collected show nitrate and ammonium concentration values exceeding the limits allowed by the National Standard and WHO and may therefore lead to exposure of age groups (men, women and children) to an increased risk of danger to human health. The spatial distribution of HItotal values illustrates that men, women and children in the southwest of the study region (Stoiceni) pose a relatively high health risk from groundwater consumption.

7.6. PARTIAL CONCLUSIONS

Chapter 7 of this doctoral thesis presented a study on human health risk assessment due to exposure to water consumption contaminated with nitrogen compounds, which included establishing the composition of groundwater in the Ramnicu Valcea industrial area, as well as a method of assessing the risk to human health on different groups classified according to age (men, women and children) associated with the consumption of water contaminated with nitrates, nitrites and ammonium.

The interpretation of the results obtained indicated that, out of twenty sampling points, five boreholes from which groundwater samples were collected show nitrate and ammonium concentration values exceeding the legal limits allowed by the National Standard and WHO, and therefore may lead to an increased risk of danger to human health arising from the consumption of these waters in the long term.

GENERAL CONCLUSIONS

Within the present doctoral thesis entitled “Evaluation of the presence in the environment of inorganic pollutants from areas affected by anthropogenic pollution” fields of research aimed at the development of methods capable of identifying and reducing the content of anorganic contaminants in contaminated environments were addressed. In order to justify decisions concerning the management of areas contaminated with these pollutants, it is necessary to assess their effects, both on the components of natural capital and on ecological systems.

The studies carried out and presented in the ORIGINAL CONTRIBUTIONS section have led to the following conclusions:

- Through the characterization of mining wastes in the Valea Călugărească and the application of chemometric methods, dangerous pollutants such as As, Pb, Zn, Cu, Fe and Al were identified and quantified in the composition of ash samples, the high content of Fe indicating the presence of pyrite.
- Metal species of Pb, Fe and Al form compounds that do not have smoothing properties being retained by the solid particles, and the nutrients are retained at the surface of the solids due to high concentrations of sulfates and fluors. Organic carbon and nitrogen showed low mobility due to the presence of high concentrations of sulfates and fluorides that may cause increased salinity in the levigat samples.
- The saturation indices of different minerals calculated on the basis of the concentrations of the elements established in the ash composition for different species indicate CaSO4 as the mineral that dominates the dissolving processes, showing a tendency to precipitation due to over-saturation.

Identification and quantification of soil pollutants in the Valea Călugărească affected by the presence of pyrite ashes, establishment of the degree of pollution with metals, the impact of toxic contaminants on the fertility of these soils and evaluation of the risk of contamination with toxic metals have revealed the following aspects:

- Soils in the vicinity of chemical waste deposits presented a high content of sulfates, soil fertility in the area of pyritic ash halls is significantly negatively influenced by the over-saturation with dissolved salts following the processes of lightening of the components of pyrite ash;
- The existence of toxic metal pollution, evidenced by the increased values of the concentration of As, Cd, Cu, Pb, Sb and Zn and the extension of contamination with toxic metals to an area of approximately 100m of abandoned deposits. The phenomenon was indicated by the spatial distribution of the values of the concentration of toxic metals in the soils in the area studied, the level of pollution being significantly reduced with the increase of the distance;
- The SQAPP application developed under the HORIZON 2020 Project, having as a partial database the information obtained in this study, recommended, among the most effective soil remediation procedures, phytoremediation using plants with deep root system, conservative agriculture and minimizing irrigation with salinated water;

From the characterization of the underground aquifer associated with the presence of pyrite ashes in the Călugărească Valley, the following results:

- ➢The existence of a high content of sulfates and chlorides in the underground water samples located on the flow direction of the aquifer;
- ➢Exceeding the permissible limits of nitrates in groundwater in agricultural areas treated with excess chemical fertilizers;
- ➢Signalling a natural source with potential for pollution of groundwater due to evaporation processes in the soil-soil water system, their mineralogy being determined by the dissolving of gypsum and precipitation of minerals of calcite and dolomite;
- ➢Assessment of the quality of groundwater for human consumption indicated that only 3% of all water samples analysed show good quality of the groundwater samples, 87% of the total samples of water show acceptable quality for consumer use, and 3 samples from the agricultural area were of poor quality due to the high nitrate content and were recommended only for irrigation.

The development of models for predicting the concentrations of arsenic and cadmium in plants, determined by the mobility of metals in the soil, led to the following conclusions:

- ➢Development of a method that combined RSM analysis with PCA analysis being used successfully to establish the extraction capacity of Cd and As from artificial contaminated soils and established the factors that influence these complex processes;
- ➢The existence of an accumulation potential of the Sinapis alba plant proved by predictive models of the concentrations of As and Cd in this plant that included the parameters of the moving fraction of metal. The method was validated by the values of the performance parameters that confirm the use as variables, the distribution coefficient values, the representative parameter of the moving metal fraction, determined on the basis of experimental values in the established solutions with the highest extraction capacity.

