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ABSTRACT

Ph. D. Thesis

The impact of CET HIDROCARBURI ARAD's activity on groundwater and soil quality

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MOTTO

” Efficiency means doing better what is already being done “

Peter Ferdinand Drucker

Founder of modern management

CONTENT

INTRODUCTION

At industrial level, electricity and heat demand is largely met by conventional thermal power plants based on the combustion of fossil fuels, coal, hydrocarbons, oil and natural gas [1].

The industrial production of energy in district heating power plants generates significant emissions of activity-specific pollutants, which can contribute to the pollution phenomenon at both zonal and global level [5].

The activity of power plants is subject to strict requirements related to environmental quality, through national and European legislation in the field of environmental protection, thus currently facing a great challenge to meet these requirements in parallel with maintaining a high efficiency of the combustion processes, respectively reducing the service life of critical technological components [3, 6].

Emissions from the energy sector directly affect the quality of air, soil, subsoil and water bodies, with heavy metals being an important category of pollutants. In the case of thermoelectric power plants, heavy metal emissions come from combustion plants, in the form of dust, which affect the soil by deposition and accumulation, both on site and in the vicinity, sometimes at long distances [7].

The harmful effect of heavy metals manifests itself at high concentrations in the composition of the air in the area of the emitting source with deposition and assimilation in water bodies and in the food chain. Heavy metal compounds participate in the global transport of substances, in the form of aerosols in the upper atmosphere in micro and nanometric sizes, in the absence of a minimum identification threshold that can demonstrate that these substances do not pose a hazard to human health [8].

High toxicity, accumulation and lack of biodegradability, cause heavy metal pollution to have a significant impact on life, seriously affecting ecosystem processes and human health, heavy metals being recognized carcinogens with genotoxic action for living beings [8, 9].

The soil is subject to contamination, usually as a consequence of anthropogenic activities, especially industrial ones, which have a major impact, as it is in the case of the land around the power plants, a particular impact being persistent pollutants, such as heavy metals [9].

Naturally occurring metals that have a density greater than 5g/cm3 are considered heavy metals. These are usually associated with toxicity and pollution, but some of them, such as essential metals, are vital for living organisms in low concentrations [10].

The persistence of heavy metals for long periods in the soil contributes to the process of geo accumulation and bioaccumulation, respectively, the soil being the interface of the ecological system of connections for the biosphere [11].

Soil is a complex system, with fundamental implications, having the capacity to store four times more organic carbon than fauna and vegetation, which gives it the attribute of the largest terrestrial carbon store, with a capacity of 2500 gigatons, and a major role in climate change [13].

The quality of groundwater is directly influenced by the activities specific to the industrial technological process carried out at ground level, through the impact of specific pollutants generated in the form of various emissions, which also include wastewater discharges into the receivers.

The monitoring of groundwater quality is a specific activity carried out systematically and periodically, according to the existing programs at zonal and national level, in order to obtain the fundamental data for an adequate assessment of the evolution of the quality of the natural water reserves.These actions also involve soil quality monitoring, given the specific nature of the activities carried out. [14].

At the level of the power plants, there are requirements established by the integrated environmental permit, respectively by the water management permit, in accordance with national and European legislation [4].

Groundwater pollution is generally an almost irreversible phenomenon and depollution is an extremely difficult, even impossible process, with harmful consequences on the use for drinking purposes.

The migration of pollutants from the groundwater aquifer to the deeper groundwater reserves is a process that takes place naturally and unfortunately easily, at the contact of effluents, when they are taken up by absorption and dissolution [14].

Due to the constantly increasing pollution, the self-purification capacity of the affected water reserves can be considerably reduced. The aquatic ecosystem is in many cases severely affected, with major consequences for living organisms.

It is necessary to be aware of the risks posed by pollution, in each field of activity. In conclusion, this approach involves the integration of policies to protect water and soil reserves, in the dynamics of modern society, for the efficient protection of the natural environment, given that soil is a finite reserve.

OBJECTIVES OF THE DOCTORAL THESIS

The main objective of the doctoral thesis was to carry out a study on the evaluation of the impact of some environmental factors on the site of S.C. CET HIDROCARBURI S.A. ARAD, respectively, the evolution of the quality parameters for groundwater and the behaviour of heavy metals in the soil and, by applying the General Pollution Index method. Authorised quality indicators for groundwater and heavy metals in soil were monitored. The period covered the period from 2010 to 2020.

The research is based on the premise that, as a result of the activities carried out on the site, groundwater can be contaminated, and the concentration of heavy metals present in the soil, in high concentrations, can negatively impact human health, both of the staff employed at the plant and of the inhabitants of the neighbouring areas, including animals, who come into contact with the area, or are located in neighbouring areas.

The CET H site is longitudinally crossed by the Mureșel Canal, which is an arm of the Mureș River and also a surface emissary for the technological wastewater discharged from the plant, after treatment. There is a very lively living environment here, which is home to species of spontaneous flora and wildlife including macroinvertebrates, fish, batrachians, birds, insects and small mammals, constituting a mixed natural habitat.

The state of this habitat is an important biological indicator for the pollution status of this area. Ensuring a favourable state for all forms of life, and the conservation of this habitat is a goal, considering its importance, for humans, plants and animals, with the impact control component. Some polluting compounds can migrate from the soil to the surface water, but also to the groundwater, or downstream groundwater, and contaminate the drinking water, groundwater is the main source of drinking water for the inhabitants of Arad.

The groundwater aquifer must be the first line of water control, at the underground level, especially in the case of industrial sites. Currently, at the level of the plant, the quality parameters for groundwater and wastewater returned to the outfall, the concentrations of heavy metals in the site's soil are monitored, in accordance with the provisions of the authorization documents, the water management authorization and the integrated environmental authorization.

Given that bioaccumulation phenomena can be initiated in the beings in the ecosystem, through various contact soil, these compounds can reach plants, are assimilated by them and then transferred to living operations or processing activities in the in the food chain.

At the same time, knowing that the groundwater in the subsoil of the power plant site constitutes the groundwater body ROMU 20, which communicates with the deep groundwater body Mureș ROMU22, of which it is part, we considered that it would be useful to investigate the state of pollution, both for the groundwater and for the soil of the site.

The methods of managing technological activities carried out on the ground may have a negative impact on the quality and quantity of groundwater, if soil-subsoil interaction is not considered a priority, in compliance with environmental protection rules.

Based on these arguments, we applied a documentation and analysis program, which generated new information on the pollution status on the plant site, being harmonized with the monitoring of environmental factors at the plant level.

The doctoral thesis is structured on 5 chapters. The presentation, in Chapters 1 and 2, of a series of theoretical concepts and notions on the state of knowledge in the field of groundwater and heavy metals monitored in industrial, urban and agricultural soils, precedes Chapter 4, dedicated to personal contributions to this case study.

Legislation and compliant monitoring, for the monitored pollutant species attributed to the plant, have been presented. We also presented the plant, which was the subject of the study, in chapter 3, and dedicated to it a consistent history, found in the appendices of this thesis, given the 127 years of technological activity on the same site at the time of writing this paper.

The legislation and compliant monitoring for the monitored pollutant species, assigned to the plant, were presented.

We also made a presentation of the power plant, which was the subject of the study, to which a consistent history was also dedicated, found in the annexes of this thesis, considering the activity carried out on the same site, for 123 years, until 2020, an activity that continues today.

The doctoral thesis had the following objectives:

- Literature review and research on groundwater and soil pollution by heavy metals;
- Analysing the quality of groundwater;
- Evaluation of the degree of groundwater pollution related to the studied site; Analysis of the concentrations of heavy metals monitored in the soil of the site;
- Evaluation of the degree of heavy metal pollution in the soil of the studied site;
- Assessment of the impact of the activity of CET HIDROCARBURI Arad on the quality of groundwater and soil.

CHAPTER 1.
STATE OF KNOWLEDGE ON GROUNDWATER QUALITY

The protection and preservation of terrestrial ecosystems is only possible in relation to surface and groundwater. The studies carried out indicate the existence of complex connections, which have been highlighted by hydrogeological methods and criteria. [22].

Groundwater contributes significantly to river flows and impacts the ecosystems that depend on it in the environment. A specific advantage of groundwater for the drinking water supply is that it is naturally protected from several contaminants [29]. The groundwater parameters are relatively stable. Groundwater has a high mineralization, a high carbon dioxide content and a low oxygen concentration, compared to surface waters, which have very different and variable compositions over time, being under the influence of numerous factors, such as: the nature of the rocks that make up the riverbeds, tributaries and precipitations, current or accidental wastewater discharges, physical, chemical and biological phenomena [29, 30]. Many regions and countries rely on naturally clean groundwater, as advanced water treatment is economically impossible [33].

Groundwater quality is important for a variety of uses, such as drinking water, ecosystems, food (especially irrigation), and energy production other industries [39, 40]. in order to have a comparable global assessment, it is necessary to implement global standards [43].

Groundwater is the main freshwater reservoir that acts in the hydrological cycle. According to the EEA (European Environment Agency) [48], groundwater abstraction accounts for 65% of total water abstraction for public water supply, but is less than a quarter of total water consumption in the EU-27 Member States. Between 2000 and 2019, the relative share of groundwater in total water abstraction increased by 4%. Poor quantitative status was reported for 9% of the total groundwater body area in the EU-27, but poor chemical status was reported for 24% of the area [49].

In the EU-27, the main source of groundwater contamination is agriculture, which affects around 19% of the total area of the body of groundwater, followed by abandoned and contaminated industrial sites (5%) and mining activities (3%). [50].

Nitrate pollution from agricultural activities, cities and industrial developments endangers aquifers around the world. The most common contaminant of groundwater resources in the world is nitrite (NO). [53]. Surplus nitrogen (N) can be quickly moved into groundwater systems after fertilizer application [54, 55]. Most water quality exceedances in Europe are caused by nitrate pollution.

The most dangerous action is on infants, who die suddenly. Excessive levels can cause "blue baby syndrome," which, if not treated immediately, can be fatal. According to the standards, water intended for children must not contain nitrates or nitrites greater than 10 mg/l [57].

On the other hand, around 6.5% of groundwater bodies in the EU-27 are negatively affected by pesticides [62]. Many pesticide-related active substances, together with their by-products, such as metabolites, degradation products and reaction products, continue to be relevant [63, 64], despite the fact that some pesticides have been restricted or banned [65].

The quality of groundwater is influenced by several factors, including the quality of the water that initially seeps into the groundwater, interaction with the groundwater environment, and the effects of human activities that take place both on the surface and underground, such as oil and gas exploration. Consequently, the 'governing factors' are the reactivity and composition of groundwater layers (geogenic contamination) and the sources of contamination from land use and other human activities (anthropogenic contamination).

Natural water-rock interactions and recharge in areas dominated by evaporation are among the many processes that can lead to higher groundwater salinity. But many groundwater salinization processes are aggravated by anthropogenic activities. These include the salinization produced by irrigated agriculture, the over-pumping that mobilizes geological old saline waters, the penetration of seawater into coastal aquifers, and the production of hydrocarbons. [75, 76].

Salinization may be linked to variations in tidal intensity and coastal flooding in low-lying areas, such as dammed areas in Bangladesh, where frequent seawater flooding can quickly contaminate soils and shallow groundwater. It is estimated that by 2060, 1.8 billion people will be affected [81, 82].

Groundwater is considered free of microbiological contamination. However, about half of groundwater sources in the United States have indicated dejection contamination, which could lead to numerous cases of waterborne transmission and disease [83].

In recent decades, urban areas have been affected by emerging organic contaminants (EOCs) from pharmaceutical residues, personal care products, pesticides, veterinary drugs, food additives, nanomaterials, industry, and other sources [90, 91]. However, despite the potential dangers to the environment and human health, these groups are not yet officially regulated by European legislation [92, 93].

Due to the fact that they are widespread and persist in the environment, microplastics have recently gained attention among emerging pollutants [94]. Although microplastics are mainly considered to be surface water pollutants, there are chances that they will end up in groundwater, for example, in a recent study microplastics were found in karst groundwater [95]. This finding is significant because about 25% of the global population depends on karst aquifers for drinking water [96].

