

Mercury determination in the environment using an advanced mercury analyzer (AMA)

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Master's thesis
2023



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Faculty of Technology

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Department of Environmental Protection Engineering

Academic year: 2022/2023

ASSIGNMENT OF DIPLOMA THESIS

(project, art work, art performance)

Name and surname: **Hagos Kiros Hagos**
Personal number: **T21695**
Study programme: **N0712A030002 Environmental Engineering**
Type of Study: **Full-time**
Work topic: **Stanovení rtuti v životním prostředí pomocí analyzátoru rtuti**

Theses guidelines

- 1. Study all literature and information sources related to the topic. Prepare the theoretical part of thesis.*
- 2. Optimize extraction of mercury from different matrices and optimize mercury determination on AMA.*
- 3. Measure mercury concentration in different environmental samples using AMA and evaluate data statistically.*
- 4. Process the measured and recorded data and critically evaluate the results.*

Form processing of diploma thesis: **printed/electronic**
Language of elaboration: **English**

Recommended resources:

1. EISLER, Ronald. *Mercury Hazards to Living Organisms* [online]. Boca Raton: CRC Press, 2006 [cit. 2022-08-29]. ISBN 9780429118401. Dostupné z: <https://doi.org/10.1201/9781420008838>.
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5. Scientific resources: such as Web of Science, ScienceDirect, SciFinder Scholar, Medline etc.

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Date of assignment of diploma thesis: **December 31, 2022**

Submission deadline of diploma thesis: **May 12, 2023**

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ABSTRAKT

Tato práce se zabývá stanovením rtuti ve vodných a půdních vzorcích. Vzorky půdy byly nejprve vyluhovány čtyřmi různými extrakčními metodami, přičemž nejúčinnější byla metoda mineralizace s využitím HNO_3 a H_2O_2 . Dále byly měřeny koncentrace rtuti, arsenu a dalších prvků ve výluzích pomocí pokročilého analyzátoru rtuti (AMA), elektrotermické analýzy (GFAAS) a plamenové atomové absorpční spektrometrie (FAAS). Nejvyšší koncentrace rtuti a arsenu byly naměřeny v místě odkaliště v koncentracích 0.763 mg.kg^{-1} a 71.7 mg.kg^{-1} . Výsledky byly zároveň porovnány např. s limity pro ukládání na skládku odpadů anebo s universálními standardy. V závěru práce je otestován způsob úpravy podobného odpadu jako na odkališti pomocí metody stabilizace a solidifikace. Výsledkem bylo zjištění, že nejlepší poměr obsahoval 60 % odpadu a 40 % portlandského cementu.

Klíčová slova: rtuť, extrakce, mineralizace, atomová absorpční spektrometrie, AMA 254, stabilizace a solidifikace

ABSTRACT

This thesis deals with the determination of mercury in environmental samples. The soil samples were first leached by four different extraction methods whereas the mineralization method using HNO_3 and H_2O_2 was the most efficient one. Furthermore, the concentration of mercury, arsenic and other elements were measured using advanced mercury analyzer (AMA), graphite furnace atomic absorption spectrometry (GFAAS) and flame atomic absorption spectrometry (FAAS). The results showed that, the highest mercury and arsenic concentrations were measured at the sludge bed (0.763 mg.kg^{-1} and 71.7 mg.kg^{-1} respectively). Furthermore, the results were compared with different limits such as universal treatment standards (UTS) or leaching limit values. Similar waste to fly ash was also tested and treated by the stabilization and solidification method in which the best ratio contained 60 % of waste and 40 % of Portland cement.

Keywords: mercury, extraction, mineralization, atomic absorption spectrometry, AMA 254, stabilization, and solidification

First and for most I would like to thank GOD. Secondly, I would like to thank my supervisor Ing. Štěpán Vinter, Ph.D., for not only being my supervisor but also for the patience, support, and mentoring he showed me throughout my studies in the past 2 years. This would not have been possible without your guidance. I will always be grateful for the things you have done for me. I would also like to thank all the professors and students in the environmental protection engineering department.

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INTRODUCTION

Mercury is a persistent toxic metal that can exist in the environment in different forms. Its source can be natural or anthropogenic. The most common mercury depositions were in the environment, soil, and aquatic environments. Methyl mercury is the most toxic form of mercury that exists in aquatic environments.

The toxicity of mercury can cause damage to human health by affecting different organs of our body. The primary source of mercury intake is through diet. Disposal of toxic effluents from industries plays a significant role in environmental toxication by pollutants. An example is fly ash disposed from a heat or wastewater treatment plant.

In this thesis, mercury was determined in soil and water samples using several techniques, mainly AMA 254. Samples were collected from the sludge bed Belov during winter and spring. The mercury content in the water sample ranges from 0.1 – 0.2 $\mu\text{g.L}^{-1}$ in winter and 0.6 – 0.9 $\mu\text{g.L}^{-1}$ in spring, whereas the highest concentration of mercury in soil was in the fly ash sample, which was 0.395 mg.kg^{-1} in winter and 0.763 mg.kg^{-1} in spring. Heavy metals like Fe, Zn, Ni, and metalloid arsenic were also present in the soil sample.

The other measured sample was a waste sample from heating plants, which shares a similar property with the fly ash sample, and it was treated by stabilization and solidification method, with an efficient reduction of mercury and arsenic from the sample.

I THEORETICAL PART

1 INTRODUCTION

One of the deadliest environmental pollutants is mercury and its compounds. Diverse environmental sources, including mine tailing, industrial effluents, agricultural drain waters, and air deposition from the production of electricity can expose biota to mercury. Elemental mercury is a rare heavy metal, but it can be extracted by heating cinnabar ores, which typically exhibit mercury oxidation states (Hg^{2+}). Mercury toxicity can occur in high trophic level feeders as a result of both inorganic and methylated mercury compound bioaccumulation in the food chain (Pavithra et al. 2023; Felix et al. 2022)

Mercury, a silvery-white metal that melts at room temperature and is highly volatile, can be found in three different oxidation states: natural mercury (Hg^0), mercurous particle (Hg_2^{2+}), and mercuric particle (Hg^{2+}). (Eisler 2006)

It is possible to find it in both organic and inorganic compounds. All mercury compounds disrupt mitosis by interfering with thiol metabolism, inhibiting or inactivating proteins containing thiol ligands. (Eisler 2006)

Although the most harmful inorganic chemical form is the mercuric species, all three types of inorganic mercury may share a common molecular mechanism of damage. (Eisler 2006)

Hg is a unique chemical element because it has a wide range of liquid and gaseous forms and exceptionally strong chemical and biological activity. Different cycles of mercury's natural circulation include compounds with very different chemical and physical properties. Due to its low melting and boiling points, conversions between chemical forms, and participation in biological cycles, mercury is a globally distributed pollutant. The global atmospheric Hg deposition rate has increased by a factor of 2–10 in and around the most industrialized regions and is approximately three times higher than it was before the industrial revolution. (Gworek, Dmuchowski, and Baczewska-Dąbrowska 2020)

Pure mercury is a cognizant, brilliant white versatile fluid with a metallic gloss. It emits bluish-violet light in thin layers. It contracts as it freezes, forming cubic crystals and a white, malleable mass that can be easily cut with a knife at around minus 39 °C. The metal expands uniformly when heated, boiling at 357.01°C and vaporizing at approximately 360.0 °C. The vapour has no colour. Mercury forms two obvious series of salts: the mercuric salts made from the oxide, HgO and the mercurous salts made from the oxide Hg_2O a crystalline powder with a bright red colour and an orange-yellow colour. The yellow structure is the most responsive and is changed into red when boiled at 400.0°C. Warming the red structure results in a dark compound, which

recaptures its variety on cooling; It breaks down into mercury and oxygen upon further heating to 630.0° C. (Eisler 2006)

Two of the most important salts of mercury are mercurous and mercuric chloride, which are known as calomel and corrosive sublimate, respectively. Halogenated mercury salts include mercuric bromide HgBr_2 , mercurous bromide, Hg_2Br_2 , mercuric iodide, mercurous iodide, Hg_2I_2 , nitrates, nitrites, sulfides, sulphates, phosphides, and ammonium salts.(Eisler 2006)

Elemental mercury is relatively inert in dry air, oxygen, nitrous oxide, carbon dioxide, ammonia, and some other gases at room temperatures. It slowly acquires a layer of mercurous oxide in the damp air. It changes into red mercuric oxide when heated in air or oxygen, which breaks down into mercury and oxygen when heated for a long time at higher temperatures. Amalgams are compounds made when mercury dissolves various metals, which are often used in dentistry to fill cavities caused by tooth decay. Mercury is used to making caustic soda and chlorine gas, components for batteries, thermometers, and barometers, electrical switches, and the extraction of silver and gold ore because it has a very high vapour pressure at room temperature.(Pavithra et al. 2023; Eisler 2006)

The worldwide mercury cycle includes mercury discharge from topographical and modern cycles into water and the air, trailed by sedimentation by means of precipitation and by microbial digestion that lets mercury out of soil and silt and changes mercury starting with one substance structure and then onto the next.(Eisler 2006)

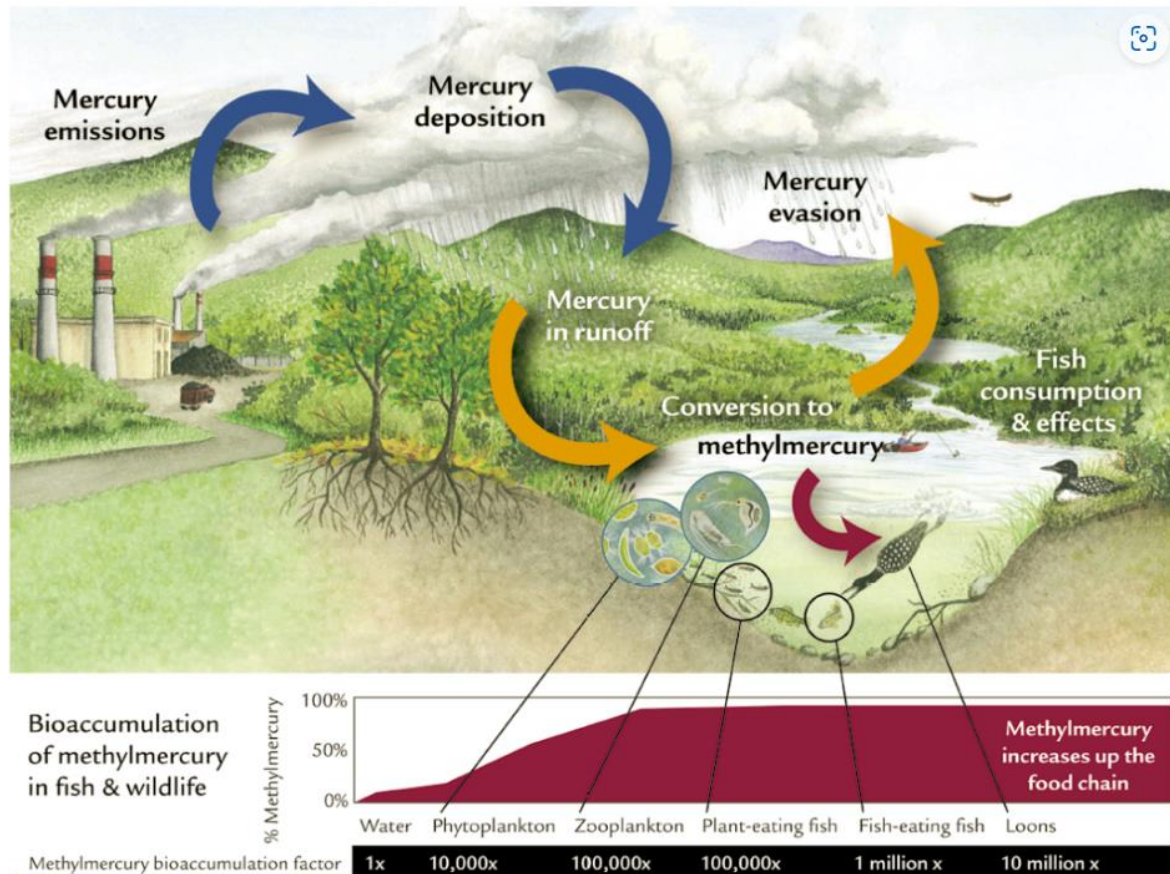


Figure 1 The Mercury Cycle (Evers 2011)

The environmental protection authority of Ethiopia's study estimates that 40,600 tons of mercury is produced annually in Ethiopia. In addition to dental amalgam fillings ("silver" fillings), laboratory chemicals and other laboratory and medical equipment containing Hg are the main sources of water ecosystems. Bioaccumulation and biomagnification of methylmercury, an organic form of mercury in fishes, can go to a thousand times higher levels than in the surrounding water. In fact, ingesting fish from seafood, including shellfish and marine mammals like whales, is the main way the public is exposed to MeHg. (Habiba et al. 2017)