The interpretation of the results obtained in the study on the elaboration of a method for assessing the risk to human health due to exposure to the consumption of water contaminated with nitrogen compounds taken from the Ramnicu Valcea industrial area concluded the following:

- ➢Identification of groundwater contamination in the agricultural area of Stoiceni locality with nitrate of two drilling samples, nitrite contamination of three water samples and contamination of four ammonium samples out of a total of 20 samples of water.
- ➢The human health risk assessment associated with the consumption of contaminated water indicated that, out of twenty sampling points, five boreholes from which groundwater samples were collected show nitrate and ammonium concentration values exceeding the limits permitted by the National Standard and WHO, and therefore may lead to an increased risk of danger to human health arising from long-term consumption of these waters.

BIBLIOGRAFIE SELECTIVĂ

CAPITOLUL 1

1.1 Pettorelli, N., Graham, N.A.J., Seddon, N., Bustamante, M.M.C., Lowton, M.J., Sutherland, W.J., Koldewey, H.J., Prentice, H.C. Barlow, J., Time to integrate global climate change and biodiversity science-policy agendas, Journal of Applied Ecology 2021, 58(11), p. 2384-2393.

1.4 Raza, M.H., Abid, M., Faisal, M., Yan, T., Akhtar, S., Adnan, K.M.M. Environmental and HealthImpacts of Crop ResidueBurning: Scope of Sustainable Crop Residue Management Practices, International Journal Environmental Research Public Health. 2022, 19(8), 4753.

1.8 Wu, W., Liao, R., Hu, Y., Wang, H., Liu, H., Yin, S., Quantitative assessment of groundwater pollution risk în reclaimed water irrigation areas of northern China,

1.13 Shiquan, D., Amuakwa-Mensah, F., Deyi, X., Yue C., Yue, C. The impact of mineral resource extraction on communities: How the vulnerable are harmed, The Extractive Industries and Society 2022, 10, 101090.

1.25 Yin, J., Wu, X., Li, S., Li, C., Guo, Z., Impactof environmental factors on gastric cancer: A review of the scientific evidence, human prevention and adaptation, Journal of Environmental Sciences, 2019, 89.

1.32 Negm, A.M., Romanescu, G., Zeleňáková, M., Water Resources Management în Romania, Springer Water, 2020, ISBN 978-3-030-22320-5 (eBook). p. 34-121

1.37 Castillo, M. (2020). Suspended sediment, nutrients, and chlorophyll în tropical floodplain lakes with different patterns of hydrological connectivity. Limnologica 82:125767.

1.47 Ministerul mediului, Strategia națională și Planul național de acțiune pentru gestionarea siturilor contaminate din România, 2014, http://www.mmediu.ro/beta/wp-content/uploads/2014/02/2014-02-13_STRATEGIA.pdf, accesat la 21.07.2023.

1.55 Zhen, Q., Ma, W., Li, M., El, H., Zhang, X., Wang, Y., Effects of vegetation and physicochemical properties on solute transport în reclaimed soil at an opencast coal mine site on the Loess Plateau, China, Catena, 2017, 148, p. 17–25.

1.62 Isqaper Interactive Soil Quality Assesment, https://www.isqaper-project.eu/, accesat 24.08.2023.

CAPITOLUL 2

2.49 Barrena-González, J., Contador, J.F.L., Fernández, M.P., Mapping Soil Properties at a Regional Scale: Assessing Deterministic vs. Geostatistical Interpolation Methods at Different Soil Depths, Sustainability, 2022, 14, 10049.

2.51 Ahmad I., Dar M.A., Fenta A., Halefom A., Nega H., Andualem T.G., Teshome A. Spatial configuration of groundwater potential zones using OLS regression method. J. Afr. Earth Sci. 2021, 177, 104147.

CAPITOLUL 3

3.1. Teng, C., Zhou, K., Peng, C.,Chen, W., Characterization and treatment of landfill leachate: A review. Water Res. 2021, 203, 117525.

3.5. Vasilache, N., Diacu, E., Modrogan, C., Chiriac, F.L., Vasile, G-G., Tenea, A-G., Iancu, V.I., Pirvu, F., Paun, I., Serban, G.V., Composition and leaching characteristics of mining ashes, International Symposium “The environment and the industry”, SIMI 2023, Book of Abstracts.

CAPITOLUL 4

4.3 Vasilache, N., Diacu, E., Modrogan, C., Chiriac, L.F., Vasile, G., Paun, I., Iancu, V., Stoica, C., Pirvu,V., Niculescu, M., Conference: International Symposium “The environment and the industry”, Assessment of soil fertility în the area of mining waste deposits, 2021, http://doi-org10-21698simi-2021-ab37.