The quantity and quality of groundwater have been affected by climate change and variability in several complicated and unprecedented ways [103–106]. In a large study carried out, which included several countries, groundwater levels were measured using satellite programs and applications [115].

In this case, groundwater level trends for 170,000 monitoring wells and 1,693 aquifer systems in countries accounting for about 75% of the world's groundwater withdrawal were analysed in site. Research results have shown that in the 21st century, groundwater levels have declined rapidly (more than 0.5 meters per year), especially in dry areas with cultivated land [115]. At the same time, the study showed that 30% of the world's regional aquifers have experienced an accelerated decline in groundwater levels over the past four decades.

The use of fluids, such as fuels, can locally cause high levels of local contamination through runoff that creates different phase (non-watery) zones in groundwater [117, 118]. These areas may continue to be sources of dissolved organic groundwater contaminants for many decades.

Organic contaminants of emerging concern (CECs) are not unknown substances, but rather groundwater pollutants about which there is relatively little information currently available on their distribution and concentrations. Their emergence is related to the existence of analytical methods and adequately advanced sampling protocols. These compounds are usually detected at concentrations below g/L in groundwater [123].

Numerous elements that dissolve from the minerals of the aquifer matrix in the natural environment and accumulate in groundwater can create problems for the functioning of the water supply system, as well as health risks. Referred to as geogenic contaminants, two of the most documented geogenic contaminants are arsenic and fluorine, but there are also iron, manganese, chromium, and radionuclides such as radium, radon, and uranium [125].

High concentrations of these natural groundwater contaminants can cause serious illnesses such as cancer (e.g., arsenic) or dental and skeletal problems (e.g., fluoride) [126].

The reddish-black colouring effect of the contact surfaces is common, being caused by the increased concentrations of iron and manganese in combination with the microbiological action.

They also affect operational components of infrastructure, causing clogging of boreholes, technical problems with the operation of pumps, extremely significant damage in the case of well fields and groundwater supply systems [127].

Arsenic (As) in drinking water sources has become a significant health problem in recent decades. Exposure can often occur through food, but most commonly through its natural presence in drinking water. Consuming a relatively small amount of arsenic over a long period of time has health effects, such as skin conditions, vascular and nervous systems, and a variety of cancers. [128] The WHO guideline for arsenic in drinking water of 10 g/L is outdated on all continents. It is estimated that there are between 94 and 220 million people who are exposed to arsenic concentrations exceeding 10 g/L, for bouth consumption and household use. [129]

Using groundwater with high concentrations of arsenic for irrigation has the potential to directly increase arsenic levels in crops and have a negative effect on crop yields. This is especially true for rice, which fixes arsenic in its grains very well. [130]

Fluoride is relatively abundant in many minerals in the Earth's crust. It is also abundant in groundwater as a result of geochemical interactions with fluorine-bearing minerals and geothermal fluids. [132] Fluoride toxicity, also known as fluorosis, occurs at higher levels of ingestion and is primarily responsible for the damaging effects it has on tooth enamel and bone tissue. [133]

The World Health Organization (WHO) establishes a guideline for fluoride in drinking water of 1.5 mg/L to prevent fluoride poisoning [134]. It is estimated that 120 million individuals, or 9% percent of the Indian population, may be vulnerable to fluoride concentrations exceeding 1.5 mg/L [135].

Two of the most abundant metals in the earth's crust are iron (Fe) and manganese (Mn). The forms and solubility of iron/manganese in groundwater are highly dependent on the pH and redox potential of groundwater. [138, 139] If not removed by in-site or post-extraction groundwater treatment, increased Fe/Mn concentrations (typically above 0.3 mg/L and 0.1 mg/L) can cause a number of operational problems, involving high investment, management and operating costs. [140]

Increasing the iron content in drinking water poses no immediate health risks. The WHO does not have a guideline on iron drinking water. Toxic symptoms appear only after excessive consumption. In young children and sensitive adults, iron concentrations of 10–30 mg/L can have chronic health effects, such as hemochromatosis (where iron buildup causes tissue damage) [140, 141].

The WHO drinking water guideline is for Mn below 0.4 mg/L, as Mn is toxic to humans [142]. Respiratory problems (e.g., pulmonary embolisms and bronchitis) and neurological problems (e.g., hallucinations, nerve damage, and Parkinson's disease) can be caused by increased manganese. Increased iron concentrations above 5 mg/l can cause iron precipitation, damaging the leaf system of plants. In contrast, high concentrations of Mn can be selectively toxic, as Mn toxicity depends on the plant species. [143, 144].

Chromium (Cr), which is also found in localized anthropogenic contamination associated with industrial activities or mining, is another potentially dangerous geogenic contaminant but is rarely monitored. [145]. There is evidence of geogenic chromium in aquifers in Europe, North and South America [146]. A provisional guideline value of 50 g/L has been set by the World Health Organization, although chromium is a vital component [147].

Because groundwater is more exposed to radioactive substances in rocks than surface water, it is more exposed to radioactive contamination. [148]. Traces of naturally occurring radioactive substances in rock and soil can accumulate in groundwater, which can affect their use. [150]. Numerous concentrations of radium activity have been reported in groundwater around the world, with radioactivity of this element being strongly represented globally. [154, 155]

Due to its moderate mobility, long half-life, and relative abundance in the Earth's crust, dissolved uranium is often present in groundwater. Uranium concentrations have been found in toxic groundwater around the world that exceed the WHO guideline for drinking water (30 g/L). [159]

Globally, the main issue with the amount of groundwater is how climate change will affect recharge. Although most European countries have been tracking the amount of groundwater since the early twentieth century, this was not common until the 1970s and 1980s [162]. Long-term groundwater quality monitoring is useful for several reasons. Efficient and sustainable groundwater management is essential.

CHAPTER 2.
STATE OF KNOWLEDGE ON HEAVY METALS IN SOIL

Heavy metals are chemical elements that occur naturally in ecological systems [165]. According to definitions established by chemists, heavy metals are those groups of metals and metalloids that possess an atomic number Z above 20 and a specific gravity exceeding 5g/cm3, such as cadmium (Cd), mercury (Hg), copper (Cu), arsenic (As), lead (Pb), chromium (Cr), nickel (Ni) and zinc (Zn) [173, 174].

Along with pesticides and polycyclic aromatic hydrocarbons, heavy metals are contaminants that environmental pollution has exposed to humans, becoming pollutants with a strong impact with industrial exploitation [176].

Heavy metals are not harmful in themselves, to plants, animals and humans, but only when their internal concentrations exceed a specific threshold. Second, trace elements and micronutrients are vital components of plant, animal, and human cells. Co, Cu, Fe, Mn, Mo, Ni, and Zn demonstrated this. They only have toxic effects when the internal concentration exceeds a certain threshold, which makes them known as heavy metals. [170]

An important characteristic of heavy metals is the anthropogenic enrichment factor, which represents for each metal a percentage of the annual emissions associated with anthropogenic sources. This factor is 97% for Pb, 89% for Cd, 72% for Zn, 66% for Hg, and 12% for Mg [177]. The anthropogenic enrichment factor, together with the risk of toxicity of metals, indicates which metals should be prioritized in research [178].

Heavy metals, unlike most organic pollutants, are not removed from ecosystems through natural processes. Because heavy metals cannot be broken down, their harmful effects continue for a long time, and the only way to neutralize them is through mineralization, dilution, and association with organic compounds. [179]

Agricultural inputs such as mulch, fertilisers and pesticides are essential for agricultural production [180]. But long-term over-application contaminated the soil with heavy metals [181].

Most pesticides are organic, but they also exist in the form of organic-inorganic combinations or pure minerals. Most pesticides are organic, but they also exist as organic-inorganic combinations or pure minerals. Some pesticides contain heavy metals such as Hg, As, Cu and Zn to increase the effectiveness of some biologically active ingredients. However, emphasis is now being placed on using pesticides that do not contain heavy metals [182].

The heavy metals present in the soil have generated special attention following the increasingly in-depth knowledge of the toxic effects they have on ecosystems, agriculture and human health, in parallel with the processes of public and scientific awareness of environmental problems, as well as with the development of high-performance analytical techniques, which have led to the more accurate measurement of their concentrations in the samples studied.

Heavy metal pollution is a major global problem. It can come from natural sources, such as volcanic eruptions or the disintegration of rocks, these substances being naturally present in the earth's crust, but the main cause of this phenomenon is industrial activities and non-compliant waste disposal, which releases heavy metals with toxic potential into the environment. In general, anthropogenic sources of heavy metals also include agricultural and transport activities [10, 184]

Heavy metals can be released into the atmosphere in the form of emissions, fixed or unfixed, on material particles, or aerosols, which will be deposited on the ground. Their sources can be diffuse, or punctual, from stationary sources, the dispersal paths representing conclusive factors for their finding in the inventory of representative ecosystems. Climatic and geographical conditions favors the deposition of heavy metal particles in the air and their transfer from industrial pollutants to residential areas [10].

The evolution of pollutants in the soil depends on the complexity of the geological environment, the transfer processes depending on their type, so that, for water-soluble pollutants, the soil represents the transport factor from precipitation to the aquifer. For some heavy metals, soil is a reservoir, as is the case with those that form hard-to-soluble compounds, these species of pollutants creating difficulties in choosing appropriate depollution technologies, especially when the polluted area is extensive. In the case of heavy pollution, the magnitude of the pollution phenomenon can affect the natural function of ecosystems, with serious effects on human health. [10, 185]

Due to the presence of anthropogenic sources of pollution, monitoring the concentration of heavy metals in soils related to urban and agricultural areas is of particular importance, especially where there is no strict delimitation of residential areas from industrial areas.

Every year, millions of tons of toxic pollutants are released into the air, both from natural sources, but especially from anthropogenic ones [186].

Due to the risk of accumulation through the food chain, heavy metal pollution endangers the health and well-being of organisms and humans, causing serious damage.

The soil is contaminated with heavy metals, it is difficult to fix. In the past, soil contamination was considered less important than air and water pollution, as soil contamination was often less visible, more difficult to manage and control than air and water pollution. Over the years, soil contamination in developed countries has steadily increased in recent years. Thus, it has become a controversial topic in the field of environmental protection globally.

A number of legislative measures have been taken or are being implemented in relation to certain metals and metalloids, in particular lead, mercury and cadmium. As a result, the contributions of these metals to arable systems appear to have declined. As for lead, air emissions from fuel combustion in Europe have fallen by around 85% in the last two decades [193]. Lead is often found in urban soils, sometimes at high levels, due to the native presence of lead in the soil and the way it has been used to pick up waste.

Children are particularly sensitive to lead exposure due to hand-mouth contact. Prolonged exposure to lead has the potential to affect children's neurological development and reduce IQ [194]. In addition, lead is not a vital component of the human body, and excessive intake can have a negative impact on the nervous, circulatory, bone, enzymatic, endocrine, and immune systems [195].

To at least one extent, there are legal regulations that limit possible entries through other sources related to agriculture, such as sludge, manure or fertilizers. These regulations include limits on the permissible content of metals in fertilizer products or soil improvers [196, 197].

Vegetable garden soils in urban areas are often affected by cadmium, especially when combined with fast-growing green crops such as endives and spinach. In the Environmental Quality Standards Directive, it is classified as a hazardous substance [198]. Therefore, it is among the most dangerous chemicals for the environment.

Another source of exposure that contains significant amounts of the metal is tobacco smoke. [199]. In addition, Cd has been shown to be responsible for the pathogenesis of myocardial infarction, peripheral arterial disease, hypertension, Itai-Itai disease, the most severe form of chronic Cd intoxication, many cancers, and diabetic nephropathy [200].

Chronic exposure to As causes different types of symptoms, including high blood pressure, neurological effects, obstetric problems, diabetes, blood vessel diseases, and of the respiratory system, as well as various skin lesions such as melanosis, Leuk melanosis, and keratosis [202].

Iron, zinc, copper, chromium, cobalt, molybdenum, manganese, and selenium are the metals considered essential for human health [206, 207]. However, high concentrations of these metals can be dangerous to humans. Although the toxic effects of metals depend on the forms and routes of exposure, disruptions of intracellular homeostasis include damage to lipids, proteins, enzymes, and DNA through the production of free radicals. [208]. Systemic toxicants include mercury, arsenic, and lead, which have the ability to induce toxicity even at low levels of exposure [209].