In Ethiopia, the exploitation of food resource present in the rivers and lakes has gained significant attention due to the country's growing population. Lake Tana, Ethiopia's largest freshwater reservoir, is located in the northern part of the country and is estimated to supply more than half of the annual fish yield from lakes. (Habiba et al. 2017)

A study of various Ethiopian lakes revealed that certain fish species contain mercury. As an illustration, the marketing restriction of the European union is $0.5 \text{ mg} \cdot \text{kg}^{-1}$ for piscivorous great

barbs, but the value exceeds the ones present in lake Hawassa, which is in the southern part of the country. (Habiba et al. 2017)

The build-up of methyl mercury in aquatic organisms poses a threat to wildlife as well as humans. More than 120 nations, including the Czech Republic, signed the Minamata mercury convention in 2017 to reduce the risk of mercury exposure in the environment. As a result of the convention, the import and export of mercury-added products, with certain exceptions, were no longer allowed since 2020. The Czech Republic has had a long history of aquaculture, with common carp being the most common species. The Czech Republic produced 21,685 tons of aquaculture in 2017, 85.1 % of which were common carp. Most of the production in the country is intended for export. Surface water represents a reservoir of numerous environmental contaminants. Aquatic organisms, particularly fish, can accumulate mercury and other heavy metals. The primary source of mercury exposure for humans is the consumption of aquatic animals, particularly fish, which come from contaminated environments and are consumed frequently and for long periods. Fish is a typical diet for many people, so it is necessary to assess the mercury content, which most of the time accumulates in the fish muscle. Regulation (EC) No. 1 of the European Commission regulates the mercury content of fish muscle. 1881/2006 setting the most extreme levels for specific toxins in staples. There are two distinct categories of fish covered by the regulation. Except for pike (*Esox Lucius*), eel (*Anguilla* spp.) and other freshwater fish, the maximum level of 0.5 mg.kg^{-1} (wet weight) has been established. Also, sturgeon (*Acipenser* spp.), In marine fish like pike, eel, and sturgeon, mercury can be found at concentrations of up to 1 mg.kg^{-1} (wet weight). The regulation specifies limits in terms of total mercury (THg). However, a MeHg fraction of 83–90% of the total mercury concentration is primarily responsible for bioaccumulation in fish muscle tissue. Hence, The World Health Organization has set the temporary average week-by-week consumption for MeHg to be $1.6 \text{ }\mu\text{g.kg}^{-1}$ human body weight/week. (Sehonova et al. 2022)

The Bilina River in the Czech Republic was chosen as a sample area to assess mercury contamination in which the mercury range was from 130 to 3390 ng.g^{-1} . The waterway positions among the most contaminated streams in the country because of various modern exercises in the district. The landscape's overall character has changed because of extensive underground and surface coal mining. In the past, a chemical plant in Zaluzí, close to Litvnov, diverted a significant portion of the river's flow. The river flowed from Zaluzí as chemical wastewater that was lifeless and heavily polluted with phenols and other chemicals. The situation significantly improved during the 1990s, when underground mining and most of the industrial activity

declined. The assessment of the levels of PAHs and mercury in fish muscles has been the primary focus of recent research in this area.(Vöröš et al. 2018)

2 MERCURY IN THE ENVIRONMENT

Mercury is a persistent toxic heavy metal that has received much attention because of its large emissions, transfer through various environmental mediums, complex biochemical cycling, and accumulation in biota. Hg, both organic and inorganic, can be found in any environment. Mining, metal smelting, industrial emissions, and other human activities can account for much of the Hg. Sulphate- and iron-reducing bacteria converted the atmospheric inorganic Hg (Hg) that was deposited on the surface of the soil or water into the most common organic form, methylmercury. (MeHg) (Qing et al. 2022)

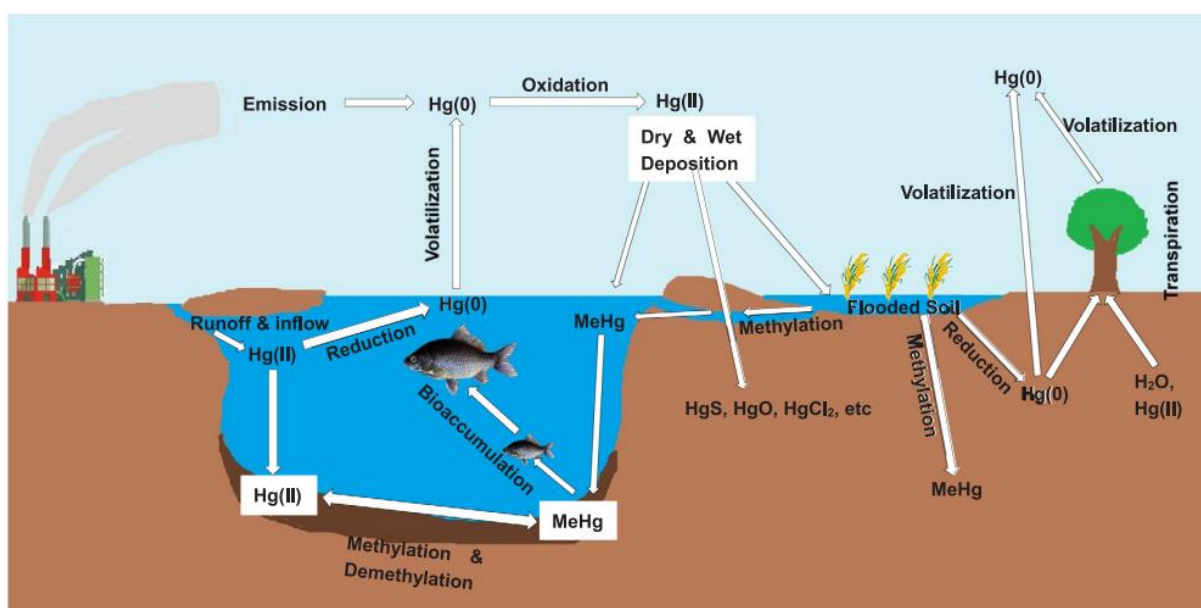


Figure 2 Transfer and Transport of mercury in soil, water, and air (Wang et al. 2020)

2.1 Atmosphere

Mercury is one of the most harmful trace metals, however, it is utilized in numerous industrial sectors. Mercury is released into the air in its elemental form (Hg^0), making up more than 95 % of the total mercury in the atmosphere. Under normal conditions, it is a stable form of Hg that is volatile and insoluble in water. This form of mercury is deposited very little in the atmosphere. Hg^0 stays in the atmosphere for several months, this makes it a long-range pollutant, transported together with air masses over long distances, thus becoming a transboundary pollution. This results in the presence of mercury in regions far from anthropogenic sources, such as the Arctic. (Korejwo et al. 2022)

Hg^0 can be oxidized to Hg^{2+} form in the atmosphere and can be less volatile and more soluble in water than mercury in its pure form (Hg^0). This transformation is crucial to the circulation of mercury in the atmosphere. As a result, its lifetime is shorter than that of Hg^0 , ranging from a few hours to several weeks. Because of this Hg^{2+} is rapidly deposited in the form of wet and dry deposition. On the other hand, the oxidation of Hg^0 to Hg^{2+} occurs mostly in the spring in the arctic. Atmospheric mercury depletion events in the arctic can result in the depletion of approximately 100 tons of mercury annually. (Korejwo et al. 2022)

Major mercury inputs to the environment are mainly from natural sources, with significant and increasing amounts contributed by human activities. With an estimated 25.0 to 30.0 % of the overall atmospheric burden of anthropogenic origin, the atmosphere is critical in the mobilization of mercury. Anthropogenic mercury emissions to the atmosphere are thought to range from 900 to 6200 tons annually. (Eisler 2006)

A portion of the mercury that is deposited is re-emitted into the atmosphere. However, the marine food web may accumulate some of the Hg deposited in aquatic ecosystems. An increase in mercury's biomagnification capacity is observed in polar fauna at higher trophic levels, whilst the highest concentrations occur in large marine mammals. (Korejwo et al. 2022)

Mercury from natural sources enters the biosphere directly as a gas, in lava (from volcanic activity on land and in the ocean), as a solution, or as particulates; cinnabar (HgS). Mercury and large quantities of lead, cadmium, and bismuth are emitted from volcanoes into the atmosphere. (Eisler 2006)

The degassing of mercury from the Earth's crust and evaporation from natural bodies of water, atmospheric transport, primarily in the form of mercury vapour, and deposition of mercury back onto land and water are all parts of the worldwide cycle of mercury. (Eisler 2006)

About 1900 metric tons of anthropogenic mercury were released into the atmosphere in 1995, primarily (75.0 %) due to the burning of fossil fuels. Asia accounted for about 56.0 % of the world's mercury atmospheric emissions, with Europe and North America providing less than 25 % of the total. Gaseous elemental mercury (Hg^0) comprised 53.0 % of the total atmospheric emissions, while gaseous Hg^+ comprised 37.0 %. (Eisler 2006)

According to USEPA (1997), electric utility mercury emissions are the largest uncontrolled source of mercury in the atmosphere and account for up to 59.0 percent of the annual atmospheric loading of mercury from both natural and anthropogenic sources worldwide. (Eisler 2006)

According to European air quality standards, atmospheric mercury levels are between 2-4 ng/m^3 in rural areas and 10 ng/m^3 in metropolitan areas. Thus, the number of airborne

contaminants that are absorbed daily into the bloodstream because of respiratory exposure varies between 32 and 64 ng in rural areas and 160 ng in metropolitan areas. However, given that the estimated average daily absorption of mercury vapors from dental fillings varies between 3000 and 17 000 ng, this exposure to mercury from outside air is negligible compared to exposure from dental amalgams. (WHO 2009)

It is crucial to consider the numerous forms of mercury in the atmosphere and the intake of these forms of mercury from other media. The only mercury vapour exposure sources are the atmosphere and dental amalgam, whereas diet is the main source of methylmercury compounds. Except for local "hot spots," outdoor mercury concentrations are normally in the range of 0.005-0.010 g/m³, which is negligible compared to exposure via dental amalgam. At current air levels, it is not anticipated that exposure to mercury will have an immediate negative impact on human health. Hg⁰, the kind of mercury that makes up most of the air, is neither mutagenic nor carcinogenic. Exposure to airborne methylmercury is regarded as minimal in this context because it is 2-3 orders of magnitude below the daily intake through food. Hence, just incorporating mercury vapor and divalent mercury will yield a numerical guideline for inhaling inorganic mercury. (WHO 2009)

2.2 Aquatic Environment

Hg comes from various foods due to biomagnification and high MeHg conversion rates in anoxic aquatic systems. Hg concentrations were typically elevated in the muscle tissue of long lived predatory fish. Feed was the main source of Hg intake for livestock which can result in contamination of animal derived foods such as meat, eggs and milk. (Qing et al. 2022)

There are three primary dissolved Hg species found in natural waters; organic Hg (monomethyl and dimethylmercury), inorganic Hg (Hg²⁺ and its complexes), and elemental Hg (Hg⁰). These species are all extremely mobile. In fresh waters, such as lake water, dissolved humic matter comprises 94–99 percent of inorganic Hg and 72–97 percent of organic Hg. On the other hand, the proportion of Hg bound to humic matter in seawater is very low due to high chloride-ion concentrations that stabilize Hg species in solution through ionic interactions. Furthermore, although Mediterranean waters exhibit a "Hg anomaly" with an organic Hg content of up to 30 % of total Hg, marine waters typically have a proportion of organic Hg that is less than 5 % of total Hg.

In contrast, freshwater systems typically have a fraction of organic Hg that is 30 % of total Hg, ranging from 1 to 5 ng Hg/L. Within the food chain, there is a wide variety of Hg species, with

methyl Hg being the most toxic and having the highest bioaccumulation factors. The concentration of mercury in prey fish can be up to 106 times that of the surrounding water, and up to 95 percent of this mercury can be methyl mercury. In clean natural waters, mercury concentrations are typically in the low ng/L range.(Eisler 2006)

An estimated 334.17 billion metric tons of mercury are present in various global reservoirs; most of this mercury is found in soils, while nearly all of it is found in ocean sediments and waters (98.75 %). Only 7.0 metric tons of mercury are believed to be present in living aquatic creatures.(Eisler 2006)

In accordance with the Safe Drinking Water Act in 1991, the EPA set a maximum contaminant level (MCL) for inorganic mercury at 0.002 mg/L or 2 ppb. The MCL for mercury in drinking water must not be exceeded by public water systems. Cost, benefits, and the capacity of public water systems to detect and remove contaminants using appropriate treatment technologies are all taken into consideration when setting MCLs that are as close to the health objectives as is practical. (Cooper and Gillespie 2001; EPA CFR 40-25-141-Subpart G 2019)

Rainwater contains mercury at concentrations ranging from 5 to 100 ng/litre, with mean concentrations as low as 1 ng/litre being reported (WHO 2009). Although local mineral deposits may result in higher levels of mercury in groundwater, the levels of mercury that naturally occur in groundwater and surface water are less than 0.5 g/liter. Mercury levels in small shallow wells and groundwaters surveyed in the United States were higher than the maximum contaminant level for drinking water set by the Environmental Protection Agency of the United States, which is 2 g.L⁻¹. Wells on Izu Oshima Island (Japan), where volcanic activity is frequent, were found to increase mercury concentration by up to 5.5 g/liter. According to IPCS (1990), the range of mercury concentrations in drinking water and rain is identical, with an average of approximately 25 ng/litre. (WHO 2009)

Water samples collected from the Mississippi River showed a mercury concentration of 0.00216 mg.L⁻¹(Cooper and Gillespie 2001) which was in the same range as the samples collected for this research.