CAPITOLUL 5

5.1 Vasilache, N., Diacu, D., Modrogan, C., Chiriac, F.L., Paun, I.C., Tenea, A.G., Pirvu, F., Vasile, G.G., Groundwater Quality Affected by the Pyrite Ash Waste and Fertilizers în Valea Calugareasca, Romania ,Water 2022, 14(13), 2022.

CAPITOLUL 6

6.1 Vasilache, N., Diacu, E., Cananau, C., Tenea, A. G., Vasile, G.G., Evaluation of the phytoremediation potential of the Sinapis alba plant using extractable metal concentrations, Plants 2023, 12(17), 3123.

CAPITOLUL 7

7.1 Vasilache, N., Mandoc, L.R, Diacu, E., Vasile, G.G. Tenea, A.G. Arcire, A. Batrinescu, G., Paun, I., Gheorghe, S., Groundwater chemistry, pollution, and health risk assessment for nitrogen compounds. a case study în a suburban region of Romania, Romanian Journal of Ecology & Environmental Chemistry, 2022, 4(2), p. 1-16.

LISTA LUCRĂRILOR PUBLICATE

ARTICOLE INDEXATE WEB OF SCIENCE CU FACTOR DE IMPACT

1. Vasilache, N., Diacu, E., Cananau, C., Tenea, A.G., Vasile, G.G., Evaluation of the phytoremediation potential of the Sinapis alba plant using extractable metal concentrations, Plants 2023, 12(17), 3123.
   https://doi.org/10.3390/plants12173123

2. Vasilache, N., Diacu, D., Modrogan, C., Chiriac, F.L., Paun, I.C., Tenea, A.G., Pirvu, F., Vasile, G.G., Groundwater Quality Affected by the Pyrite Ash Waste and Fertilizers in Valea Calugareasca, Romania,Water 2022, 14(13), 2022.
   https://doi.org/10.3390/w14132022

ARTICOLE INDEXATE WEB OF SCIENCE FĂRĂ FACTOR DE IMPACT

1. Vasilache, N., Diacu, E., Modrogan, C., Lucaciu, I., Vasile, G.G., Paun, I.C., Iancu, V., Forecasting methods for assessment of the biodegradability of wastewater from organic separators, University Politehnica of Bucharest Scientific Bulletin Series B-chemistry and Materials Science 2021, 83 (4), p. 95-108.
   http://hdl.handle.net/123456789/1791

ARTICOLE NEINDEXATE WEB OF SCIENCE, INDEXATE BDI

1. Vasilache, N., Mandoc, L.R., Diacu, E., Vasile, G.G., Tenea, A.G., Arcire, A. Batrinescu, G., Gheorghe, S., Groundwater chemistry, pollution and health risk assessment for nitrogen compounds. A case study in a suburban region of Romania, Romanian Journal of Ecology & Environmental Chemistry, 2022, 4 (2), p. 7-22.
   https://doi.org/10.21698/rjeec.2022.201

2. Vasilache, N., Diacu, D., Vasile, G.G., Modrogan, C., Paun, I.C., Pirvu, F., Groundwater quality assessment for drinking and irrigation purpose using GIS, Piper diagram, and water quality index, Romanian Journal of Ecology & Environmental Chemistry 2020, 2 (2), p. 109 – 117. https://doi.org/10.21698/rjeec.2020.214

CONFERINȚE

1. Vasilache, N., Diacu, E., Modrogan, C., Chiriac, F.L., Vasile, G-G., Tenea, A-G., Iancu, V.I., Pirvu, F., Paun, I., Serban, G.V., Composition and leaching characteristics of mining ashes, International Symposium “The environment and the industry”, SIMI 2023, Book of Abstracts. http://doi.org/10.21698/simi.2023.ab26

2. Vasilache, N., Diacu, E., Vasile, G.G., Paun, I., Pirvu, F., Gheorghe, S., Iancu, V. Chiriac, L.F., Assessment of the Corrosion and Scaling Potential of Groundwater from an Area Affected by Industrial Activities, 22nd Romanian International Conference on Chemistry and Chemical Engineering Sinaia, Romania - September 7 – 9, 2022.

3. Vasilache, N., Diacu, E., Chiriac, F.L., Vasile, G.G., I.P., F. Pirvu , A.G., Tenea, G.V., Serban , A.,Trandabat, Nitrate pollution and health risk assesment of groundwater in rural areas from Botosani, Romania, International Symposium "The environment and the industry", E-SIMI 2021, Book of Abstracts.
http://doi.org/10.21698/simi.2021.ab27

4. Vasilache, N., Diacu, E., Modrogan, C., Chiriac, F.L., Vasile, G.G., Paun, I., Pirvu, F., Iancu, V.I., Niculescu, M., assessment of soil fertility in the area of mining waste deposits, International Symposium "The environment and the industry", SIMI 2023, Book of Abstracts, SIMI 2021. DOI: http://doi.org/10.21698/simi.2021.ab37