Wastewater treatment continues to be improved as a result of the growth of industry and the acceleration of the construction of the urban environment. Soils are the best places to treat soil sludge due to the high content of organic matter, nitrogen, and phosphorus in sludge. [210]. It is known that apart from chemicals that protect plants, a variety of organic contaminants can be found in waters and soil.

These substances are not usually actively introduced by farmers, unlike chemicals that protect plants. Instead, the emissions of these substances end up in the soil. The application of sewage sludge, which adds a variety of organic compounds to the soil, including PFAS, is an exception [211].

The chemicals most commonly found in soil include persistent organic pollutants (POPs), which are chemicals, persistent in the environment, and can bioaccumulate in the food chain.

They can be naturally present (e.g. polycyclic aromatic hydrocarbons (PAHs) or can be derived from industrial processes (e.g. polychlorinated biphenyls (PCBs) or organochlorine pesticides such as DDT, dieldrin and hexachlorobenzene HCB).

Polycyclic aromatic hydrocarbons (PAHs) form another important, widespread group of soil contaminants. [212]

Persistent organic pollutants (POPs) are chemicals that persist in the environment and can bioaccumulate in the food chain. These are among the chemicals most commonly found in soil. They can be found naturally, such as polycyclic aromatic hydrocarbons (PAHs), or they can be obtained from industrial processes, such as pesticides or polychlorinated biphenyls (PCBs). [213]

Heavy metal contamination of soil, water, and air has emerged in historical industrial practices in highly developed countries such as the United States, China, Russia, and certain European countries [214].

From coal-fired power plants to waste incinerators, the number of metals entering the environment from natural sources has increased significantly.

The risk of exposure to such metals continues to increase as a result of their prevalence. In the past, accidental exposure was mostly caused by inadequate regulations of recycling programs. [215]

2.1. Impact of heavy metal contamination in soil

2.1.1. Impact on soil microbial and enzymatic activity

Soil microbial and enzymatic activity can have a significant impact on soil quality [216]. Some researchers argue that soil microbial biomass is a significant indicator that can indicate the level of soil contamination [217]. It was found that increasing the concentration of heavy metals reduced the activities of almost all enzymes in the soil by 10 to 50 times. [219] These reactions have dramatic effects on soil.

2.1.2. Impact in plants

Plants have developed complex mechanisms throughout evolution to overcome these biotic and abiotic challenges. Elements such as Zn, Cu, Al, Pb, Cd, and As are among the most diverse types of metals and metalloids that influence plants. Hyperaccumulation, tolerance, exclusion and chelation with organic molecules are important strategies. [220]

Recent studies in the field have improved the understanding of the plasticity of the plant genome to help them cope with these stimuli [221].

2.1.3. Impact on animals

Exposing animals to heavy metals through contaminated food and water is the leading cause of exposure to pollution from humans. Heavy metals remain in the body after ingestion for a long time. The type of exposure determines whether heavy metals cause acute or chronic, clinical, subclinical, or subtle toxicity.

Toxic metals disrupt cellular homeostasis by creating free radicals, which cause oxidative stress [226]. Highly toxic metals such as As, Cu, Hg, Cd, and Pb can exert adverse effects even in minute concentrations, without providing beneficial biological effects in animals [229].

Contamination with metals in the animal environment endangers both the health of animals and human consumers in the food chain. Therefore, this topic is extremely important for informed decision-making in agricultural and veterinary practices.

2.1.4. Impact on humans

Current research indicates that heavy metals from urban soils can reach the body through skin absorption and inhalation of dust, among other things, which has a negative impact on people's health, especially children. [234]

Cd poisoning has had many detrimental effects on cellular molecules, mainly by creating an oxidant-antioxidant imbalance. The Committee of the Agency for the Management of

Toxic Substances has classified Cd as the sixth most toxic substance harmful to human health. [236]

Pb is very organizational pro. It affects and destroys numerous organs and systems of the body, including the kidney, liver, reproductive system, nervous system, urinary system, immune system, and fundamental cell and genome processes. [237]

Although the human body needs the trace elements Cu, Zn and Ni in excessive quantities from the external environment, excessive consumption of them would harm human health. Because they have carcinogenic effects, Ni and Cu are tumour favouring factors. [238]

A recent report says that As has greatly harmed farmers in Heshan Village, Shimen County, Changde City, Hunan Province, China. In this village there was an arsenic processing factory, between 1951 and 1978. Currently, the As content in the soil is 10 times higher than the allowed limit, at 92.7 mg/kg. Many plants have disappeared, and crops cannot be used for animal feed. About 1800 employees of the factory, who are also farmers from the village, were affected by persistent poisoning with As. [235]

Industrial waste, from power plants, coal burning, the metallurgical industry, car repair plants, chemical plants, etc., household garbage, construction and weathering particles on the pavement, precipitation, as well as transport emissions (exhaust gases, tire wear debris, etc.) are the main sources of heavy metal contamination of urban soils. [241]

Assessing heavy metal pollution of farmland soil is essential for managing and mitigating heavy metal pollution that is becoming increasingly hazardous. It is also the basis for reducing the risk of heavy metal contamination. There is currently no common standard for assessing soil environmental quality at home and abroad. [248]

The type and content of heavy metals in soil caused by human activities have gradually increased in recent years as a result of the growth of the global economy. This has led to a significant deterioration of the environment.

To eliminate this type of pollution, physical, chemical, biological and integrated methods have been used [249]. Metals are relatively immobile in underground systems as a result of absorption and precipitation reactions.

Therefore, in such contaminated sites, remediation methods have focused on solid-phase metal sources such as sludge, debris, contaminated soils or waste. [250]. Naturally, all soil has traces of metals. Consequently, the presence of metals in the soil cannot be considered an indication of contamination. First, the geology of the parent material from which the soil was formed affects the concentration of metals in uncontaminated soil. The concentrations of metals in a soil can exceed ranges depending on the local geology.

CHAPTER 3.
CET HIDROCARBURI ARAD

3.1. Location

CET Hidrocarburi Arad (S.C. Hydrocarbons District Heating Power Plant S.A. Arad) is located in the municipality of Arad in the eastern part of the central area, about 1 km from the Arad train station, on both sides of the Mureşel Canal. This is a branch of the Mureș River, being a restitution emissary for wastewater, resulting from the technological process carried out in society. The plant occupies an area of 3.62 ha of land, which is not part of the protected natural area. [251]

3.2. Object of activity

CET Hidrocarburi Arad is a joint stock company established in 2009, being under the authority of the Arad Municipal Council, which manages the patrimony, production capacities, primary heating networks, thermal points and manages by concession the secondary heating networks and thermal modules in the municipality of Arad. [251]

CET Hidrocarburi Arad was designed to operate on hydrocarbons (fuel oil and natural gas). It produces electricity and heat in its own power plant, takes thermal energy from S.C. C.E.T. Arad S.A. and ensures the transport, distribution and supply of thermal energy in the form of hot water in the municipality of Arad. [254]

It has the license of the National Regulatory Authority for Community Services of Public Utilities (A.N.R.S.C.) for the public service of centrally produced thermal energy [253] The district heating system in Arad is composed of two sources of thermal energy production, CET Arad S.A. and CET Hidrocarburi Arad (CET H Arad), which operate interconnected by the DN 900 supply pipeline. [251]

Since 2015, there are only four large combustion plants on the site, each with a thermal output of more than 50 MW. The plant's installations consist of an energy group consisting of two steam generators and a TA1 electric turbogenerator, and two hot water boilers (CAF), the total capacity of the four combustion plants being 362 MWt, and that of the turbogenerator, of 12 MWe. [251]

Subsequently, the thermo-energy group was put into conservation. Since 2018, only CAFs have been in operation at the plant, the fuel used to be exclusively natural gas. According to Article 33 of Law 278/2013 on industrial emissions, CET H Arad has been notified to operate until December 31, 2023, with a maximum of 17,500 hours of operation for each production unit. [254]

3.3. Investements

The old installations are in the perspective of scrapping, considering the construction of new installations. By achieving this investment objective, the aim is to build a new source of thermal energy production in high-efficiency cogeneration.

The general objective is the modernization of the centralized heat supply system of the Municipality of Arad, in order to increase the efficiency and quality of the public heat supply service to the connected consumers, with minimal impact on the environment. [255, 256, 257]

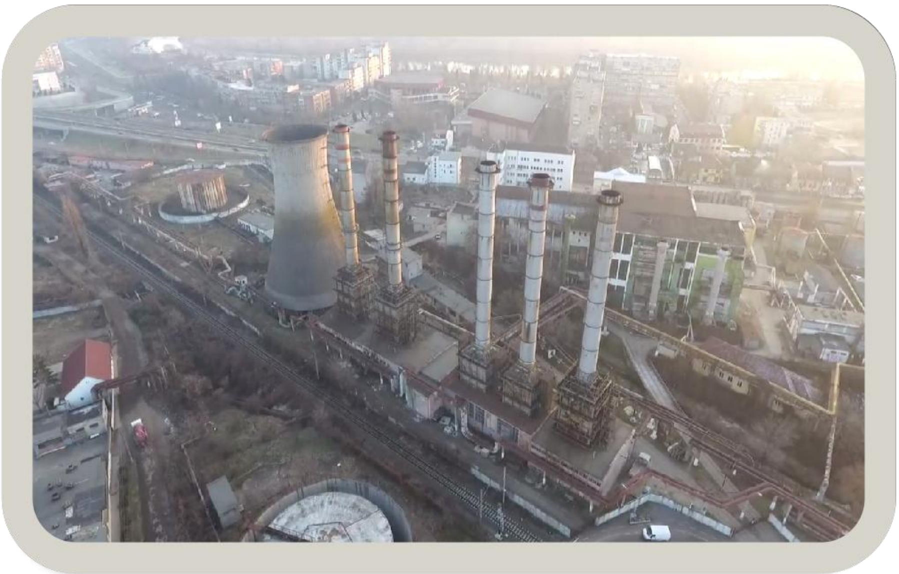

Figure 3. CET H ARAD, year 2015 [258]

Figure 4. CET H ARAD, year 2023 [259]

CHAPTER 4.
PERSONAL CONTRIBUTIONS

4.1. Evaluation of the quality of groundwater on the site of CET H ARAD

4.1.1. Introduction

The accelerated industrialization of the last decades has generated excessive contamination with various toxic substances, especially synthetic chemical compounds, in concentrations that have caused harmful transformations in the planet's ecosystems. In particular, the aquatic ecosystem is severely affected, due to discharges of water loaded with persistent pollutants, such as heavy metals or hydrocarbons, with multiple consequences for living organisms. [265]

The emissions of specific pollutants generated by the activity of district heating plants require careful monitoring. The soil around the plants is often subject to direct contact with them, as a result of the technological activities carried out on site, with the risk of chemical pollution produced by various substances released into the environment.

The quality of groundwater is directly influenced by the activities specific to the industrial technological process carried out at ground level, through the impact of specific pollutants generated in the form of various emissions. At the level of the plant there are requirements established by the integrated environmental permit, the water management permit, in accordance with national and European legislation.

The aim of this study was to assess the groundwater quality and perform a groundwater pollution analysis at the site of a hydrocarbon-fired power plant, currently fueled exclusively by natural gas, which was previously fueled by coal and fuel oil.

The assessment methodology is based on the use of the Global Pollution Index *($*I_{GP}$)* and has been applied for three sampling points, analyzing four authorized quality indicators.

This is one of the methods applied for environmental impact assessment and has been proposed by Zaharia [267] with applicability on environmental factors including groundwater. A number of chemical factors have an impact on groundwater quality.

The result of the pollution index *(I^*_{GP})* gives a single value that shows the total pollution rate, in this case of groundwater. The method applied is simple, based on data processing and provides accurate and impact-oriented information. The value *(I^*_{GP})* also provides an accurate representation of the degree of well contamination [268].

4.1.3. Materials and methods

4.1.3.1. Materials

Three groundwater boreholes located on the CET H Arad site were used. The interception boreholes are called Control Wells and have the following coordinates in the STEREO 70 stereographic projection system, which are shown in Table 1. The depth of the groundwater aquifer is about 10 m, the control wells being provided with metal protection fences and covers.