2.3 Soil

Mercury can be deposited on the Earth's surface as elemental Hg (Hg^0) or divalent Hg ($\text{Hg}(\text{II})$) by a variety of natural and anthropogenic processes. After being deposited, $\text{Hg}(\text{II})$ interacts with soil in various chemical and biological ways. As a result, the soil is the largest terrestrial Hg reservoir and plays a significant role in the global biogeochemical cycle. (J. H. Huang, Shetaya, and Osterwalder 2020)

Soil plays a significant part in the mercury cycle by acting as a medium and source for the hydrological cycles, atmosphere, and biota metabolisms. Through chemical, physical, and biological processes, soil can influence different mercury species, altering their solubility, biological accessibility, ecology, and environmental toxicological impacts. (Jatnika Effendi, Lestari, and Irsyad 2020)

The forms of mercury determine the fate, route, and toxicity of mercury in soil. Compared to inorganic mercury, organic mercury species like methyl mercury are more biologically soluble and have a higher level of toxicity. This is because organic mercury is more mobile than inorganic mercury. A less harmful species of mercury can be found in soil and is classified as semi-mobile. While only mercury sulfide is non-toxic, non-mobile mercury species are chemically toxic. (Jatnika Effendi, Lestari, and Irsyad 2020)

Due to the disposal of artisanal and small-scale gold mining tailings, it is necessary to remediate mercury-contaminated soil. One remediation innovation that can be applied in the recuperation of semi-unpredictable or unstable mixtures of mercury-polluted soils is by washing the dirt or supposed a dirt washing strategy. Soil washing is a method for recovering contaminated soil that has several advantages, including the fact that the recovery process only takes a short amount of time, can be used extensively, is financially feasible, and can be applied to soil that has been contaminated with mercury or other semi-volatile or volatile compounds. (Jatnika Effendi, Lestari, and Irsyad 2020)

When leaching, runoff, and erosion occur in polluted soils, measuring the water-soluble fraction of mercury in the soil is a particularly useful tool for determining the potential risk of groundwater contamination, biological uptake, and toxicity for aquatic organisms. (Reis et al. 2014)

The health and ecological risks posed by metal(loid)s are often underestimated by estimating their total concentrations in soil. This is since most of the estimated content will be in forms that are not immediately accessible to living organisms and are either permanently or

temporarily fixed to soil components. Because it is immediately susceptible to surface runoff and leaching into ground waters, the soil solution's soluble metals (and metalloids) fraction is typically regarded as "mobile." A significant portion of the metals held in the soil solid phase and the submicron colloidal particulates suspended in the soil solution is "labile" in addition to the soluble pool of soil metals. This labile pool of metal is "potentially mobile" because it can move to the solution phase in response to changes in the equilibrium physicochemical conditions of the soil. The "available" or "reactive" fraction of soil metals is frequently called the combination of the soluble and labile pools. (J. H. Huang, Shetaya, and Osterwalder 2020)

Because it is "presumably" readily available for plant uptake and assimilation by soil microorganisms, the available/reactive (soluble plus labile) pool of soil metals has been widely recognized as "bioavailable." However, the available/reactive pools should only be defined as "potentially bioavailable" because the actual uptake of metals by plants and microorganisms is more dependent on defence and selection mechanisms, which plants and organisms use to protect themselves against toxic elements or preferentially uptake certain elements necessary for their biological functions. Mass transfer parameters, which include physicochemical processes governing dissolution, desorption, diffusion, and hydrology, may also have an impact on pollutants' bioavailability. Because of this, establishing a reliable connection between pollutants and their bioavailability is extremely challenging. Therefore, the definition of the pool of metals that is taken up by plants or assimilated by soil microorganisms should be limited to the use of the term "bioavailable. (J. H. Huang, Shetaya, and Osterwalder 2020)

For an accurate assessment of the potential toxicity of soil Hg to animals and humans, it is essential to comprehend its bioavailability. To better understand the possibility of biotic Hg methylation, which could result in the formation of the highly toxic methyl Hg, it is also necessary to evaluate the bioavailability of Hg in soils. (J. H. Huang, Shetaya, and Osterwalder 2020)

The one-of-a-kind physicochemical quality of Hg, in contrast with other exemplary hard metals, for example, zinc, nickel, cadmium, copper and lead, has delivered endeavours to concentrate on its (profile)- accessibility extremely testing. For instance, the chemical form of Hg has a significant impact on its toxicity; Organic Hg, particularly methyl Hg, poses a significantly greater threat to living things than inorganic Hg. Since some Hg species, such as methyl Hg and Hg⁰, are volatile, any developed protocol for assessing its (bio)availability must account for Hg evasion. Hg's behaviour, including its (bio)availability, can be largely controlled by the presence of low to average amounts of soil organic matter, as well as levels of sulfur and

selenium. Since Hg is a soft metal, it is known to have a strong affinity for soft ligands. Ligands are ions and molecules (like chloride and hydroxide in soil or dissolved organic matter) that can form a coordination complex. Their presence in natural soils may significantly alter the solubility of mercury. In addition, in contrast to hard metals, the formation of $\text{Hg}(\text{OH})_2$ and HgCl_2 results in the maximum Hg $(\text{OH})_2$ and HgCl_2 sorption in soil between pH 3 and pH 4. (J. H. Huang, Shetaya, and Osterwalder 2020)

Because mercury is recycled between the surface environment and the atmosphere, its half-life in surface soils is relatively long. Once buried in mineral soils, anthropogenic Hg will be permanently removed from the biologically active portion of the environment. Soil plays an important role in biogeochemical Hg circulation because it accumulates this element and is a source of other environmental components. Naturally, Hg can exist from different sources, such as forest fire, volcanic eruptions, and soils from geological sources. A total of 200–300 Gg of mercury is thought to have built up in the soils of terrestrial environments worldwide. (Gworek, Dmuchowski, and Baczevska-Dąbrowska 2020)

While Hg-contaminated sites typically have soil concentrations that are two to four orders of magnitude higher, the average background Hg concentration in soil typically ranges from 0.03 to 0.1 mg kg^{-1} . (Gworek, Dmuchowski, and Baczevska-Dąbrowska 2020)

Over 23,000 topsoil samples (upper 20 cm) were collected from all European Union countries on land except Croatia by the LUCAS Topsoil Survey of the European Union Organization. The concentration of Hg in Europe topsoils ranged from 0 to 159 mg kg^{-1} , with the average value being 0.04 mg kg^{-1} . Numerous polluted and isolated locations have been identified in studies, and Hg concentrations are higher in larger historical and contemporary industrial and Hg mining areas. (Gworek, Dmuchowski, and Baczevska-Dąbrowska 2020)

3 TOXICITY OF MERCURY

The toxicity of the chemical element mercury is a global concern. It can cause damage to human health, which includes the kidney, liver, digestive system, lungs, heart, and central nervous system, all of which can sometimes be irreversible. Mercury can also cause cardiovascular issues like coronary heart disease, hypertension, and myocardial infarction. The most harmful form of mercury is methylmercury, which is produced by methylating aquatic bacteria and encouraging bioaccumulation in fish. (Felix et al. 2022).

Most of the Hg exposure occurs through diet. The nervous, cardiovascular, and immune systems, as well as the kidneys and liver, can be damaged by excessive Hg intake. Psychological and neurological impairment was linked to low-dose, long-term Hg exposure. (Qing et al. 2022)

In numerous studies, the consumption of aquatic foods was regarded as the primary dietary source of MeHg. MeHg can damage the central nervous systems of individuals and their offspring by passing through the blood-brain and placental barriers. (Qing et al. 2022)

Eating fish exposes us to many contaminants through oral intake. Fish typically have mercury levels below 200 mg/g, and other meals typically have below 20 mg/g. Less than 10 g/d of inorganic mercury is thought to be consumed overall. Although there is little dermal exposure to mercury, the compounds used to clean diapers with mercury can poison people. The brain and kidneys are the main affected organs. Mercury is toxic, and the body builds up mercury and its salts to make matters worse. As a cumulative poison, mercury can cause major health issues even when only small amounts are ingested over time. The most common cause of acute mercury poisoning is toxic exposure to soluble inorganic salts. Afterwards, stomatitis, loosening of the teeth, and gastrointestinal disorders (abdominal discomfort, nausea, vomiting, bloody diarrhoea, and shock) can occur. (Csuros and Csuros 2016)

In the digestive tract, bleeding and ulceration cause death. Erosive bronchitis, bronchiolitis, and interstitial pneumonia are all brought on by mercury vapours. Erosive bronchitis, bronchiolitis, and interstitial pneumonia are all brought on by mercury vapours. Due to the cumulative nature of mercury, mercurialism, or chronic intoxication by elemental mercury vapour or mercury salts, is significantly more frequent than acute toxicity. Some symptoms are headache, weariness, weakness, memory loss, drowsiness, sleeplessness, muscle tremor, and general neuralgia. The victim often experiences mental and emotional disorders (becoming melancholy, irritable, and irascible, especially when reprimanded). Gingivitis, stomatitis, intestinal issues, and eye abnormalities are other symptoms. The signs of mercury salt intoxication are similar,

although kidney problems are more common. The sort of metallic mercury used in thermometers, sphygmomanometers, and other devices is not absorbed by the digestive tract, making it less dangerous.(Csuros and Csuros 2016)

However, lung tissue absorbs it. Mercury fumes are hazardous, especially when heated. Because of the widespread industrial discharge of mercury compounds into streams and lakes, mercury poisoning has recently become a serious issue. Before, it was thought that mercury, a heavy metal, would sink to the bottom of lakes and rivers, where it would be covered by sand and remain inert. Nevertheless, some microbes transform mercury metal into organic mercury compounds, primarily methylmercury and dimethylmercury. Dimethylmercury quickly evaporates from water, whereas methylmercury is trapped in bottom sediments and released slowly into the water, where it enters food-chain creatures and is biologically amplified (by a build-up of chemical elements or substances in organisms in successively higher trophic levels). Methylmercury is concentrated in fish, and people who eat the contaminated fish can get mercury poisoning. (Csuros and Csuros 2016)

Minamata illness, which has the clinical appearance of encephalitis, was created when mercury was deposited in Minamata Bay in Japan and other alkylmercury compounds. The first symptoms include a gradual loss of taste, smell, vision, hearing, and touch as well as numbness in the fingers, toes, lips, and tongue (which develops to complete blindness). Other symptoms include tremors and mood swings, as well as loss of balance and lack of coordination. 17 persons died and 23 were left permanently crippled out of the 52 instances that were documented in Japan. The number of recorded cases of mercury poisoning sharply decreased once tainted foods were taken off the market.(Csuros and Csuros 2016)

The Minamata Convention was agreed upon in 2013 to "protect human health and the environment from anthropogenic emissions and releases of mercury and mercury compounds" in light of the dangers posed by mercury and mercury exposure (UNEP, 2013). However, environmental issues like heavy metal pollution have become prevalent in China as a result of widespread industrialization and rapid urbanization.(Qing et al. 2022)

Contamination with methylmercury during pregnancy can significantly impact fetus development, resulting in irreversible damage such as congenital malformation, cognitive deficit, hearing loss, and brain problems, as well as a delay in the development of the new-born (Felix et al. 2022).