Table 1. STEREO 70 coordinated of the sampling sites [260]

Authorised sampling point	**STEREO 70 Coordinates**	
Location CET H Arad **Authorized Area**	Coordinate X	Coordinate Y
Control well No. 1 (PC1)	217188.26	526720.76
Control well No. 2 (PC2)	217343.56	526687.81
Control well No. 3 (PC3)	217182.34	526835.62

Figure 5. Satellite image - CET HIDROCARBURI ARAD, ROMANIA
with the location of groundwater sampling points in the authorized areas [272]

4.1.3.2. Methods

In this study, values measured at groundwater were collected for the following parameters: *pH, Total Suspended Matter, Fixed Residue at 105°C* and *Chemical Oxygen Consumption (COD-Cr).* The sampling was carried out for a period of 11 years, between 2010 and 2020, in an annual database. The determinations were carried out in compliance with the approved official methods.

The measured values for groundwater were compared with five benchmarks, respectively, with the authorized reference values, with those in accordance with the historical level of the CET H in the period 2008-2017, with the legal values allowed (A) for drinking water and exceptionally admitted (AE), and with the legal values provided for technological wastewater discharged into the aquatic environment.

The results obtained for the Global Pollution Index *(*I_{GP})* have been illustrated graphically for each sampling point considered in this study.

The authorized reference values are presented in Table 2 together with the historical level values from 2008-2017.

4.1.4. Legislation

The legislation applicable to groundwater on industrial sites in Romania includes several normative acts that regulate the protection and management of groundwater, but does not explicitly provide for the accepted values for the quality indicators monitored in this study.

In the case of industrial units, local and national environmental authorities may issue additional regulations or specific requirements for certain activities carried out.

In the case of CET H Arad, for the monitoring of groundwater, the regulatory authority has provided, in the Water Management Authorization, as quality indicators, the following parameters: *pH, Total suspended solids, Fixed residue at 105°C* and *Chemical oxygen consumption (COD-Cr),* which were also provided in the Integrated Environmental Authorization issued by the local environmental authority.

The admissible values for the quality indicators stipulated in the authorizations are the values measured at the time of authorization, according to the Bulletin of physico-chemical analysis dated 14.11.2008, CET H Arad, which were considered as control samples and legal reference for the determinations to be carried out later [274].

The CET H site is not a designated area for water abstraction for drinking water purposes. The groundwater aquifer related to the site belongs to the groundwater body ROMU20, and the deep groundwater aquifer belongs to the groundwater body ROMU22, according to the Water Management Authorization CET H [260].

OM 621/2014, which sets out the permissible values for the quality indicators for groundwater bodies in Romania, does not provide permissible values for the groundwater aquifer, nor does it contain provisions for the parameters *pH, Total suspended solids, Fixed residue at 105°C* and *COD-Cr.* [277]

Each country or region within a country has its own quality standards. However, worldwide there is a tendency towards a common basis, resulting from the experience and needs of all. [278]

In this respect, the World Health Organization has issued and periodically reissues the necessary guidelines and international bodies such as the European Union also promote detailed or at least indicative common standards, such as the Directive on the quality of water intended for human consumption [279]. In Romania, the quality standard for drinking water in the 1980s was STAS 1342/84, and currently, it is STAS 1342/1991.

The authorized reference values are presented in Table 2, together with the historical level values.

Table 2. Reference levels for groundwater at CET H ARAD [260, 261].

Sampling point	Legal reference level *Test control_ Year 2008 cf. W. M. Auth. and AIM CET H Arad				Historical reference level CET H Arad for the period 2008-2017 according to W. M. Auth. and AIM CET H Arad documentation			
Location CET H Arad	**Quality indicators (i) Maximum Allowable Values (MAC_i)**				**Quality indicators (i)**			
Authorised zone	**pH**	**TSS**	**Fixed residue at 105°C**	**COD-Cr**	**pH**	**TSS**	**Fixed residue at 105°C**	**COD-Cr**
	[pH units]	[mg/l]	[mg/l]	[mg/l]	[pH units]	[mg/l]	[mg/l]	[mg/l]
Control well No. 1	7.00	3.00	401.10	8.40	7.00-7.50	17.40-19.00	303.00-411.60	5.70-8.40
Control well No. 2	7.50	2.10	503.00	5.60	7.00-7.50	8.20-14.00	264.00-417.20	2.40-5.80
Control well No. 3	7.00	1.60	458.20	4.90	7.00-7.50	9.40-13.00	192.00-421.60	4.90-5.50

The values admitted according to STAS 1342/91 – DRINKING WATER for the quality indicators considered in the study are presented in Table 3.

Table 3. Quality indicators for drinking water [262, 263].

STAS 1342-91-DRINKING WATER Quality indicators (i)							
Allowed values (A)				**Values exceptionally allowed (AE)**			
pH	**TSS**	**Fixed residue at 105°C**	**COD-Cr**	**pH**	**TSS**	**Fixed residue at 105°C**	**COD-Cr**
[pH units]	[mg/l]	[mg/l]	[mg/l]	[pH units]	[mg/l]	[mg/l]	[mg/l]
6.50 -7.40	-	100.00-800.00	3.00	max. 8.50	-	30.00-1200.00	5.00

Table 4. Quality indicators for technological wastewater discharged into the aquatic environment cf. DECISION no. 188 of 28 February 2002 for the approval of some norms regarding the conditions of discharge of wastewater into the aquatic environment [264]

TECHNOLOGICAL WASTEWATER **Quality indicators (i)**			
Permissible values (A)			
pH	**TSS**	**Fixed residue at 105°C**	**COD-Cr**
[pH units]	[mg/l]	[mg/l]	[mg/l]
8.50	60.00	2000.00	-

A groundwater mirror in wells is an indicator of groundwater levels. Groundwater flows under the action of gravity, just like surface water. However, the flow velocity of groundwater is slower because of the type of rock (grain size or pore size) which also acts as a filter. The water positions are shown on hydrographic maps. [306]

The shallow subsurface groundwater aquifer level, known as the water table, was found at the site at a depth between 8.0 m (PC2) and 8.2 m (PC1 and PC3) with varying levels depending on rainfall.

Samples were taken from the control wells after pumping an appropriate volume of water from each well equal to at least three times the borehole volume. Sampling was carried out using a special device (bailer) according to the sampling standard in force, ISO 5667-11:2009. A visual examination was carried out during sampling, after which the water samples were placed in plastic containers, prepared and labeled accordingly, and transported to the laboratory under controlled temperature conditions, where physico-chemical analyses were carried out within 24 hours after sampling.

4.1.5. Study area

The site of CET H Arad is located in the municipality of Arad, in the eastern part of the central area, about 1 km from Arad railway station, on either side of the Muresel Canal, which is a branch of the Mures River, and also a restitution emissary for wastewater resulting from the technological process. The plant occupies an area of 3.62 ha of land, which is not part of the protected natural area. [251]

4.1.6. Hydrographic network

On the territory of Arad County, the hydrographical network is formed by two main river basins: BH Mures and BH Crișul Alb. The Mureș River flows through Arad County in the south, and the Crișul Alb River, together with its tributaries Dezna, Chicher and Teuz, flows in the north.

4.1.6.1. Mures alluvial fan

The Mures river alluvial fan has a total surface area of 2,210 km2, of which 2,040 km2 is on Romanian territory. The aquifer at medium depth, in the fluvio-lacustrine deposits, is the largest source of groundwater from which most uses are supplied. The hydrostatic level is influenced by variations in the climatic regime, which also affects the flow rate of the surface aquifers that supply the underground aquifer. [280, 281]

4.1.7. Sources of water pollution in Arad County

On the territory of Arad County, there are a variety of polluting sources affecting the quality of surface and groundwater. They can be both point sources (industrial, agricultural, local) and diffuse (chemical fertilizers and pesticides used in agriculture, animal husbandry, etc.).

The report on the state of the environment in Arad County in 2007, issued by APM Arad, indicates the areas that are in a critical state in terms of surface and groundwater pollution due to human activities.

In Romania, groundwater, phreatic and deep water bodies have been established following the implementation of the EU Water Directive. The regional authorities responsible for managing these resources will oversee these water bodies [293].

According to the multi-annual assessment carried out by the National Administration "Romanian Waters" in 2021 and summarized in the document "Synthesis of water quality in Romania in the period 2018-2020", 141 groundwater bodies were monitored and assessed in the period 2018-2020.

The individual assessments also included the groundwater body ROMU20, which belongs to the Mureș River Basin, which also includes the groundwater related to the CET H Arad site. The results showed exceedances of the quality standard for nitrogen in several areas.

According to the assessment methodology, the groundwater body ROMU20 is classified in poor chemical status, because the areas occupied by boreholes with exceedances of the quality indicator for nitrogen represents 22.31%. [283]

4.1.8. Deep groundwater body ROMU22 - Mures alluvial fan (Lower-Middle Pleistocene).

It is a groundwater body of medium depth, confined in the porous-permeable deposits of the alluvial fan of the Mures River.

4.1.8.1. Assessment of the chemical status of the water body ROMU22

Between 2018 and 2020, 6 boreholes in the national hydrogeological network were qualitatively monitored. Water body status indicators include nitrate (NO^{3-}), total chromium (Cr^{3+} + Cr^{6+}), nickel (Ni^{2+}), copper (Cu^{2+}), zinc (Zn^{2+}), lead (Pb^{2+}), cadmium (Cd^{2+}), arsenic (As^{3+}) [283].

Slight exceedances of the threshold values for ammonium and orthophosphates were recorded at the Păuliș F7MA borehole, so that, by applying the assessment methodology, the area with exceedances occupied by the borehole represents less than 20% of the total surface area of the water body, leading to the classification of the ROMU22 water body in good chemical status. [283]

4.1.10. Methodology for environmental impact assessment

The assessment methodology is based on the use of the *Global Pollution Index* (I^*_{GP}) and was applied to three sampling points, analysing four authorized quality indicators.

One of the methods applied for assessing the impact on the environment is the *Global Pollution Index* $^*I_{GP}$ proposed by Zaharia [267]. The value of the groundwater pollution index (I^*_{GP}) provides a single value that shows the total groundwater pollution rate. A number of chemical factors have an impact on groundwater quality.

The value (I^*_{GP}) provides an accurate representation of the degree of contamination of the well [268].

First of all, *the Quality Index* (EQ_i) was calculated according to the following equation:

$$EQ_i = C_i / MAC \quad (1)$$

Where:

EQ_i is the Quality Index for parameter i,

C_i is the measured value for the parameter under consideration, and MAC_i is the maximum allowable value for parameter i.

After the *(EQ_i)* was calculated, an Evaluation Score *(ES_i)* was assigned for each parameter, according to the values presented in Table 5, which can be consulted in the thesis.

To assess the impact on the groundwater aquifer, a correlation of the *Global Pollution Index ($*I_{GP}$)* with the effects in the water body was made, as shown in Table 6.

Table 6. Correlation of Global Pollution Index I^*_{GP} with effects in the water body [267]

Values I^*_{GP}	**Consequences in the body of water**
1	body of water untouched by human activity
$1 \leq I^*_{GP} < 2$	body of water where human activity is permitted within reasonable bounds
$2 \leq I^*_{GP} < 3$	aquatic body where human activity is bringing distress to living forms
$3 \leq I^*_{GP} < 4$	human activity-damaged body of water that disrupts biological forms activity
$4 \leq I^*_{GP} < 6$	body of water where human activity has seriously impacted and endangered living forms
$I^*_{GP} > 6$	degraded body of water unfit for all living forms

4.1.11. Results and discussions

This study was conducted by applying a previously developed method for the calculation of a *Global Pollution Index (I^*_{GP})* that can be used for the assessment of groundwater quality at the CET H Arad site.

For this purpose, the measured values for the authorized quality indicators in water samples taken from the authorized sampling points, identified by three monitoring wells, were collected annually for eleven years.

The results obtained for (I^*_{GP}) show that effects related to the state of discomfort for life forms predominate in 93.94% of all cases, with 6.06 values within the permissible limits, in relation to the legal reference set in the water management authorization, respectively in the integrated environmental authorization, which refers to the 2008 control sample, considered legal reference for subsequent determinations.

The most affected by the state of pollution is PC3, which over the entire study period recorded values of *(I^*_{GP})* correlated with the state of discomfort for life forms.

The values of the Global Pollution Index show that the state of the groundwater aquifer has not changed even after 2014, the year corresponding to the implementation of European regulations, harmonized at national level.

By analyzing the technological data recorded in the plant's documents, as well as the emission monitoring data reported to the environmental authorities, it is not possible to make a direct correlation of the results obtained for *(I^*_{GP})* based on the existing records.

In comparison with the historical level of CET H Arad, corresponding to the period 2008-2017, it can be concluded that there was no significant worsening of the pollution state, given that values within the permissible limits predominate, in the percentage of 78.79%.

However, taking into account the predominance of exceeded values recorded for the *Global Pollution Index (I^*_{GP})*, in relation to the authorized permissible values, which correspond to the discomfort effect for life forms, as well as the fact that the groundwater on the site of CET H Arad is part of the groundwater body ROMU20, which upstream and downstream, outside the perimeter studied, is used as a source for drinking water, I consider that it would be advisable to develop and implement a sustainable water management plan.

Even if, at present, decommissioning works of the old installations continue on the site, in parallel with the construction of new technological units, and monitoring is carried out in accordance with the operating permits, it would be beneficial to identify and monitor emerging pollutants.

I believe that, in the future, it would be appropriate to carry out a study to assess the quality of groundwater on the site, at the same time as assessing the groundwater aquifer upstream and downstream, outside the perimeter of the Arad CET H, taking as a reference the law on the approval of threshold values for groundwater in Romania.

An explanation for the fact that the COD-Cr was low in 2017 compared to the other years studied cannot be issued on the basis of the technological data existing in the documents recorded in the plant's database or in the reports submitted to the environmental authorities, so that the results obtained can be correlated with the plant's activity, respectively with the number of operating hours of the combustion installations, stack emissions, falling within the permissible limits for all pollutant species emitted into the atmosphere, in each year of the period studied, 2017, not being recorded with a lower number of operating hours compared to the other years of study. CET H Arad does not release any emissions leading to variations in COD-Cr.

In aquatic ecosystem research, the chemical oxygen consumption (COD-Cr) value is very important. This quantity indirectly describes the content of organic and mineral substances in the water that have been oxidized by a strong oxidant under specific conditions. The amount of oxygen that is required to oxidize organic substances in a given volume of water is known as chemical oxygen consumption. The determination (COD-Cr) measures the amount of organic compounds, including those that are hardly degradable.

The specific technological activities carried out on the soil were at the usual level. A probable explanation could be the variation of the hydrogeologic level in the water table with increasing loading, which would cause a decrease in the concentration of organic and mineral substances present in the water table.

In 2017, the city of Arad recorded heavy rainfall in terms of quantity, which produced increases in the Mures River flows and groundwater aquifer recharge.

In the framework of this study, precipitation changes were not monitored, strictly following groundwater quality based on the results of monitoring carried out according to the legal requirements laid down in the operating permits issued by the environmental authorities for CET H Arad, but the plant emissions into the air, treated technological waters and soil were monitored.

During the period studied, there were no exceedances of the permissible values for the quality indicators monitored for these environmental factors, as required by the company's operating permits.

Chemical oxygen demand has increased at PC1, especially in the last four years. Concerning the factors that could have led to this increase, as a hypothetical factor, a possible external contribution could be considered, caused by the existence of an underground sewage collection tank, located in the vicinity of PC1, at about 15 m, belonging to an economic unit located in the immediate vicinity of the CET H Arad site. This tank is below the level of the municipal sewage network, the wastewater being pumped into this network.

Another hypothetical factor would be the existence of a fuel oil reservoir, which was decommissioned in 2010, in this area a series of works were carried out, which have continued to the present day, the area being allocated to the storage of sections of the decommissioned installations, on the site of CET H Arad, carrying out activities related to the plant's retrofitting.

CET H Arad did not pollute, taking into account the environmental factors monitored, air, treated technological water, soil, which did not show exceedances during the period studied.

Only in the groundwater aquifer were results recorded indicating a level of pollution correlated with discomfort for life forms.

The changes at the monitoring well PC3, which showed I^*_{GP} values producing discomfort effects for life forms during the whole period studied, could be potentially caused by the existence of the reagent storehouse used for chemical water treatment in its immediate vicinity, where different substances used in the technological process are discharged, stored and handled.

Currently, the reagent storehouse has been decommissioned and is located in the perimeter allocated for the construction of the new production units of the plant, which is undergoing a major process of modernization.

It is likely that, in order to obtain the necessary operating permits for the new production units, the environmental authorities will have to reconfigure the sampling points for groundwater and other environmental factors that will be subject to authorized monitoring.

Considering 123 years of technological activity on the same site, even if PC3 pollution is present, in the range $2 \leq I^*_{GP} < 3$, we consider these results for I^*_{GP} satisfactory, given that the negative effect represents only discomfort for life forms, which places it in the range of the accepted values, $1 \leq I^*_{GP} < 2$, given the range $I^*_{GP} > 6$, which indicates a degraded water body, unsuitable for any life forms.

The data collection process was carried out on an annual database, obtained from the physico-chemical determinations performed on each monitored quality indicator, from momentary water samples, as stipulated in the operating permits of CET H Arad, for a period from 2010-2020.

The results obtained for (I^*_{GP}) from the study were also represented in the form of graphs, in the figures below:

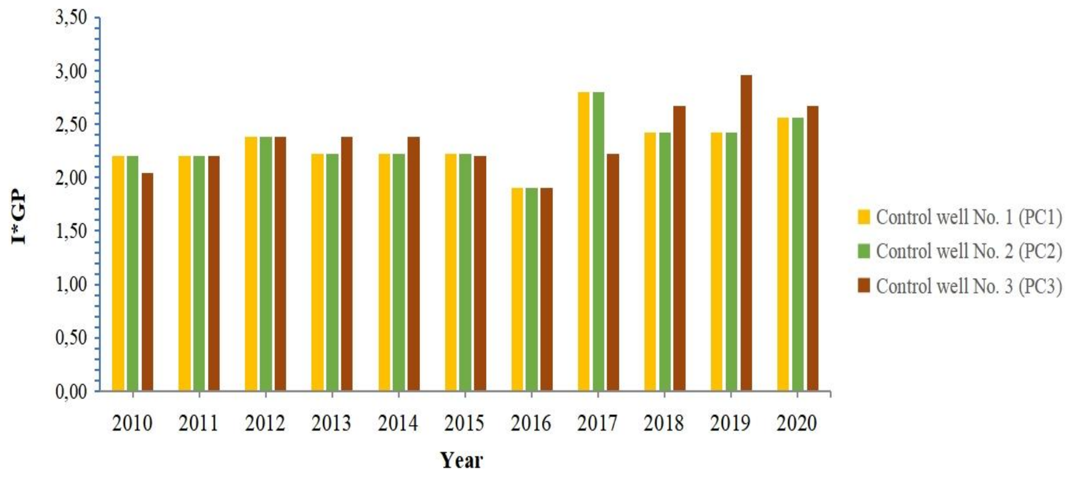

Figure 12. Results obtained for $\mathbf{I^*_{GP}}$ according to the reference Water Management Permit/ Integrated Environmental Permit CET H Arad

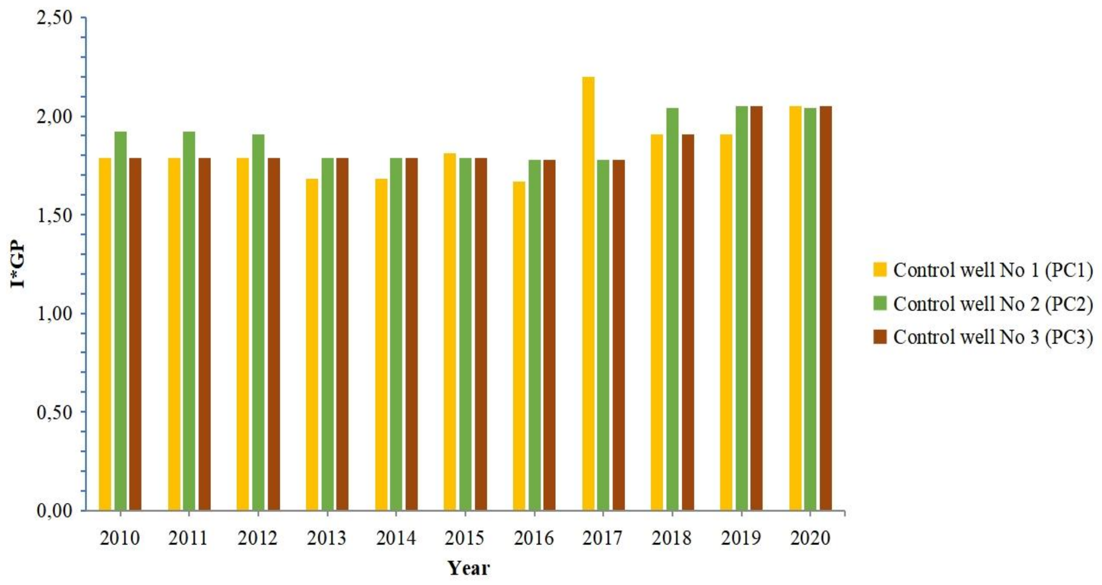

Figure 13. Results obtained for I^{*}_{GP} according to the reference Historical level of annual average values CET H Arad - Period 2008-2017

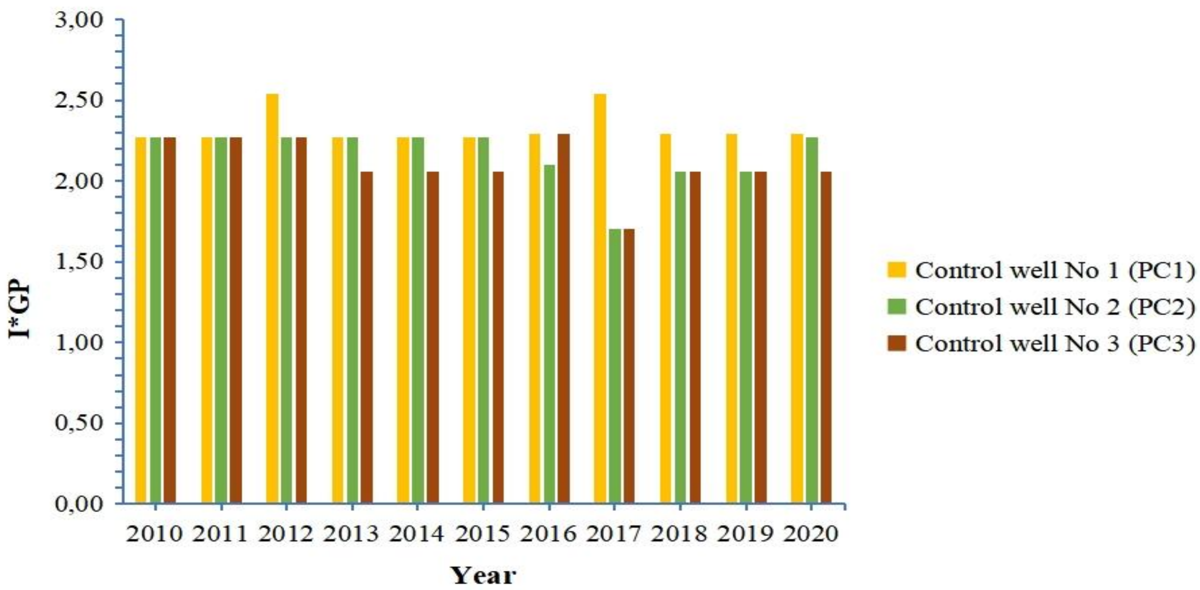

Figure 14. Results obtained for I^{*}_{GP} according to the reference STAS 1342-91 DRINKING WATER - Permissible values (A)