To monitor human mercury exposure, particularly that resulting from dietary intake, hair is an appropriate indicator. Hair samples can be collected, stored, and transported in a straightforward manner. Even though mercury levels in the blood are an indicator of ongoing or recent exposure, mercury levels in hair represent a much longer time frame, possibly several years (the average scalp hair growth has been reported as 1 cm per month). Several studies have reported a convincing relationship between the mercury content in hair and its content in the blood. Additionally, hair samples generally contain higher mercury concentrations than blood or urine, which are other indicators used to monitor human mercury exposure. WHO proposed a minimum threshold value for methylmercury in the hair of $50 \mu\text{g g}^{-1}$, which the US-EPA lowers to $10 \mu\text{g.g}^{-1}$ based on impact studies of mercury on human health.(Gao et al. 2010)

4 DETERMINATION OF MERCURY

It is important to develop trustworthy analytical techniques for the speciation analysis of mercury in seafood to safeguard the environment and ensure food safety. Environmental and dietary samples include traces or ultra-traces of Hg species. Although most analytical chemistry laboratories have access to flame atomic absorption spectrometry (FAAS), analysis can only be done down to the mg/l (ppm) level. As a result, this method cannot be used to determine most heavy metals at trace and ultra-trace levels. Sensitive analysis methods like high performance liquid chromatography-inductively coupled plasma-mass spectrometry (HPLCICP-MS), GC-ICP-MS, GC-CV-AFS, cold vapor atomic absorption spectrometry (CVAAS), cold vapor atomic fluorescence spectrometry (CV-AFS), graphite furnace atomic absorption spectrometry (GF-AAS), inductively coupled plasma atomic emission spectrometer are used for Hg determination and speciation. Despite being frequently employed to identify T-Hg and MeHg species, HPLC, GC-ICPMS, GC-ICP-AES, and GC-AFS are sophisticated, expensive, large-scale devices that are not common in many laboratories. Therefore, it is essential that novel techniques be used to determine T-Hg and/or MeHg in various matrices using devices that are less expensive. Additionally, achieving adequate sensitivity and selectivity for the speciation of the Hg species at trace or ultra-trace level in environmental and biological samples with complex matrices is crucial. Therefore, it is crucial to perform a selective preconcentration before measuring different Hg species. (Atasoy et al. 2023)

Two major and significant issues for mercury measurements in environmental samples are lower levels of the analytes than the quantitation limits of the analytical techniques and larger levels of the concomitant ions in the real samples. For mercury, methyl mercury, and heavy metals, separation and preconcentration techniques include solvent extraction, coprecipitation, cloud point extraction, ion-exchange, flotation, and solid phase extraction.(Tuzen et al. 2009)

Trace amounts of heavy metals can be quantitatively absorbed by higher species like mosses, bacteria, and algae. Because there isn't the metabolic activity required for intracellular metal accumulation, non-living material accumulates metals by biosorption. The immobilization of the organisms on natural or synthetic polymeric materials forms the basis of a significant portion of studies on biosorption. The biosorption systems for preconcentration, speciation, and separation of mercury species are based on the biosorption of the mercury species on the organisms and the desorption of adsorbed mercury from the organisms. (Tuzen et al. 2009)

The two most common methods used to determine mercury are CV-AAS and AMA 254. The cold vapor method (CV-AAS) makes use of the fact that mercury has sufficient vapor pressure at room temperature. As a result, it was possible to directly measure the radiation loss that corresponds to the concentration of free mercury atoms at this temperature. Stannous chloride or borohydride is used in the liquid phase to transform divalent mercury into elemental mercury. A stream of inert gas moves the reduced elemental mercury vapors, which are then transferred to a measuring cuvette that is 10 to 20 cm long and dried with a layer of CaCl_2 or $\text{Mg}(\text{ClO}_4)_2$. An asymmetric peak is observed in the absorbance trend after it reaches equilibrium on the line 253.65 nm. In 10 ml of aqueous sample, the detection limit is less than 1 ng Hg. When compared to standard flame atomic absorption spectrometry, the assay's sensitivity is roughly two orders of magnitude higher due to the mercury atoms' lengthy delay time in the tube. Tin chloride only breaks down mercury that is bound inorganically. If total mercury is to be determined, total mercury must be decomposed or determined after the reduction of the sample with sodium borohydride. The treatment of the sample prior to the determination is the main issue with mercury determination, not the analysis itself. Mineralization can make the mercury in the sample ionic, which is necessary for the complete reduction of mercury. In the case of mercury, this is extremely complicated and results in significant errors due to losses. The sorption of mercury in the measuring apparatus or the contamination of the chemicals used could also be a problem. (Gao et al. 2010)

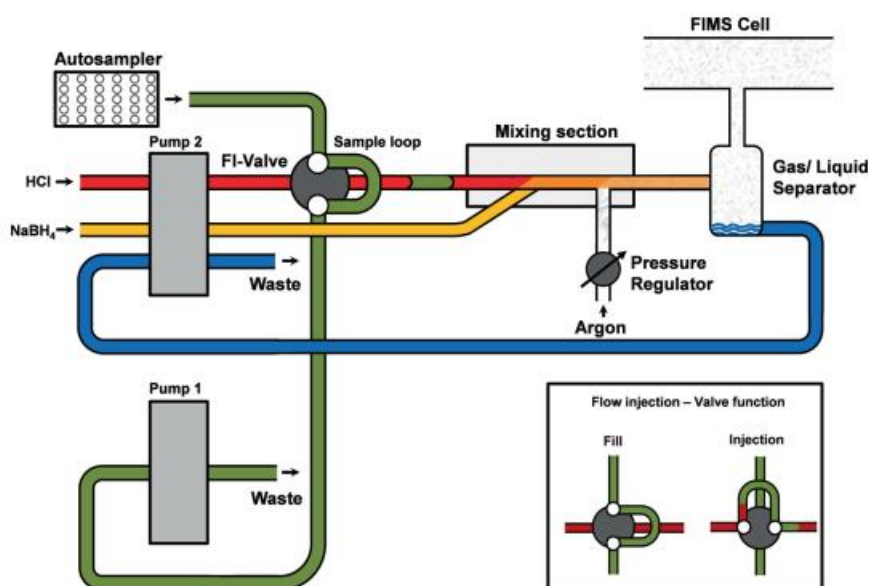


Figure 3 CV-AAS Scheme (Heitland, Göen, and Hartwig 2019)

There are a variety of methods for total Hg analysis, including non-destructive methods like Neutron Activation Analysis (NAA), destructive methods like an aqueous mineralization step followed by AFS or ICP-MS, and thermal decomposition methods like the AMA analyzer. (Gao et al. 2010)

The advanced mercury analyzer AMA 254 is a mercury-determining single-beam atomic absorption spectrophotometer. It is made to directly measure the amount of mercury in both liquid and solid samples without the need for chemical sample preparation (mineralization, etc.). An extremely high sensitivity of the determination and the independence of the determination result from the sample matrix is achieved by generating metallic mercury vapors and then enriching them on a gold amalgamator. (Cizdziel, Hinnners, and Heithmar 2002)

Inside the instrument, oxygen flows over the sample at approximately 200 mL min^{-1} while the temperature is raised to $120 \text{ }^\circ\text{C}$ to allow the sample to dry for a pre-specified time. The sample is then combusted as the temperature is raised to $750 \text{ }^\circ\text{C}$. The combustion products are carried through a $\text{Mn}_3\text{O}_4/\text{CaO}$ -based catalyst (kept at $750 \text{ }^\circ\text{C}$), where oxidation is completed; different chemical forms (species) of mercury are converted to elemental mercury vapor; and sulfur oxides, nitrogen oxides, and halogens are trapped. Mercury and other decomposition products are carried to an amalgamator chamber containing gold-coated sand. There, mercury is selectively trapped while other products are flushed out of the system. Later, the trap is rapidly heated to $700 \text{ }^\circ\text{C}$ to release the mercury vapor, which is carried in a pulse through a spectrophotometer. The mercury concentration in the sample is determined by the software from the absorbance measured at 253.7 nm and the amount of the sample used. An interference filter filters the radiation before a semiconductor UV diode detects it from a mercury lamp with low pressure. The analyzer operates in two ranges, which the software of the instrument chooses for itself to avoid exceeding the absorbance value of 0.8. The first range can analyze up to 500 ng Hg , while the second range covers roughly $0\text{-}30 \text{ ng Hg}$. (Cizdziel, Hinnners, and Heithmar 2002)

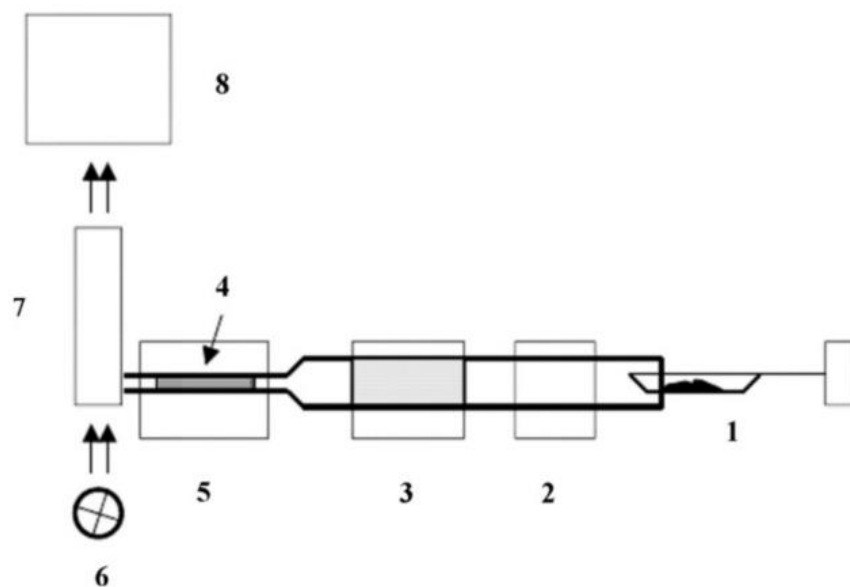


Figure 4 Scheme of AMA 254 spectrometer 1) sample boat, (2) decomposition furnace, (3) catalytic column, (4) gold amalgamator, (5) releasing furnace, (6) mercury cathode lamp, (7) optical cell system, (8) detector (Tomáš et al. 2013)

5 EXTRACTION OF MERCURY

The parent rocks determine where mercury in soils of any kind comes from. In the case of agricultural soils, it is the use of mercury-containing commercial and natural fertilizers, lime, and fungicides. In the case of surface soils, atmospheric mercury contributes significantly to pollution, particularly in areas with increased anthropogenic activity. The explanation of mercury's retention and mobility, as well as the equilibrium between the solid phase and the soil solution and its bioavailability for plants, require an understanding of the speciation and transformation reactions occurring in the soil. Using a technique known as speciation, it is possible to identify and determine the chemical forms or oxidation states of the element, making it possible to differentiate the various forms of mercury found in the soil. The oxidation state of an element, operationally (based on the extraction reagents or the methods used for their isolation), and functionally (such as bio accessible forms), can all be used to define a species. Typically, the use of simultaneous or sequential extraction is the foundation of operationally defined speciation. However, species are frequently extracted from other phases of the soil, so the extractants used in simultaneous extraction are rarely specific. Since the residue from one extraction is extracted by the next extractor in the sequence, we can increase the specificity of the extraction by combining individual extractants during sequential extraction. For the speciation of elements in soils and sediments, numerous sequential extraction procedures have been developed that vary in the number of extraction steps, the extraction reagents used, and the extraction procedure. (Reis et al. 2014)

One example of how to extract mercury can also be sequential extraction procedures. These methods have been developed for the speciation of elements in soils and sediments, which differs in the number of extraction steps, the extraction reagent used, and the extraction procedure. The outcome can be the separation of soil Hg into five fractions: water-soluble; diluted hydrochloric acid soluble; organically bound; elemental Hg; and mercuric sulphide. (Araújo et al. 2019)

Another study also used sequential methods to extract mercury from the soil. 1M $\text{CH}_3\text{COONH}_4$ (ammonium acetate) can be used to extract mercury from carbonates. However, the mercury bound into iron and manganese oxides can be extracted using CH_3COOH (acetic acid), HCl (hydrochloric acid) bound to organic matter, NaOH (sodium hydroxide) bound to humic and fulvic acids, HNO_3 (nitric acid) bound to Phosphates and sulphides bound to silicates, 2M Nitric acid solution, for metals bound to iron and manganese oxides, the combination of acetic acid, and Hydroxylamine hydrochloride, $\text{NH}_2\text{OH}\cdot\text{Cl}$ can be a suitable extraction method. Digestion

with HNO_3 and H_2O_2 can also be used to extract metals from sulfides and phosphates. (Závodská, Žemberyová, and Farkašová 1999)

Other extraction techniques include reagents like, Boric acid solution, Aqua regia, hydrofluoric acid and stannous chloride. (Pamela Heckel 2007)

6 REMOVAL OF MERCURY

As a result, the removal of Hg^0 is necessary for mercury removal from coal-fired power plants. The most common methods for removal are adsorption and catalytic oxidation. The other method was lignin, in which the mercury was extracted by soil. (Li et al. 2023)