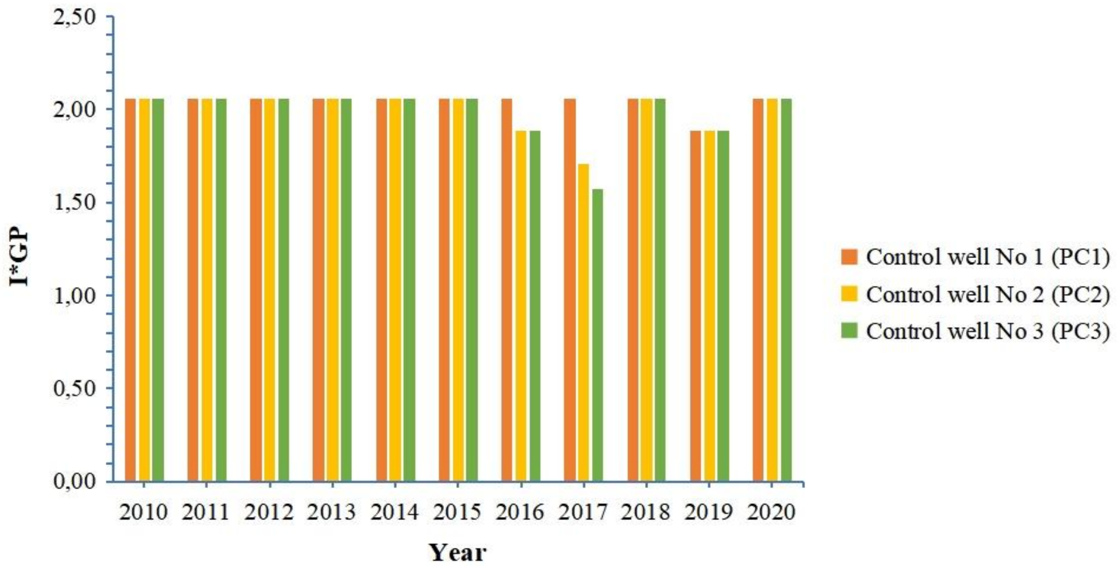

Figure 15. Results obtained for $\mathbf{I^{*}_{GP}}$ according to the reference STAS 1342-91 DRINKING WATER - Exceptionally permissible values (EA)

Figure 16. Results obtained for $\mathbf{I^{*}_{GP}}$ according to the reference HG 188/2002 on technological wastewater discharged into the aquatic environment

4.1.12. Conclusions on groundwater quality at the site

In conclusion, in the studied period, covering the years 2010-2020, the state of the groundwater aquifer related to the site of CET H Arad, indicates for the values of the *Global Pollution Index* (I^*_{GP}) effects correlated with the state of discomfort for life forms, which predominate in all the referential cases used, except for the values obtained in relation to the historical level of CET H Arad, for the period 2008-2017, where values within the permissible limits predominate, in percentage of 78.79%.

In the case of the values obtained for (I^*_{GP}) in relation to the water management authorization and the integrated environmental authorization, effects related to the state of discomfort for life forms predominate in 93.94%, with 6.06 values within the permissible limits.

The same percentages were also obtained when using the standardized values for drinking water (A) as a reference. 78.79% of the standardized values for drinking water (AE) were related to the discomfort state and 21.21% to values within the permitted limits.

In the case of the values obtained for (I^*_{GP}) in relation to the permissible values for technological wastewater discharged to the aquatic environment, the same percentages were obtained as in the case of the reference standardized values exceptionally permissible for drinking water (AE)

In relation to the permitted permissible values admitted, the results obtained show as an effect a state of damage to the groundwater body, causing discomfort to life forms, except in 2016, at PC1 and PC2, when the values obtained are within the permissible limits.

ROMU20 is a phreatic groundwater body formed in the upper part of the alluvial cone of the Mures River, in deposits classified as Upper Pleistocene-Holocene age, with an area of 2222.68 km^2, on the Romanian territory. [283]

Precipitation falling over the entire alluvial cone and seepage from the Mures River feed the groundwater aquifer. The river contributes a flow of 640 l/s to the aquifer over a 16 km length between Păuliș and Arad, according to borehole studies carried out by ISPIF Bucharest (National Research and Development Institute for Land Improvement Bucharest) in the Mures riverbed. [261]

According to the multi-annual assessment carried out by the National Administration "Romanian Waters" in 2021, reproduced in the document „Synthesis of the quality of Romanian waters in the period 2018-2020 in the period 2018-2020, 141 groundwater bodies were monitored and assessed [283].

The individual assessments also included the groundwater body ROMU20, which belongs to the Mureș River Basin (ROMU22), and of which the groundwater related to the CET H Arad site is part.

Between 2018 and 2020, twenty hydrogeological boreholes that are part of the ROMU20 body were monitored. According to the assessment methodology the medium deep groundwater body ROMU22 was classified in good chemical status however, the groundwater body ROMU20 was classified in poor chemical status. [283]

Considering this result we can deduce that the groundwater body ROMU20, implicitly the aquifer related to the site, is not supplied with good quality water, therefore there would be a possibility of affecting the groundwater quality in the studied perimeter to some extent, implicit of the result related to the Global Pollution Index (I*GP), which indicates 93.94% of effects correlated with the state of discomfort for life forms in the groundwater aquifer located on the site of CET H Arad, in relation to the permissible values provided in the water management authorization, respectively in the integrated environmental authorization.

Considering these results, a study on the quality of the groundwater body ROMU20, upstream and downstream, outside the CET H Arad site, taking into account a unitary set of quality parameters, would be appropriate in order to exclude a possible contributing influence from outside the studied perimeter.

4.2. Evaluation of heavy metal concentrations in soil on the CET H ARAD site

4.2.1. Introduction

The soil is subject to contamination, as a consequence of anthropogenic activities, especially industrial ones, which have a major impact. Emissions from the energy sector directly affect the quality of air, soil, subsoil and water bodies, with heavy metals aa an important category of pollutants. [313]

In the case of district heating power plants, heavy metal emissions come from large combustion plants, in the form of dust, and affect the soil, by deposition on site and in the vicinity, sometimes over long distances [311].

The negative effect of heavy metals can be a result of high levels in the concentration of the air around the emitting sources with deposition and assimilation in water bodies and in the food chain. Heavy metal compounds participate in the global transport of substances, in the form of aerosols in the upper atmosphere having micro and nanometre dimensions. [314]

There is no identifiable threshold below which these substances do not pose a risk to human health. Heavy metal pollution has a significant impact on life due to its extreme toxicity, lack of biodegradability and accumulation, severely affecting ecosystem processes and human health [315]. Heavy metals are recognized carcinogens with genotoxic action for living beings.

Industrial district heating power plants have strict requirements related to the quality of the soil in the area of the site, imposed by national and European legislation in the field of environmental protection, for an effective monitoring of emissions, in order to prevent and reduce the impact on the environment [316].

4.2.3. Materials and methods

4.2.3.1. Materials

Soil samples were taken, from the site of the plant, from the authorized area, from two depth profiles, 10 and 40 cm respectively.

It is not recommended to collect soil samples after rain or when the moisture level is high, as it may cause errors in the estimation of pollutant levels and homogenization. When the soil does not stick together and can be crumbled in the hand, this is a correct sample. The sample can be collected using a spade, probe or any clean instrument available.

Figure 21. Satellite image of CET HIDROCARBURI ARAD, ROMANIA with the positioning of the authorized sampling area for heavy metals [325]

4.2.3.2. Methods

In this study, values were collected for a number of 120 soil samples from the sampling points located in the authorized area on the CET H Arad site, analyzing the following parameters, foreseen in the AIM of CET H Arad as quality indicators for heavy metals: Cu, Zn, Pb, Ni, Cd, Ni, Cd and total Cr.

The table shows the stereo coordinates of the sampling points for soil samples in the authorized area.

Table 10. STEREO 70 coordinates for authorized soil sampling points on the CET H Arad site [254]

Soil sampling point Authorized Area Location CET H Arad Heavy metals	**Sampling profile**	**STEREO 70 Coordinate**	
	Depth	X Coordinate	Y Coordinate
S3	10 cm	211955.01	461053.96
S3*	40 cm		

The sampling was carried out over ten years, between 2011 and 2020, on an annual database. The determinations were made in accordance with officially approved methods. The identification and quantification of heavy metals contained in the soil can be used as a pollution fingerprint in the targeted industrial areas.

4.2.4. Legislation

The plant has strict requirements regarding the quality of the soil in the site area, imposed by the authorization, in accordance with the national and European legislation in the field of environmental protection. It contains monitoring requirements appropriate to pollutant discharges, specifying the measurement methodology and frequency.

The monitoring was carried out on the basis of annual programs and provides, according to *the Integrated Environmental Authorization*, respectively *OM 756/03.11.1997, that the values of the concentrations of heavy metal pollutants specific to the activity, present in the soil of the company's land, must not exceed the alert threshold for less sensitive use land, and it is advisable not to exceed the values determined in 2008, according to *the CET H Arad Site Report,* carried out to obtain the authorization.

The authorised reference values for heavy metals in soil are presented in Table 8.

Table 8. Legal reference values for heavy metals in soil - CET H Arad [254]

Sampling point	Quality indicator	Sampling profile	Legal reference values for heavy metals in soil			
			cf. Site Report CET H Arad Year 2008	cf. AIM CET H Arad *OM 756/03.11.1997 for land of less sensitive use		
Location CET H Arad	Heavy metal	Depth	Measured value	Value Normal	Alert threshold	Intervention threshold
Authorized area		[cm]	Concentration ($C_{s,i}$) [mg/kg s.u.]			
S3	Copper	10	34.10	20.00	250.00	500.00
S3*		40	40.70			
S3	Zinc	10	87.50	100.00	700.00	1500.00
S3*		40	96.20			
S3	Lead	10	47.80	20.00	250.00	1000.00
S3*		40	109.80			
S3	Nickel	10	16.90	20.00	200.00	500.00
S3*		40	27.00			
S3	Cadmium	10	1.70	1.00	5.00	10.00
S3*		40	1.50			
S3	Total chromium	10	11.80	30.00	300.00	600.00
S3*		40	20.30			

4.2.5. Study area

The location of CET Hidrocarburi Arad, Iuliu Maniu Blvd., no. 65-71, Arad city, Arad County, Romania.

4.2.7. Applied methodology

For the calculation *of the Global Pollution Index (PLI),* the methodology presented by Kowalska [329, 330, 331] was applied. The *CF* and *PLI indicatives* were used to assess the heavy metals individually, respectively, the general pollution status.

The results of the analyses performed were centralized in xls (Excel Binary File Format) documents and were interpreted by summary statistical methods.

First, the *Individual Pollution Index* (CF_i) was calculated. It is used to determine the heavy metal that poses the greatest threat to the soil. It is calculated separately for each heavy metal analyzed according to the formula:

$$CF_i = C_{s,i} / B_i \quad (1)$$

where:

$C_{s,i}$ is the concentration of the heavy metal i at the point s,

B_i is the value of the geochemical background level of the heavy metal in the study area.

It represents the native endowment of the soil with the heavy metal, respectively the concentration of heavy metal in the natural soil background. The obtained results can be consulted in the table in figure 30 of the thesis.

In the calculation of the *Individual Pollution Index (CF_i),* the Value of the geochemical background level (B_i) for heavy metals in Romania [332] was taken into account. Considering that there is no database for the geochemical background level of heavy metals in Arad County, the comparison of the obtained values for heavy metal concentrations was made with the national geochemical background values for heavy metals. It would be useful to conduct a study in this field, and it could constitute a research topic in the future.

4.2.7.1. Individual assessment for heavy metals and general pollution status

The CF levels are classified as follows: CF ≤ 1 – unpolluted; 1 < CF ≤ 2 – low level of pollution; 2 < CF ≤ 3 – moderate level of pollution; CF > 3 – very high level of pollution.

These levels must be equated by calculation with the values of O.M. 756/03.11.1997 for land of less sensitive use.

Considering that the soil of the studied site is of an industrial type, being legally classified according to O.M. 756/03.11.1997 in the category of land of less sensitive use, we have calculated the corresponding *Individual Pollution Index CF_i* for the authorized values and also for the values initially determined in 2008, provided in the Site Report CET H, to have an equivalent CF comparison term, necessary in this case.

Also, the CF levels classified as well as the expression of the *Global Pollution Index (PLI)* had to be reconsidered in relation to the values admitted according to O.M. 756/03.11.1997 for the category of land of less sensitive use, for a correct and adequate assessment.

Initially, the concentrations of heavy metals ($C_{s,i}$) were evaluated in relation to national legislation for less sensitive land use and against the reference determinations from 2008, according to the authorization.

The details regarding the obtained results can be consulted in Table 11 of the thesis, where they are presented. The values that exceeded the accepted limits according to AIM CET H Arad are marked in yellow cells.

Then, the individual pollution index CF_i corresponding to the authorized values and the values initially determined in 2008 was calculated to have an equivalent CF comparison term, necessary in this case. The obtained results can be visualized in the Table 12, in the thesis.

The results obtained for the Individual Pollution Index (CF_i) of heavy metals at the two sampling profiles, 10 and 40 cm respectively, are graphically illustrated in Figures 31 and 32.

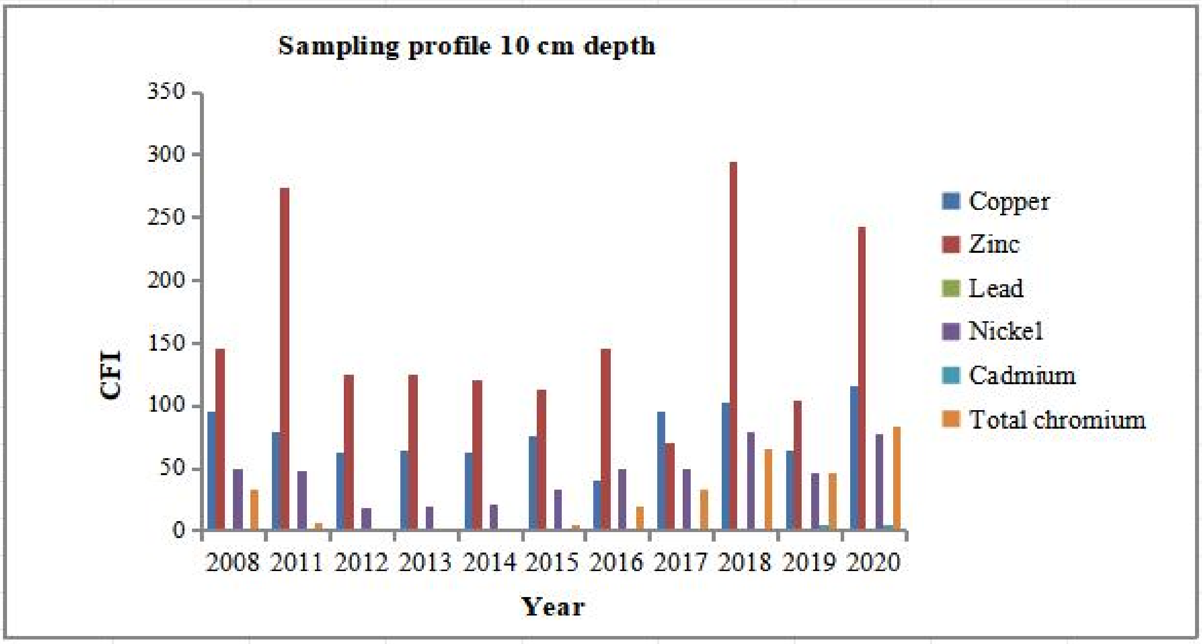

Figure 31. Results obtained for the Individual Pollution Index (CF_i) of heavy metals, sampling profile at 10 cm depth

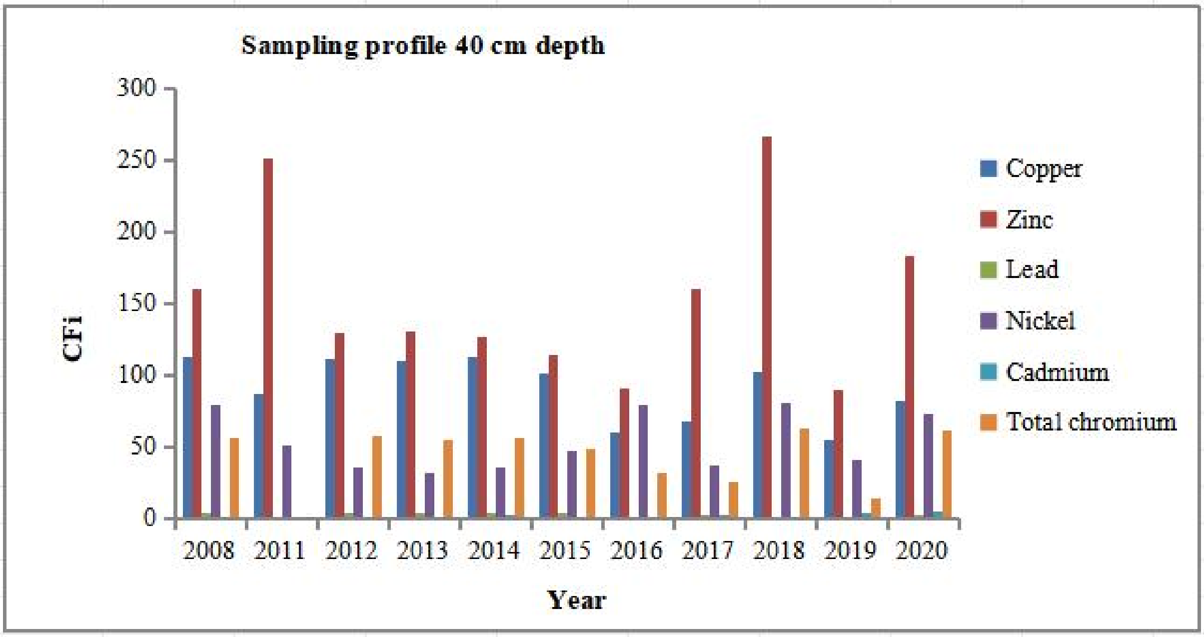

Figure 32. Results obtained for the Individual Pollution Index (CF_i) of heavy metals, sampling profile at 40 cm depth

The assessment of the degree of soil pollution was carried out by calculating *the Global Pollution Index (PLI).* This index shows the level of heavy metal contamination of the soil and is obtained based on *the Individual Pollution Index (CF_i)*. PLI is calculated as a geometric mean of CF_i according to the formula:

$$\text{PLI} = \sqrt[n]{(CF_1 \times CF_2 \times CF_3 \times \ldots CF_n)} \qquad (2)$$

where:

n – the number of heavy metals analysed;

CF – individual pollution index calculated for each heavy metal analysed.

The Global Pollution Index (PLI) was calculated for the authorized legal reference values, according to O.M. 756/03.11.1997 and the *Site Report of the plant*, from 2008, in order to have an equivalent comparison term in the case of land of less sensitive use, as in the case of this study. The results are presented in Table 14.

Table 14. Results Global Pollution Index for Heavy Metals (PLI) calculated based on legal reference values for CET H

<table>
<tr><th>Sampling point</th><th>Sampling profile</th><th colspan="4">Global Heavy Metal Pollution Index (PLI) calculated based on legal reference values</th></tr>
<tr><td>Location CET H Arad</td><td rowspan="3">Depth [cm]</td><td>cf. Site Report CET H Arad Year 2008</td><td colspan="3">cf. AIM CET H Arad *O.M. 756/03.11.1997 for land of less sensitive use</td></tr>
<tr><td rowspan="2">Authorized Area</td><td>Determined value</td><td>Normal value</td><td>Alert threshold</td><td>Intervention threshold</td></tr>
<tr><td>(PLI)</td><td>(PLI)</td><td>(PLI)</td><td>(PLI)</td></tr>
<tr><td>S3</td><td>10 cm</td><td>19.38</td><td rowspan="2">17.22</td><td rowspan="2">155.98</td><td rowspan="2">367.66</td></tr>
<tr><td>S3*</td><td>40 cm</td><td>27.00</td></tr>
</table>

Then, *the Global Heavy Metal Pollution Index (PLI) for the* authorized area was calculated based on soil samples taken, in the period 2011-2020.

The results obtained are presented in the graph in Figure 34. Details regarding these results can be found in Table 15 of the thesis.

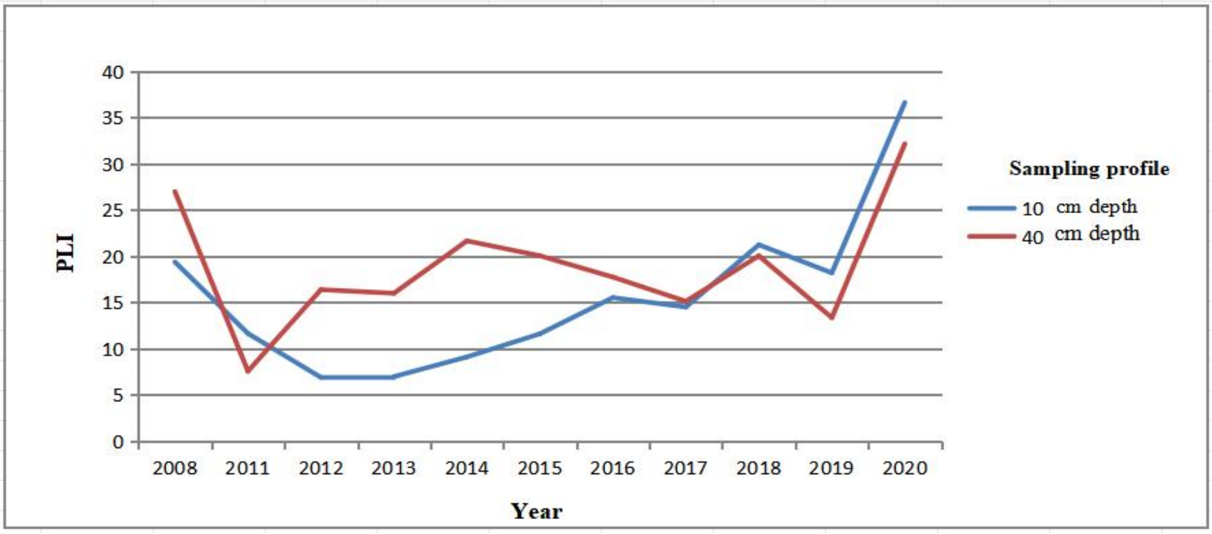

Figure 34. Results obtained for the Global Heavy Metal Pollution Index *(PLI)* on the CET H Arad site

The values obtained for the *Pollution Index (PLI)* based on soil samples collected annually from the authorized sampling area were compared with the (*PLI)* results calculated for the legal reference values.

According to the (*PLI)* results for heavy metals obtained for the authorized area, it can be observed that there is no value exceeding the (*PLI)* value of 155.98 corresponding to the alert threshold, which represents the accepted limit, indicating good soil quality at the CET H Arad site concerning heavy metal pollution during the studied period.

Based on the determined (CF_i) values and the Toxicity Factor (T_i) corresponding to heavy metals, the environmental impact was evaluated through ecological risk analysis, using the Risk Indices method (ER_i and *RI*). The values of the toxicity factors for heavy metals are presented in Table 16, which can be consulted in the thesis.

Next, the Individual Ecological Pollution Risk (ER_i) for the studied heavy metals was calculated based on the authorized reference values, applying the formula:

$$ER_i = CF_i \times T_i \quad (3)$$

The results of the calculations performed based on formula (3) are presented in Table 17, which can be consulted in the thesis.

Next, a comparative analysis was conducted on the results obtained for the Individual Ecological Pollution Risk with heavy metals (ER_i) during the period 2011-2020 at the CET H Arad site with the reference values determined in 2008, the results being presented in Table 18, which can be consulted in the thesis.

Finally, the *General Ecological Pollution Risk (RI)* was calculated based on the legal (authorized) reference values for the CET H Arad site by applying the formula:

$$RI = \sum ERi \quad (4)$$

The results are shown in Table 20, presented below:

Table 20. Results obtained for the General Ecological Risk of Heavy Metal Pollution (RI) on the site of CET H Arad

Sampling point	**Sampling profile**	**Overall ecological risk of heavy metal pollution (RI) calculated on the basis of legal reference values**			
Location CET H Arad		cf. CET H Arad Site Report 2008	cf. AIM CET H Arad *OM 756/03.11.1997 for land of less sensitive use		
Authorized area	**Depth [cm]**	Determined value	Normalvalue	Alert threshold	Intervention threshold
		(RI)	**(RI)**	**(RI)**	**(RI)**
S3	**10 cm**	98.07	933.87	9421.97	20561.87
S3*	**40 cm**	1293.59			

Analyzing the annual data calculated for the General Ecological Risk of Heavy Metal Pollution (RI) on-site, over the entire studied period, compared to the reference values determined in 2008 during the preparation of the Site Report for obtaining the integrated environmental permit, we found that the determined values exceed these reference values in only two cases out of 10, namely in 2020, at the 10 cm depth profile, when a value of 1541.94 for RI was recorded, compared to 987.07, the value obtained in 2008.