Adsorption is the method that is used most often to get rid of Hg (II) from a solution of water. Adsorbents typically have a large surface area and a high porosity, and the primary sorption mechanism is the formation of chelates. To remove Hg^{2+} and $\text{Hg}(0)$ from water, covalent triazine nanospheres were created that function with thioether. The kinetic study revealed a rapid adsorption rate, which was 9 times faster than that of TAPB-BMTTPA-COF and 7 times faster than that of PAF-1-SH. Excellent adsorption capability was also observed (1253 and 813 mg/g, respectively, for Hg^{2+} and $\text{Hg}(0)$). The maximum adsorption capacity achieved when using a novel synthesized mesoporous conjugate adsorbent based on pentasil zeolite to adsorb Hg (II) in an aqueous solution was $172.6 \text{ mg}\cdot\text{g}^{-1}$. The adsorption of mercury ions onto the imine (C-NH-) groups around the surface of the nanoparticles was discovered when using silica-coated magnetic nanoparticles to extract Hg (II) from wastewater. Adsorption occurs primarily through chelation between chitosan's nitrogen atoms and Hg (II). Adsorption is also frequently used to get rid of gas-phase elemental mercury ($\text{Hg}(0)$). Hg preferentially forms complexes with soft ligands like sulfur to form insoluble and stable compounds, according to the "hard and soft acid-base" (HSAB) theory. Adsorbents with a high sulfur content were found to increase $\text{Hg}(0)$ adsorption capacity. While involving adsorbents for Hg evacuation, it is important that security and reusability ought to be truly thought of. (Wang et al. 2020)

Selective catalytic reduction and advanced oxidation methods can also be used for removing Hg. (Wang et al. 2020)

The stabilization and solidification method has been extensively used to treat mercury-contaminated waste and soil. In addition, numerous pilot and bench-scale studies have been conducted to identify binders and reagents that outperform conventional methods like cement. S/S entails physically binding or enclosing contaminants within a stabilized mass (solidification) or triggering chemical reactions between the stabilizing agent and the contaminants to reduce mobility (stabilization). (EPA-542-R-07-003 2007)

Mixing soil or waste with binders like Portland cement, sulfur polymer cement (SPC), sulfide and phosphate binders, cement kiln dust, polyester resins, or polysiloxane compounds to create a slurry, paste, or another semi-liquid state that is given time to cure into a solid is the

stabilization process. Polyester resins used in ex-situ S/S processes are mixed with waste at a low rate for five to ten minutes until a homogeneous mixture is formed. After that, a catalyst is added to this mixture to start the polymerization reaction. Mixing at a high rate for another 2 to 5 minutes continues until the temperature rises, which means that curing has begun. After that, the waste-resin mixture is allowed to cool and harden.(EPA-542-R-07-003 2007)

In addition, pH adjustment agents, phosphates, or sulfur reagents may be added to the S/S process to shorten the setting or curing time, increase compressive strength, or reduce contaminants' leachability.(EPA-542-R-07-003 2007)

7 FLY ASH PRODUCTION

Since almost all of the Hg contained in coal will be released into flue gas during coal combustion, which accounts for about half of the world's anthropogenic atmospheric Hg emissions during the early 2000s, coal combustion has been a significant source of Hg in the atmosphere over the previous 50 years. China has had difficulty lowering its Hg emissions from coal combustion, particularly from coal-fired power plants (CFPPs), which account for around 50 % of its national consumption and are the world's largest coal consumers. Over the past 20 years, CFPPs in China have improved their air pollution control technologies to reduce particle, SO₂, and NO_x emissions, with the clear added advantage of lowering mercury emissions. For instance, field surveys revealed that the atmospheric Hg emissions from four ultra-low emission power plants only accounted for 0.4 % – 14 % of the total Hg intake, which was significantly less than the statistics (64 % – 78 %) in China in the middle of the 1990s, when there were no limitations on SO₂ and NO_x emission for CFPPs.(Y. Huang et al. 2022)

Despite an increase in coal fly ash discharge, only about half of global production is used. About 130 and 190 million tonnes of coal-fired fly ash were produced annually in the United States and India, respectively, in 2015. Fly ash outputs from CFPPs in China were over 748 million in 2019, and in recent years, the fly ash utilization rate was around 70%. Unused fly ash is frequently heaped, where it may leak out with water or be re-emitted into the atmosphere, releasing Hg into the environment. Therefore, it is important to consider how mercury behaves in these CFPP by-products of flue gas cleaning.(Y. Huang et al. 2022)

The average Hg removal efficiency for pulverized coal (PC) furnace power plants in Guizhou province was 94 %, while the rate for circulating fluidized bed (CFB) utility boilers was 98% in the middle of the 2010s. For 11 of the pulverized CFPPs, 40% of the Hg in the feed coal ended up in the fly ash and 54 % in desulfurization gypsum in Guizhou province after upgrading SO₂, NO_x, and particulate emission control devices. In contrast, for CFB utility boilers, 97 %–99 % of Hg in the feed coal was ultimately removed into captured fly ash.(Y. Huang et al. 2022)

The export of Hg produced by CFPPs is mostly accomplished through the storage of Hg in fly ash. Numerous research has looked at the Hg level of fly ash from Chinese CFPPs. Another study stated that fly ash from a CFPP in North China had $465.0 \pm 89.0 \text{ g.kg}^{-1}$ Hg and that the Hg level of fly ash in Guizhou varied from 169.3 ± 0.8 to $889.0 \pm 0.9 \text{ g.kg}^{-1}$.(Chen et al. 2022)

II Experimental Part

8 EXPERIMENTAL PART

8.1 Materials

- Mercury calibration standard solution, 1 g/L (Analytica Co. Ltd, Czechia)
- Arsenic calibration standard solution, 1 g/L (Analytica Co. Ltd, Czechia)
- Multi – element calibration standard solution, 10 mg/L, AN M1004 Analytica Co. Ltd, Czechia)
- Nitric Acid 65% G.R. (Lach-Ner, Ltd, Czechia)
- Acetic acid, CH₃COOH
- River sediment (QCM 01, Analytica.Ltd, Czechia)
- Environmental samples for mercury determination (QCM 17, Analytika, Ltd, Czechia)
- Ice Acetic acid (PENTA Czechia)
- AAS ETA Modifier (Pd/ Mg (NO₃)₂), 3 g/L, 2 g/L (Analytica Co. Ltd. Czechia)
- glass fibre filter paper with pore size 0.45 µm. (Papirny Pernstejn Ltd., Czechia)
- Portland Cement (CEM 1 42.5 R, Cement Hranice, Czechia)

8.2 The laboratory equipment's

- Advanced Mercury Analyzer, Atomic absorption spectrometer AMA 254, Altec, Czech Republic
- ElvaX, X-Ray Fluorescence Spectrometer, Ukraine
- Atomic absorption spectrometer ContrAA 800, Analytikjena, Germany
- Analytical balances Kern ABJ 220-4NM, Germany
- Electromagnetic mixer MM4, Lavat, Czech Republic
- Dryer UM 100, Memmert, Germany
- pH meter 720 WTW series InoLab - Combined pH electrode: pH electrode SenTix 41, WTW, pH range 0-14 /0-80 °C/ store in 3 mol/l KCl, Germany

- Conductivity meter 730 WTW series InoLab conductivity cell: TetraCon 325, WTW, Germany
- Shaker Yellow line, RS 10 basic IKA, Germany
- Laboratory furnace MP 05-1.0, Laboratory furnace Martínek, Czech Republic
- Mineralizer MLS 1200, digestion/drying module, exhaust module EM-30, Milestone - microwave laboratory systems, Switzerland
- RZR 2020 overhead stirrer (Heidolph & Co.KG. Germany)

9 METHODS

9.1 Sampling

The sampling site was in the west outer Carpathians. The region is represented by clays and sandstones, whereas the main type of soil present in the area is luvisol. (Nejeschlebova Ludmila 2013)

The samples were sampled during the winter and spring time nearby (or) at the disposal site of fly ash from the heating plant shown in Fig 4. In total, 5 soil samples and 3 water samples were collected at different locations. In the case of soil samples, the sampling area had a dimension of 5 x 5 cm, and the soil samples were taken at a depth of 0.3 cm using a small shovel into transparent 250 ml plastic containers closed by plastic cover. Moreover, the water samples were taken from surface water, well water and small lake water (named green water), which was located on the site directly. The water samples were taken into 500 ml plastic bottles and closed tightly. Both soil and water samples were transferred in a dark box to the laboratory for analysis.

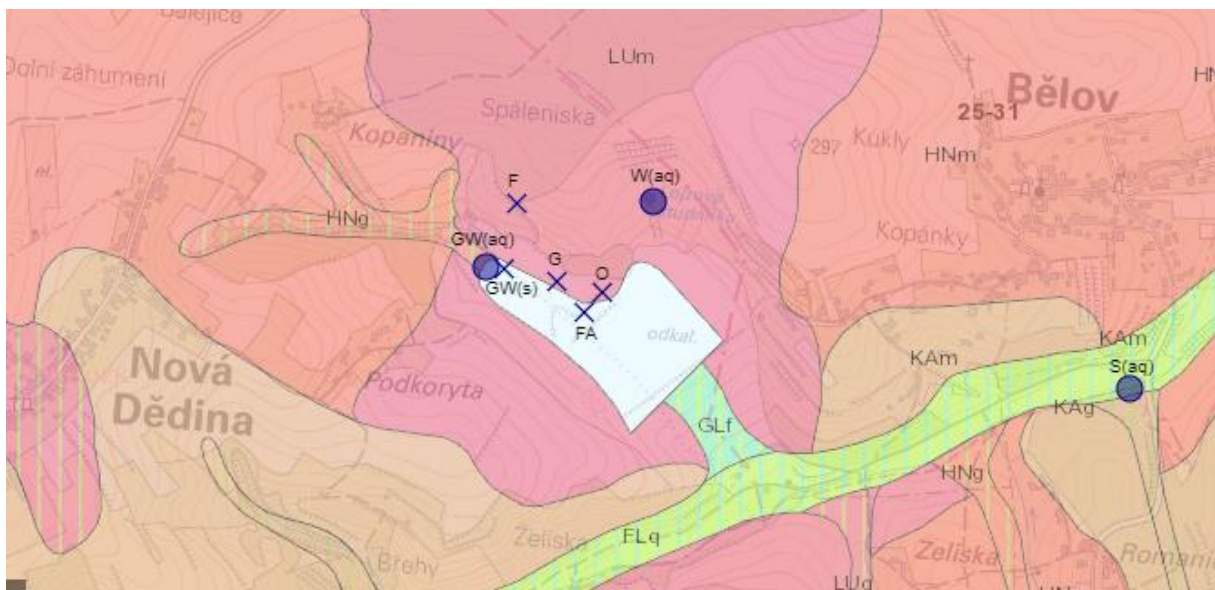


Figure 5 The map of the sampling site

The first sampling was carried out on 12/01/23. The sampling method was a random one conducted at a location with a height of 208 meters above sea level at 49.21965° N and 017.66312° E. The samples were taken between 13:30 and 15:30 in the afternoon. The day was cloudy, with a temperature of 7°C , 70 % precipitation, 83 % humidity, and a wind speed of 14 km/h. The site treatment activity was under progress in the nearby area where samples were

collected. In the case of springtime, the second sampling was conducted on 19/04/22 between 10:00 and 12:00 in the morning. The day was wet, with 8 °C, 1017.6 kPa pressure, 77 % humidity, and a wind speed of 18 kilometres per hour. The whole sampling procedure was like a winter one. The other sample used was a waste sample from a heat plant, which was taken in 2008 and exhibited almost similar characteristics to the fly ash sample collected from the site. The goal was to find the difference between seasonal changes in the metal content on site. The sampling spots are summarized in Table 1.

Table 1 Labeling of samples

Sample	Name	Abbreviation
Soil samples		
1	Original	O
2	Fly ash	FA
3	Grassland	G
4	Forest	F
5	Green water	GW (s)
Water Samples		
1	Well	W (aq)
2	Green water	GW (aq)
3	Stream	S (aq)

In addition, the disposal site of fly ash has roughly 15.25 hectares, and it was previously a lake from the 1970's on, it has become an area where fly ashes from heating plant are landfilled. Nowadays, the landfilling procedure continues in the form of stabilized mortar called OTOSAN (see table 2), which is a mixture of fly ash, slag, CaO, and desulphurization product. The heat plant is a producer of heat, and electricity that combines brown coal, natural gas, and biomass as sources for the combustion. The common composition of fly ashes is made from organic and inorganic parts (SiO_2 , Al_2O_3 , CaO, CaSO_4 , Fe_2O_3 a MgO) with some trace elements such as Cr, Pb, Ba, Zn, Ag, Mo, Se, Hg a As (Hower 2012). The annual emission of As and Hg from the heating plant is determined to be 12.8 kg of As and 4.3 kg of Hg in 2021. (Czech Meteorology Institute 2023)

Table 2 Composition of OTOSAN

Mixture	Dry matter of the raw material [% w]			
	Fly ash	Desulfurisation product	CaO	Slag
OTOSAN 1	45-60	30-45	0-5	20-30

9.2 The measurement of dry matter

To determine dry matter of the soil, each sample was weighed on an analytical balance and then dried for two hours in an oven at 105 °C. (ZBÍRAL et al. 2011)

Dry matter can be calculated by:

$$DM = \frac{m_2 - m_0}{m_1 - m_0} \cdot 100 \quad (1)$$

Where:

m_0 = weight of the dry petri dish [g]

m_1 = weight of sample + petri dish [g]

m_2 = weight of dry sample + petri dish [g]

DM = Dry matter [%]

9.3 The measurement of pH and conductivity

Before the actual measurement, the pH meter was first calibrated using three buffers solutions in the case of leachates from samples, and then with constant stirring, measured samples and determined pH. The samples were measured in 5:1 ratio (ISO 10390 2021). The conductivity was measured according to international standard ISO 11265. (CSN ISO 11265).

9.4 The measurement of organic matter content

To determine the organic matter content of the soil, 5 g of wet soil sample was weighed on a laboratory scale and dried in the oven for 24 hours.

From the wet sample, 5 g were weighed on a scale and dried in an oven for 24 hours at 550 °C (ZBÍRAL et al. 2011).

$$C (\%) = \frac{100(m_1 - m_2)}{m_1} \quad (2)$$

Where:

$C (\%)$ = content of organic substance by weight [g]

m_1 = weight of the sample before drying [g]

m_2 = weight of the dry sample after drying [g]

9.5 The method validation

To validate the measurement on AMA 254, two quality certified materials of fly ash sample from the coal power plant and wastewater sludge were measured using 50 mg of each material with the machine's setup 60/150/45 (see chapter 8.7). These materials were obtained from the Czech company Analytika, Ltd. under the commercial name METRANAL 17. The result was then compared with values provided by the company, and the recovery values were calculated using an equation (3) according to the US EPA methodology. (J.A.Shoemaker 2009)

$$\%R = \frac{\text{measured concetration}}{\text{theoretical concetration}} (\%) \quad (3)$$

9.6 Metal content analysis using X-ray fluorescence.

The XRF machine works in a way when the percentage of elements in a sample is exposed to a source of high-intensity X-rays, fluorescent X-rays will be emitted from the sample at energy levels unique to those elements.

An energy dispersive spectrometer with a rhodium-ray lamp was used for the measurement, along with a computer running ElvaX 2.8.2 software, and the following circumstances were monitored with no filter: For the spectra of light elements, an X-ray lamp with current $I = 64$ A and voltage $U = 10$ kV was used. The heavy element spectrum was also measured with the

following parameters in three filters: X-ray lamp voltage $U = 45$ kV, X-ray lamp current $I = 99.9$ μ A.

The samples were measured in dual mode, which measures the spectra of both light and heavy elements for 60 s (live time). Furthermore, samples have been measured in special containers made of polyethylene (30 x 22 mm). One side is stretched by special polypropylene film (Prolene film, CAT. NO: 416, Chemplex INDUSTRIES, INC.; Palm City, USA, foil thickness 4 μ m)

9.7 Mercury analysis

A sample of known weight (100 μ l for water sample and 50 mg for soil sample) was used to measure the mercury concentration on the AMA 254. The machine used a setup of 60 seconds for drying, 150 seconds for decomposition and 45 seconds for reading. In order to improve the element's detection, various machine configurations were tested by varying the decomposition time. At 150 seconds, a satisfactory detection was achieved.

The concentration of the unknown samples was calculated using a calibration standard with two calibration curves ranging from 0 – 40 ng and 0 – 500 ng, respectively.

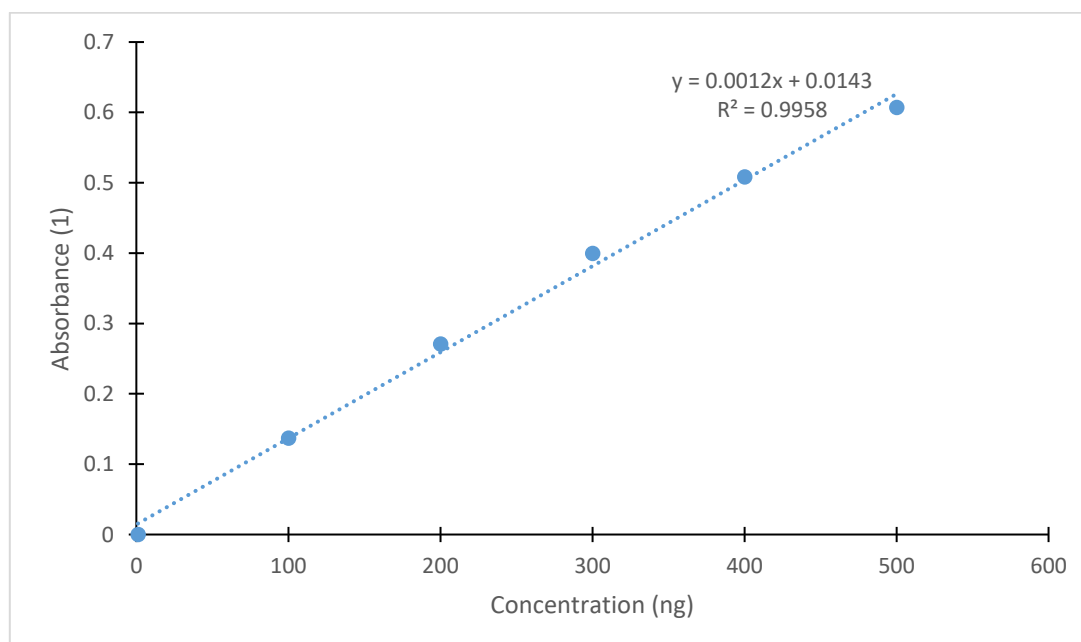


Figure 6 Calibration curve for higher mercury concentration range

9.8 Sample digestion

To evaluate the total metal content, all samples were decomposed using a microwave instrument (MLS 1200). A soil and fly ash sample of 0.2 g was weighed and digested with a special Teflon container containing 2.5 mL of HNO₃ and 0.5 H₂O₂. The digestion program is shown in table 3.

Table 3 The digestion program

Step	Time (min)	Power (W)
1	2	250
2	2	0
3	5	400
4	2	0
5	2	500
6	2	0
7	6	600

After the digestion, the sample was transferred into 25 mL volumetric flasks and diluted by distilled water. The method was also controlled by the digestion of certified material green algae. (Metranal 31, Astasol, Czech Republic).

The results for concentration were presented in mg/kg, and this can be calculated by:

$$C \text{ (mg/kg)} = \frac{C \text{ mg/l} * V \text{ (ml)} * 100}{m \text{ (g)} * (100 - w)} \quad (4)$$

Where

C = concentration (mg/l)

V = final volume after the digested is diluted (ml)

m = mass of the soil sample (g)

w = moisture content (%)

9.9 The measurement of metal content

9.9.1 Flame AAS

The metal contents in leachates made from the soil and ash samples were measured using an air-acetylene flame on the contrAA 800D atomic absorption spectrophotometer (contrAA 800D, Analytical Jena., Germany). To determine unknown concentrations in the samples, multielement standard diluted with 2M HNO₃ and HF was used as a calibration standard solution, in which the concentration was 10 mg/L of selected elements. The calibration standards were then prepared from 0 – 10 mg/L. Measured elements and their wavelength are summarized in table 4.

Table 4 The wavelength of the elements detected on AAS

Measured elements	wavelength[nm]
Cu	324
Zn	213
Cd	228
Co	240
Ni	232
Fe	248
Pb	217
Mn	279

9.9.2 Graphite furnace AAS

Arsenic concentrations in the soil from all the samples were measured by graphite furnace atomic absorption spectroscopy at a wavelength of 197.197 nm. Firstly, a working solution of 500 µg/l was prepared from a 1 g/l Astasol standard solution. Other calibration standards were prepared by diluting a working solution in a range of 0 – 375 µg/l. After that, the samples were measured with pyrolysis and atomization temperatures at 1100 °C and 2200 °C, respectively. To increase pyrolysis temperature, 0.05 % Pd and 0.1 % Mg (NO₃)₂ diluted in a 2% HNO₃ were used as a modifier. The sample volume injected into the machine was 20 µl plus 5µl of a modifier.

9.10 Stabilization and solidification of Fly ash sample from heat plant

The solidifying mixture was prepared by mixing binder and waste in different ratios. The type of binder was Portland cement (CEM 1 42.5 R) manufactured by Cement Hranice. Samples were weighed according to the cement waste ratio. In total, the 7 mixtures were prepared in which the waste content ranged from 20 to 70 %wt. The total mass of solidifying mixture was 50 g. After weighing the samples, an overhead stirrer RZR 2020 was used to mix the waste and cement for 10 minutes. To improve the paste's workability, 25-50 ml of distilled water was added to the mixture. Then, the paste was poured into a cylindrical mould with dimensions of 30 x 50 mm and stored for 28 days in a dark place. Solidified samples were subjected to leaching tests 28 days later in distilled water and acetic acid. (See sub-chapter 8.11)

After 28 days, the leachates were filtered through a 0.45 µm glass fibre filter paper to remove suspended solids and measured on AAS for heavy metals present.

9.11 Leaching Methods

There are different extraction methods that are used to extract elements from a soil sample. In this paper, three extraction methods were used:

9.11.1 Modified 2M HNO₃

By decree 271/2019 Coll., a soil leachate ratio of 1: 10 was used to extract metals from a soil sample, which was 2.5 g of the soil sample and 25 ml of 65% (w/v) HNO₃. Then the mixture was shaken for 24 hours with 150 RPM on an automatic shaker. After that, the solution was filtered using filter papers made from glass fibres with a pore size 0.45 µm. (Papirny Pernstejn Ltd., Czechia) (Czech Ministry of the Environment 2019)

9.11.2 Acetic acid

All samples were extracted using acetic acid leachate. As per the norm TPLC 1311, liquid solid ratio of 20:1 with particle size ≤ 1 mm were used for the mixture. Then the mixture is shaken on a mechanical shaker for 18 ± 2 hours with 150 RPM on an automatic shaker. After that, the solution was filtered using filter papers made from glass fibres with a pore size of 0.45 µm. (Papirny Pernstejn Ltd., Czechia) (EPA 1992).

9.11.3 Distilled water

Another extraction leachate medium was distilled water according to the European norm EN 12457-4, a liquid-solid ratio of 10:1 with particle size ≤ 10 mm was used for the preparation of the mixture. After that, the mixture was shaken for 24 hours at 150 rpm on an automatic shaker (EN 12457-4 2002).

9.11.4 Statistical analysis

The statistical analysis was carried out using the calculation of standard deviation. In the whole document it was presented in the form of brackets () in tables or in error bars in tables. The standard deviation can be calculated by the formula: (4)

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (x_i - \mu)^2}{n - 1}}$$

Where

σ – is a symbol that denotes standard deviation

x_i – is the i^{th} number of observation in the data set

n – is the number of observation in the data set

μ - is the mean of the sample

$\sum x$ – is the sum of all values in the data set

10 RESULT AND DISCUSSION

10.1 Basic characterization of soil samples

As the first step, the soil property parameters were determined for samples collected in both sampling events. The results are summarized in table 5:

Table 5 Measurements of soil property parameters

Sample	Winter				Spring			
	Dry matter [%]	pH	Conductivity [$\mu\text{S}\cdot\text{cm}^{-1}$]	organic matter content [%]	Dry matter [%]	pH	Conductivity [$\mu\text{S}\cdot\text{cm}^{-1}$]	Organic matter content [%]
Forest	73.92	6.99	200	10	82.78	6.86	29	9.2
Original	74.97	6.89	105	7.7	80.12	8.52	115	9.9
Green water	80.68	8.07	322	5.2	61.32	8.54	2235	7
Grassland	74.06	4.52	171	9.2	79.92	6.76	182	7.9
Fly ash	79.55	7.74	215	10	63.82	12.06	5208	11.9

All the samples had dry matter ranging from 60 to 80 %. Additionally, samples collected in winter had a pH value that ranged from 4.52 to 8.07, where the grassland sample showed a strongly acidic condition, whereas the green water sample showed a slightly alkaline condition. In contrast, the spring samples have a pH range of 6.76 - 12.06. A strong alkaline condition were implicated in the fly ash sample, which can be caused by the presence of materials cementitious materials at the site. The conductivity of samples collected in winter had a value in close proximity to $200 \mu\text{S}\cdot\text{cm}^{-1}$. However, the green water and fly ash samples collected in spring had a higher conductivity than the other samples, with the fly ash sample being the highest with $5208 \mu\text{S}\cdot\text{cm}^{-1}$. Moreover, the organic matter content of the soil samples collected during winter and spring time had a close value between each other. The result showed a similar organic matter content with mineral soils.(Oades 1989)

Table 6 measured the parameters of water samples.