The second exceeded value was recorded in 2018, at the 40 cm depth profile, with RI having a value of 1323.96, compared to 1293.59, the value obtained in 2008. The percentage of exceedances is not significant, except in the first case.

The results obtained are presented in Table 22, being graphically illustrated in the figure 35 of this summary.

It can be concluded that the results obtained for RI indicate values that generally demonstrate a good evolution of soil condition concerning the heavy metals in the studied series, these quality indicators having values that do not exceed the authorized limits, except in two cases, when the alert threshold for cadmium was exceeded.

From the series of heavy metals evaluated over the entire study period, we found that the alert threshold was exceeded only for Cd, in 2019, by 18.20% at the 10 cm depth profile, respectively by 1.20% at the 40 cm depth, as well as in 2020, by 8.00% at both depth profiles, for this heavy metal.

In the case of the other heavy metals, no exceedances above the alert threshold were recorded, and all determined values fell within the accepted limits. The determined results have been presented in Table 11, which can be consulted in the thesis.

The General Ecological Pollution Risk (RI) with heavy metals is very low, which is particularly important and encouraging, considering the 123 years of operation of the power plant at this site, through the burning of fossil fuels in large combustion installations.

The results of the Index (PLI) indicated that the majority of the samples fall within normal limits for industrial land, specifically for the less sensitive type of use. Details regarding these results can be found in Table 15, inserted in the thesis.

Soil analyses conducted in the years 2020, 2021, 2022, and 2023 recorded values that fall within the permissible limits, both for cadmium and for the other heavy metals monitored according to the provisions of AIM CET H Arad.

The study period included the years 2011-2020. The results of these analyses can be found in the annual reports on the state of environmental factors submitted by CET H Arad to APM Arad.

Figure 20. Suggestive image of sampling for soil analysis [324]

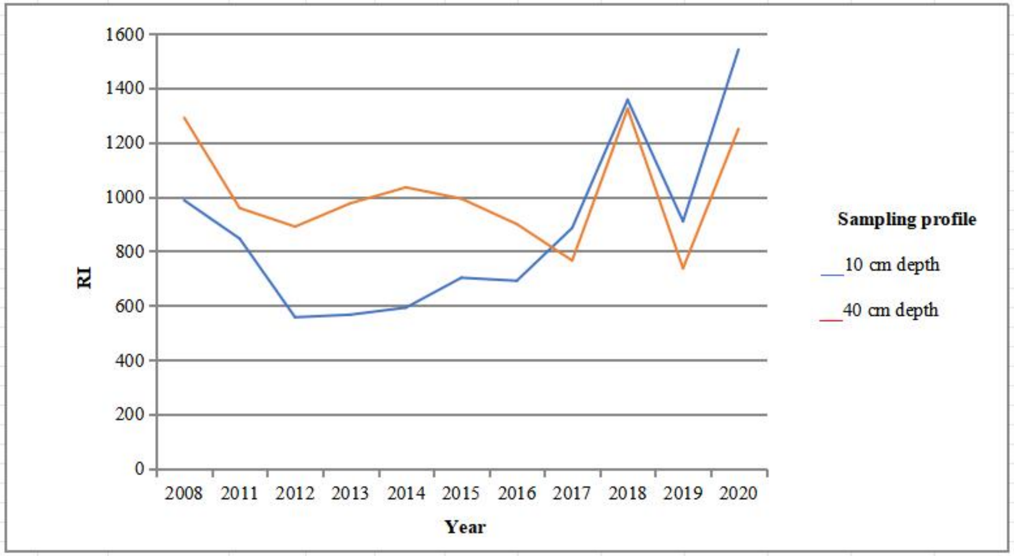

Figure 35. Results of RI obtained compared to the year 2008

Table 22. Results obtained for the General Ecological Risk of Heavy Metal Pollution (RI) at the CET H Arad site

Period 2011-2020		**Results of values determined during the study period compared to the legal reference values according to *AIM CET H Arad (Year 2008)**				
Total value **(RI)**	Average value **(RI)**	Average value **(RI)**	The lowest annual value **(RI)**		The highest annual value **(RI)**	
∑ ER_i				**Year**		**Year**
S3 /10 cm depth **8650,47**	865.05	< 12,36%	557.02	**2012**	1541.94	**2020**
S3*/40 cm depth **9829,8**	982.99	< 23,83%	736.84	**2019**	1323.96	**2018**

4.2.10. Conclusions on heavy metal concentrations in soil at the site

In conclusion, the analyzed indicators are within the legal limits, except for Cd, for which the alert threshold was exceeded in 2019 and 2020 at both sampling points. It can be stated that the burning of fossil fuels in the power plant installations has contributed to some extent to the accumulation of heavy metals over time in the soil of the investigated area, but a decrease compared to the reference values in 2008 was observed, the average value of the overall *Pollution Risk (RI)* in the period 2011-2020 being lower by 12.36% for point S3, 10 cm depth profile, and 23.83% for point S3* corresponding to the 40 cm depth profile, respectively.

The results indicate minimal source-related risks for heavy metals in the study area, except Cd. For Cd, the percentage of normal values is 80%, with a percentage of 20% exceeded values for the alert threshold and 0% values for the intervention threshold, according to O.M. 756/03.11.1997 for less sensitive land use. The concentration for Cd was exceeded in 2019 by 18.20% at point S3 at 10 cm depth, respectively by 1.20% at point S3* at 40 cm depth, and in 2020 by 8.00% at the two points at each sampling profile, the determined values exceeding the alert threshold.

We cannot exclude, without a scientific investigation, the possibility of an external contribution from a major pollution source present in the immediate vicinity of the sampling area, approximately 15 m away, this being a heavily trafficked DN artery, positioned parallel to the south longitudinal side of the studied site. This doubt should determine the subject of future research.

The results of the *(PLI)* index indicated that most of the samples fall within the permissible limits, in relation to the type of industrial land use, of less sensitive use, the analysis of the obtained results proving a minimal impact on environmental factors, in terms of heavy metals as well as the minimal existence of risks related to the source, in this case, CET H Arad. These results are good and indirectly demonstrate that, over time, the combustion processes have been run efficiently, with satisfactory yields, even if in the past, there were no filtering equipment for the pollutants emitted from the IMA stacks, as they were installed relatively recently.

The analytical data used were collected from documents uploaded on the official website of the Arad Environmental Protection Agency.

CHAPTER 5.
GENERAL CONCLUSIONS AND PERSPECTIVES

5.1. General conclusions

The results for the overall Heavy Metals *Pollution Index (PLI)* showed that most of the samples fall within the permissible limits, in relation to the type of industrial land use, less sensitive land use, the analysis of the results obtained proving a minimal impact on environmental factors, in terms of heavy metals and the minimal existence of risks related to the source, in this case, CET H Arad.

These good results indirectly demonstrate that, over time, the combustion processes have been run efficiently, with satisfactory yields, even if in the past, there was no filtering equipment for the pollutants emitted from the IMA stacks, as they were installed relatively recently.

Given that the site is located in a central area with a high population density, the results of the research contribute to the health and tranquility of the city, with the degree of soil pollution, heavy metals and other environmental factors being within normal limits.

The law requiring landowners and operators to keep the environment healthy and to pay for the damage caused by pollution establishes the regulatory framework of environmental liability in order to prevent and repair environmental damage [337].

Looking at the situation from the point of view of these legal provisions, it is very important to know the state of pollution of the environmental factors mentioned above, in order to prevent undesirable events with a negative impact on the environment, but also on the activity of the plant. First of all, it is important to monitor the soil in parallel with monitoring the subsoil, considering their existence as a unit.

Even though the results of the research carried out have shown that the pollution level on the CET H Arad site is at a minimum level, it is mandatory to continue to apply the existing measures to eliminate/minimize emissions to the soil and groundwater.

It can be stated that the burning of fossil fuels in the power plant installations has contributed to a certain extent to the accumulation of heavy metals (Cd) over time in the soil of the investigated site.

However, for the overall *Pollution Risk (RI)* a decrease compared to the 2008 baseline values was observed, its average value in the period 2011-2020 being lower by 12.36% for point S3, 10 cm depth profile, and 23.83% for point S3* corresponding to the 40 cm depth profile, respectively.

5.2. Perspectives

In the context of a sustainable development, according to the legislation in force, and in view of the major potential impact for heavy metals, studies and research are needed on finding solutions to protect, prevent and combat environmental pollution.

Concentrations of heavy metals have recorded only two exceedances for cadmium as exceptions during the whole studied period 2011-2020.

The possible external anthropogenic anthropogenic contribution, due to the heavily trafficked artery in the southern neighborhood, constitutes a new topic for future research, in parallel with geochemical background level studies for heavy metals in the soil of Arad Municipality, given that such a study has not been done so far.

We cannot exclude, without a scientific investigation, the possibility of an external contribution from a major pollution source present in the immediate vicinity of the sampling area, approximately 15 m away, which is the DN 7E artery with heavy car traffic, positioned parallel to the longitudinal south side of the studied site. This doubt should determine the subject of future research.

At the same time, I consider it opportune, in the future, to investigate the heavy metals in the series studied for the soil, and in the atmospheric basin adjacent to the site area and its surroundings. Air traffic has also increased sharply in recent years and a possible contribution cannot be excluded.

This scientific study is the first to be carried out at CET H Arad to assess the impact of the activity and the risk related to the source. The study was started in 2010, after the company was administratively reorganized by splitting into two units, the new company, CET H Arad, which was established in 2009, continuing the monitoring of environmental factors, namely the annual groundwater and soil monitoring since 2010.

The reasoning for the selection of the wells is necessarily subject to the existing provisions in the operating permits issued by the environmental authorities for CET H Arad.

The frequency of sampling is also laid down in the operating permits, which, in the case of groundwater, provide for an annual sampling of momentary samples for each monitoring well, from the three wells existing on the site.

The operator is obliged to take all measures for effective pollution prevention.

It should be noted that there are only 3 groundwater monitoring wells on the site of CET H Arad, namely PC1, PC2 and PC3.

Therefore, the selection criteria for the sampling points are subject to the provisions mentioned in the operating authorizations of CET H Arad, which are mandatory.

The possibility that the pollutant species being monitored could reach groundwater exists only if accidental pollution would occur at ground level or in the Muresel Canal, the surface outfall that crosses the plant site, used for the discharge of the technological wastewater, properly treated before discharge. There was no accidental pollution on the site of CET H Arad during the period 2010-2020.

Groundwater quality trends cannot be estimated, given the influences present on the site, which are not related to the emissions of the power plant, i.e. to the technological production activity.

A more in-depth analysis of pollution sources and long-term trends, addressing seasonal variations, would have been advisable, but given the strong dynamics of the major technological restructuring process of the entire plant, which is in full progress, there were too many variables during the period of the study that would have induced various interferences with the monitored reference sources.

In the near future, the existing installations will be entirely decommissioned and the current plant will only continue to operate until the new production units are commissioned according to an ongoing investment project. The estimated commissioning date for the new production capacity is June 2026 on the existing site.

In view of the above, I recommend, in the perspective, the establishment of a sustainable aquifer quality management plan based on (I^*_{GP}) and through the assessment of emerging pollutants, in line with a unified legislation for groundwater bodies.

The legislation applicable to groundwater on industrial sites in Romania includes several normative acts regulating groundwater protection and management, but does not explicitly stipulate permitted values for the quality indicators monitored in this study.

The common objective at European level aims to protect essential sources of drinking water, reducing treatment costs by reducing pollution of surface and groundwater.

In the case of industrial establishments, local and national environmental authorities may issue additional regulations or specific requirements for certain activities. Industrial companies must comply with all such regulations to ensure adequate groundwater protection at their sites.

To show how important they are in different industrial sectors, potential pollutants from industrial activities can be conveniently grouped for different industries [273].

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