Samples		pH	Conductivity [$\mu\text{S}\cdot\text{cm}^{-1}$]	ORP [mV]
Winter sample	Stream water	6.7	788	388.8
	Green water	6.01	3242	328.4
	Well water	6.6	695	315
Spring sample	Stream water	7.6	880	387.2
	Green water	6.97	6392	441.5
	Well water	6.87	700	454.1

Similarly, water samples were also collected from the site, and the parameters of the samples are shown in table 6. All of the water samples that were taken in the winter and spring had pH values between 6.01 and 7.6, which is in a neutral range. A study carried out in 2012 at the same area on water samples shows a pH value within the range of 7.48 – 7.9. (Nejeschlebova Ludmila 2013) .

The conductivity of the green water sample showed a higher value than the other samples. The reason for a higher result for the green water sample might be its location because the green water sample was located near a fly ash landfill area, which can probably be the cause for some parts of the fly being dissolved in the water.

In addition, surface and well water samples had conductivity ranging from 698 to 880 S/cm, which shows that the samples were moderately saline. However, the green water sample had saline water characteristics and a conductivity range of 3242–6392 $\mu\text{S}/\text{cm}$. The conductivity value also indicates a lot of dissolved ions present in the water sample.

Another parameter measured was oxidation-reduction potential (ORP), where the values range 315 – 454.1 mV, representing oxidizing conditions in the area.

10.2 Metal content analysis using X-ray fluorescence

The elemental content of each soil sample was measured on X-ray fluorescence. The Spectrum of samples are illustrated in figure 7 and figure 8.

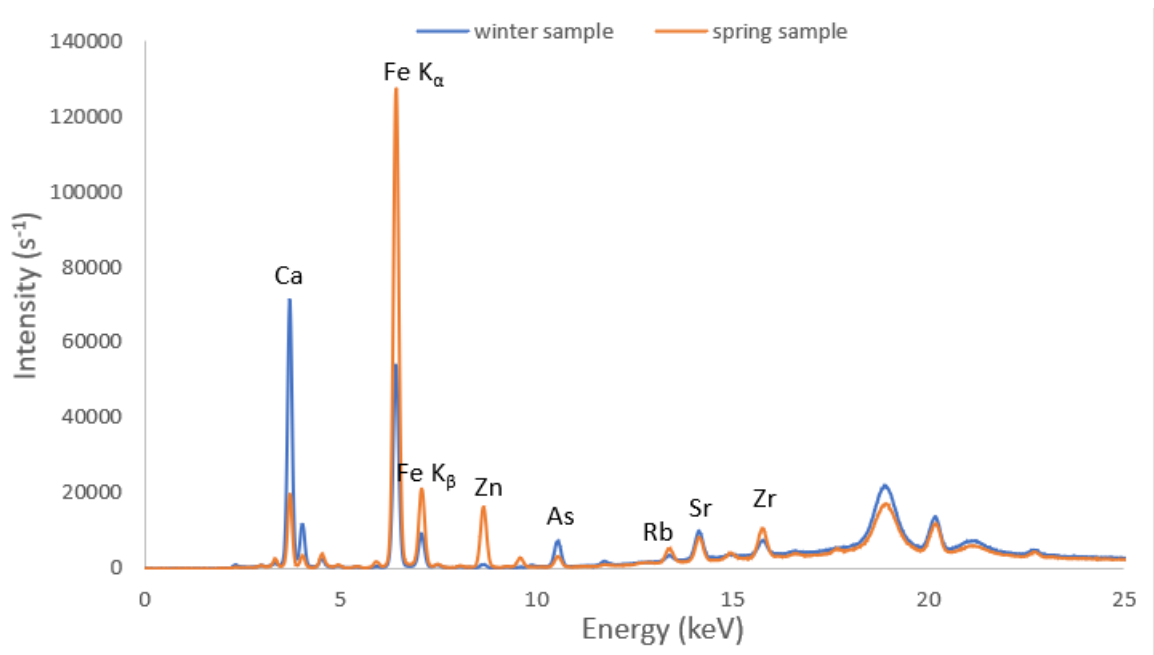


Figure 7 XRF spectrum of 1st and 2nd fly ash sample

In the fly ash sample, the elements found in abundance include, Fe (approx. 25.9% in winter and 15.0% in spring), Ca (44.2% and 70.7%), Sr, and S. Various metals were also present in the fly ash sample, however, they are only found in trace amounts. The origin of calcium and sulfur can be from coal combustion.

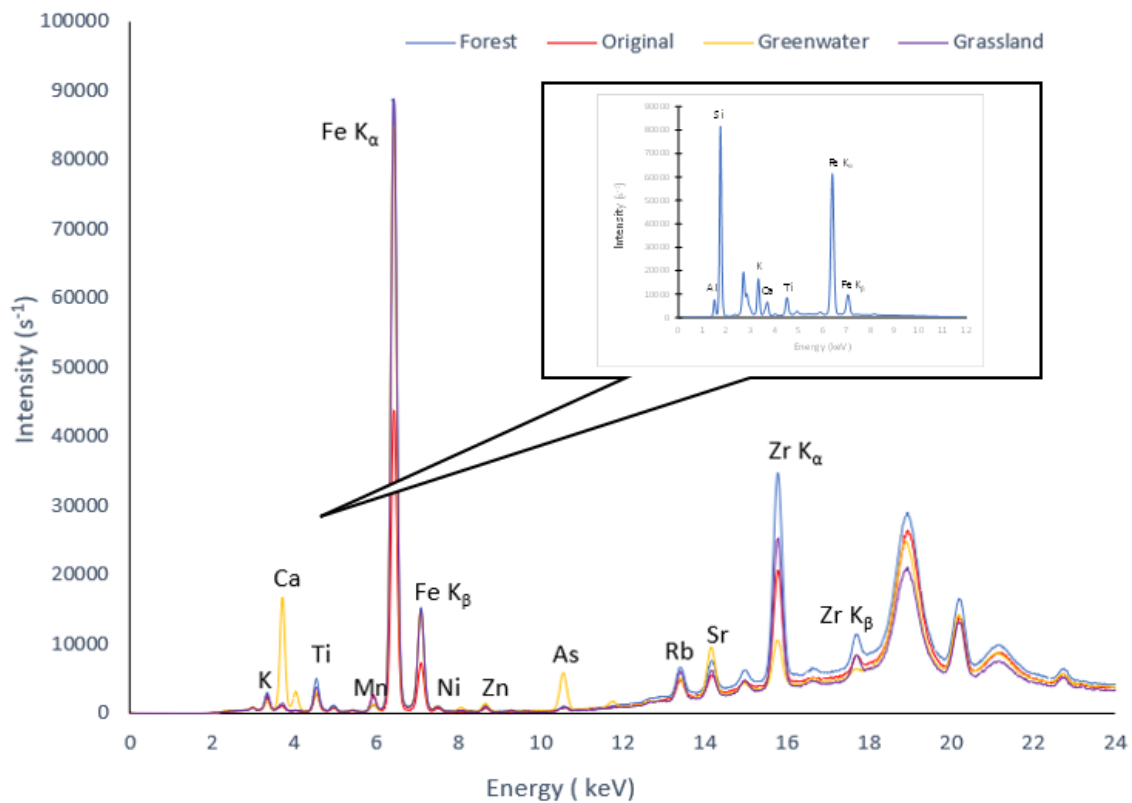


Figure 8 XRF spectrum of different soil samples

During the analysis, all soil samples contained a significant amount of Fe, as depicted in figure 8. Likewise, Zr and Sr were found in a generally high amount in every one of the samples. However, most of the samples contained low concentrations of Ca, K, and As. During the analysis of the soil samples, it was found that there is a significant arsenic content in all the places where samples are collected. The highest content was found in the fly ash sample, with abundance ranging between 0.4 and 0.6 %. Moreover, mercury was not detected in the samples. The reason can be the amount was less than the detection limit of the machine. On the other Al and Si were found in a significant amount.

10.3 Mercury analysis in samples

10.3.1 Method Validation

The instrument used to measure the concentration of mercury (AMA 254) was first validated by measuring quality control materials (Metranal 17). As shown in table 7, the recovery of test samples was up to 125 %, which is a good recovery range because it was less than 150 %.(J.A.Shoemaker 2009)

Table 7 Hg concentration in model samples

	Sample	Hg concentration [mg.kg ⁻¹]	standard Hg concentration [mg.kg ⁻¹]	Recovery (%)
Quality control materials	fly ash from heat plant	1.642	1.32	124.39
	sludge	6.518	5.2	125.35

10.3.2 Mercury determination in water

The concentration of mercury in all three water samples was measured. The results are shown in table 8.

Table 8 Mercury concentration in the water sample

Samples	Winter time	Spring time	drinking water limit [µg.L ⁻¹]
	Hg concentration [µg.L ⁻¹]	Hg concentration [µg.L ⁻¹]	
Well	0.1	0.6	2
Surface	0.2	0.6	
Green water	0.2	0.9	

From the result above, samples collected during winter and springtime showed an almost similar concentration of mercury in the range from 0.1 to 0.9 $\mu\text{g}\cdot\text{L}^{-1}$. However, the green water sample had a relatively higher mercury concentration, and the value was also lower than the mercury concentration limit for surface water in the Czech Republic which is set to 0.07 $\mu\text{g}\cdot\text{L}^{-1}$. In the case of well water, the concentration was below the limit for drinking water, which is 0.002 $\text{mg}\cdot\text{L}^{-1}$. This result can be compared with a study carried out on three rivers in Poland, which shows the mercury concentration in the surface waters to be 0.42 - 0.89 $\mu\text{g}\cdot\text{L}^{-1}$ (Jabłońska and Kluska 2020). Most importantly, a study carried out on the same area around Belov showed an average mercury concentration in water to be 4.1 $\mu\text{g}\cdot\text{L}^{-1}$, which was a slightly higher concentration. (Nejeschlebova Ludmila 2013; Government regulation No 401/2015 Coll 2015; EPA CFR 40-25-141-Subpart G 2019).

10.3.3 Mercury determination in soil

Mercury measurement results for the five soil samples are presented in figure 9. The mercury concentration for original, forest and grassland samples collected in winter showed insignificant differences between the results. However, fly ash and greenwater samples collected in spring had a much higher concentration, with values of 0.763 $\text{mg}\cdot\text{kg}^{-1}$ and 0.664 $\text{mg}\cdot\text{kg}^{-1}$ respectively, than samples from winter, with the concentration of 0.395 $\text{mg}\cdot\text{kg}^{-1}$ for fly ash and 0.099 $\text{mg}\cdot\text{kg}^{-1}$ for green water. The main reason for the difference in results might be caused because of the sampling technique used, which was random sampling.

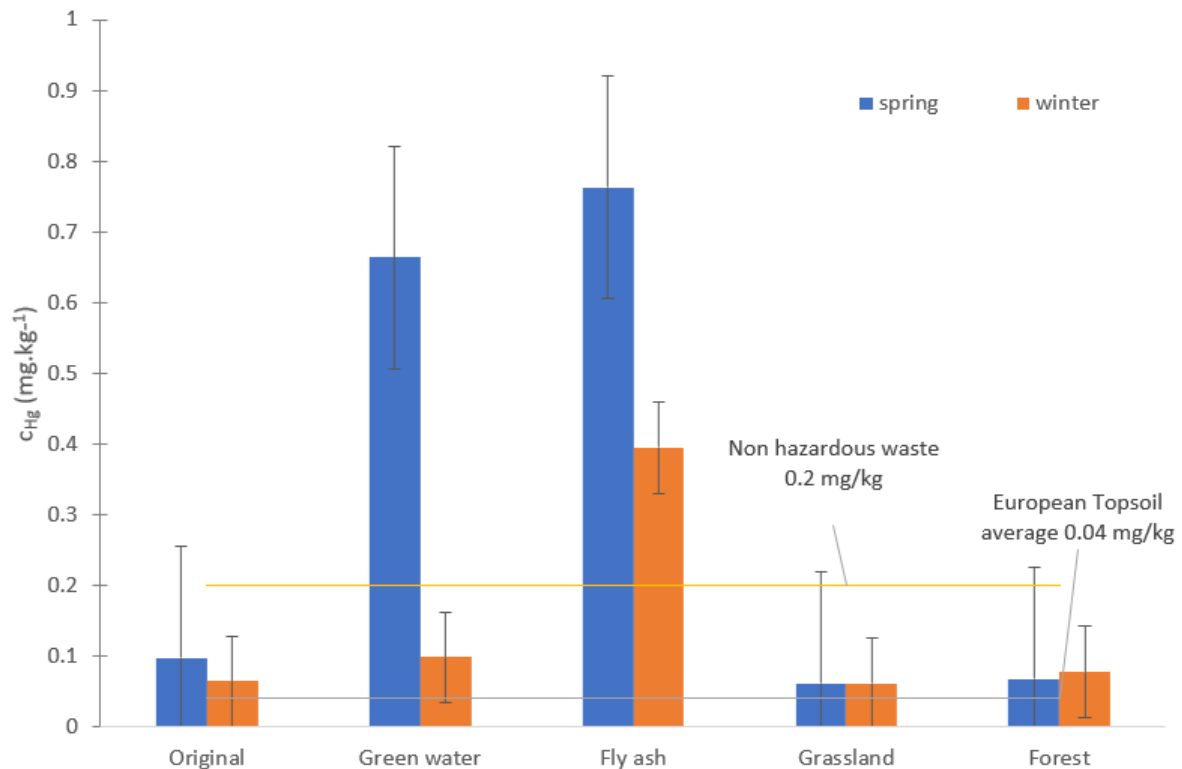


Figure 9 mercury concentration in different soil samples

On the other hand, a high concentration of mercury was seen in all the samples when compared with the average mercury concentration for European topsoil's, which is 0.04 mg/kg, (Gworek, Dmurchowski, and Baczewska-Dąbrowska 2020). In other study the mercury content was measured on the upper layer of a soil, in selected areas of two districts in Warsaw, ranging 0.0334 – 0.4004 mg/kg, 0.2320 – 1.3098 mg/kg and 0.2544 mg/kg, which is the same as the mercury content in a landfill site. (Małuszyński, Dabrowski, and Małuszyńska 2019)

In contrast, fly ash samples can be considered as waste. For example, a comparison made with non-hazardous waste which has an average mercury concentration limit of 0.2 mg/kg, showed a relatively high value when compared with the three soil samples but lower than the fly ash and green water samples. (European commission 2003)

10.3.4 Mercury extraction methods from soil samples

In order to estimate the available fraction of an element present in a soil sample, it is important to use a suitable extraction method. Commonly used extraction methods include the use of leachates. It can be with 2M HNO₃, acetic acid or distilled water. Since all the leachates have different pH, their extraction capacity is also different. Practically the HNO₃ leachate has a high extraction efficiency because it is a strong acid with a 0.5 pH value. On the other hand, the second best leaching medium is acetic acid, with pH value of 2.5, and the least effective leaching medium is distilled water, with pH close to 7.

As shown in table 9, soil samples collected in the winter season using 2M HNO₃ leachate had a mercury concentration range of 0.0095 – 0.064 mg.kg⁻¹, whereas for spring samples, the range was 0.0003 – 0.0529 mg.kg⁻¹ which do not have a significant variation of results. However, the mercury concentration was in the range of 0.0031 – 0.0595 mg.kg⁻¹ compared to soil samples extracted by acetic acid. The result also showed that the soil samples leached in HNO₃, had a slight edge in mercury concentration than the acetic acid leachates. Relatively low concentrations of mercury were measured in the distilled water leached soil sample with a concentration range of 0.00011 – 0.0017 mg.kg⁻¹.

Table 9 Hg concentration with different leaching medium

Samples	Winter	Spring		
	Hg Concentration [$\text{mg}\cdot\text{kg}^{-1}$]			
	2M HNO_3	2M HNO_3	Distilled water	Acetic acid
Original	0.0095 (0.0055)	0.0529 (0.013)	0.0017 (0.001)	0.003 (0.0031)
Forest	0.064 (0.0014)	0.0009 (0.0015)	0.00011 (0.0001)	0.0133 (0.001)
Grassland	0.05 (0.004)	0.0003 (0.0011)	0.00024 (0.00012)	0.0262 (0.001)
Greenwater	0.026 (0.004)	0.0882(0.015)	0.00011(0.0001)	0.0595 (0.002)
Flyash	0.042 (0.014)	0.0529 (0.0013)	0.00013 (0.0001)	0.0063 (0.003)

10.3.5 Digestion of soil samples

Digestion is also one mechanism used to extract elements from a soil sample. In this research, the mineralisation was carried out by microwave digestion with HNO_3 and H_2O_2 , which is very often used in the determination of metal content in soil. As shown in table 10, the mercury concentration of the digested samples was determined. All the samples digested show very close results except the fly ash and forest samples with concentrations of $0.154 \text{ mg}\cdot\text{kg}^{-1}$ and $0.184 \text{ mg}\cdot\text{kg}^{-1}$. Quality control material (river sediment) shows a mercury concentration of $0.075 \text{ mg}\cdot\text{kg}^{-1}$, lower than the standard concentration of $1.3 \text{ mg}\cdot\text{kg}^{-1}$.

Table 10 Hg concentration in digested samples

Digested samples	Hg Concentration [mg.kg ⁻¹]
Green water	0.053 (0.008)
Original	0.285 (0.089)
Grassland	0.210 (0.028)
Fly ash	0.154 (0.0005)
Forest	0.184 (0.01)
River sediment	0.075 (0.0064)

The digestion method with other extraction methods, like 2M HNO₃ leachate extraction, shows a higher extraction capacity. For example, the average mercury concentration for digested soil samples was 0.16 mg.kg⁻¹, whereas for the soil samples leached using 2M HNO₃, the average mercury concentration was 0.03 mg.kg⁻¹.

10.4 Metal content analysis using Atomic Absorption Spectrometry

Furthermore, the presence of heavy metals in the soil samples was measured by AAS. The results are summarised in table 11. From the results, it can be concluded that the iron concentration for the fly ash sample was, on average, 411 mg.kg⁻¹ in all soil samples, whereas the green water soil sample was the highest with 637.3 mg.kg⁻¹. Other elements presented in a high concentration in all sampling spots were manganese and zinc because their occurrence is more likely controlled by geochemical processes. For comparison, the concentrations of Manganese and Zinc in the same type of soil were 154 mg.kg⁻¹ and 18 mg.kg⁻¹. Moreover, moderate amounts of Ni, Pb, Cu, Co were found at every place. The only metal that was not detected was Cadmium, probably because of the detection limit of the machine used.(Reedy 1976)

Table 11 Concentration of heavy metals in the soil samples

Sample	Winter								Spring							
	Concentration [mg.kg ⁻¹]								Concentration [mg.kg ⁻¹]							
	Cu	Zn	Cd	Co	Ni	Fe	Pb	Mn	Cu	Zn	Cd	Co	Ni	Fe	Pb	Mn
Greenwater	16.7 (1.18)	110.7 (2.14)	0	8 (1.27)	20.3 (0.45)	637.3 (24.29)	14.1 (1.41)	271.5 (29.44)	17.5 (1.75)	45.7 (4.02)	0	0.8 (1.28)	0.8 (21.85)	195.4 (171.4)	0	85.6 (105.81)
Original	15.2 (0.87)	84.2 (6.93)	0	5.6 (1.51)	25.3 (1.3)	664 (21.39)	10 (1)	276.7 (21.39)	3.7 (0.37)	42.3 (0.9)	0	0.7 (0.32)	0.3 (2.99)	169.1 (16.24)	1.7 (0.17)	163.9 (103.77)
Grassland	8.9 (0.84)	38.3 (32.58)	0	6.6 (0.88)	6.1 (0.5)	547.3 (13.11)	17.1 (1.71)	277.4 (11.50)	3.7 (0.34)	36.6 (0.62)	0	0.3 (0.2)	2.4 (11.73)	230.5 (36.29)	0.3 (0.03)	11.8 (36.54)
Fly ash	19.7 (9.81)	110.9 (9.81)	0	5.4 (1.34)	15.9 (2.41)	591.1 (28.77)	7.5 (0.75)	171.7 (17.19)	6.8 (0.68)	32.5 (2.21)	0	0	0.6 (11.29)	125.7 (98.82)	0	34.2 (30.32)
Forest	5.4 (7.41)	53 (7.41)	0	6.4 (0.65)	6.9 (0.2)	519.5 (9.13)	15.2 (1.52)	284.9 (1.56)	2.2 (0.12)	37.1 (0.38)	0	0.3 (0.13)	0.5 (2.3)	202 (11.88)	2.1 (0.21)	98.7 (9.87)

*0 – Not detected

In general, soil samples collected in winter had the highest concentration of Fe, which was 406.4 mg.kg⁻¹ than the Fe concentration for spring samples was 238.98 mg.kg⁻¹.

From the heavy metals present in the soil samples, lead and nickel were also found in a moderate amount, with average concentrations of 8.5 and 128.68 mg.kg⁻¹. When comparing the results with other studies, such as a study carried out on European top soils, which had Pb and Ni concentrations of 15.3 mg.kg⁻¹ and 18.36 mg.kg⁻¹. (El-Naggar et al. 2021)

Table 12 Heavy metal concentration in the digested samples

Digested samples	Concentration [mg.kg ⁻¹]							
	Cu	Zn	Cd	Co	Ni	Fe	Pb	Mn
Green water	10.23 (0.62)	7.16 (0.8)	Not detected	0	20.11 (1.2)	3958 (515.3)	1.04 (0.02)	828.2 (2.63)
Orignal	27.61 (1.2)	2.95 (0.52)	Not detected	8.14 (5.6)	65.9 (12.5)	2690 (142.6)	0	738.1 (7.2)
Grassland	4.4 (0.52)	4.7 (1.02)	Not detected	Not measured	2.12 (0.2)	3544 (313.2)	6.11 (2.5)	834.1 (43.9)
Fly ash	Not measured	1.79 (0.45)	Not detected	Not measured	3.93 (3.4)	Not measured	Not measured	Not measured
Forest	27.86 (1.02)	6.69 (2.1)	Not detected	Not measured	17.51 (5.6)	3567 (512.1)	Not measured	510 (120.5)
River sediment	88.61 (25.1)	717.5 (52.7)	Not detected	Not measured	26.4 (4.56)	3943 (236.2)	71.4 (3.5)	877.8 (26.5)

The findings of the sample digestion, as shown in table 12 reveal that the soil samples had the highest concentration of Fe in all the samples, ranging from 2689.8 to 3957.9 mg/kg. Manganese, with a concentration in the soil of 238.35 - 877.82 mg/kg, was the other very prevalent metal. All other heavy metals, such as Cu, Zn, Co, Ni, and Pb, exhibit modest concentrations.

A study on heavy metals in European topsoils showed that there is a high Mn content in the soils with values ranging 600 – 900 mg.kg⁻¹. Other heavy metals present in the European topsoils show relative results with the samples measured in the Belov area.(Tóth et al. 2016)

Research carried out in eastern Spain on soil collected from a river basin and processed using microwave-assisted digestion revealed significant concentrations of Fe and Mn with respective levels of 15,274 mg/kg and 320 mg/kg. The soil sample also included other heavy metals like Co, Cr ,Cu Ni, and Zn. (Carolina Mico 2007)

10.4.1 Arsenic content in the soil samples

During the analysis of heavy metal content and mercury, it was found that arsenic was also present in the soil samples in a significant amount. As concentration was determined using graphite furnace atomic absorption spectroscopy. The results are shown in table 13.

Table 13 Concentration of arsenic in different leaching methods

Samples	Winter	Spring		
	Concentration [mg.kg^{-1}]	Concentration [mg.kg^{-1}]		
	2M HNO_3	2M HNO_3	Distilled water	Acetic acid
	As	As	As	As
Green water	1.64 (0.058)	9.7 (1.04)	1 (0.02)	11.8 (1.5)
Original	0.22 (0.036)	2.8 (2.08)	0.2 (0.05)	0.3 (0.05)
Grass land	1.4 (0.86)	0.3 (0.05)	0.1 (0.06)	0.2 (0.06)
Fly ash	3.82 (2.98)	17 (7.07)	0.9 (0.02)	71.7 (15)
Forest	0.92 (0.109)	0.7 (0.02)	0.2 (0.001)	0.2 (0.001)

Arsenic was one of the heavy metals discovered in the soil samples at a significant quantity compared to its toxicity. There were three different leaching techniques used: 2M HNO_3 , distilled water, and acetic acid leachates. Fly ash is the sample with the highest concentration of arsenic across all three leaching techniques, with values ranging from 3.82 to 71.7 mg/kg. Like the other samples, arsenic was detected in the green water sample but at a considerably higher concentration.

Soil samples collected in winter showed a high concentration of arsenic than samples collected in spring. The reason for the difference in results could be the random sampling technique used.

For comparison, a study carried out on soil samples collected from the Mississippi River alluvial flood plain located in northwest Mississippi shows the arsenic concentration to be 5.73 mg.kg^{-1} . (Cooper and Gillespie 2001)

10.5 Stabilization and solidification

10.5.1 Waste Analysis

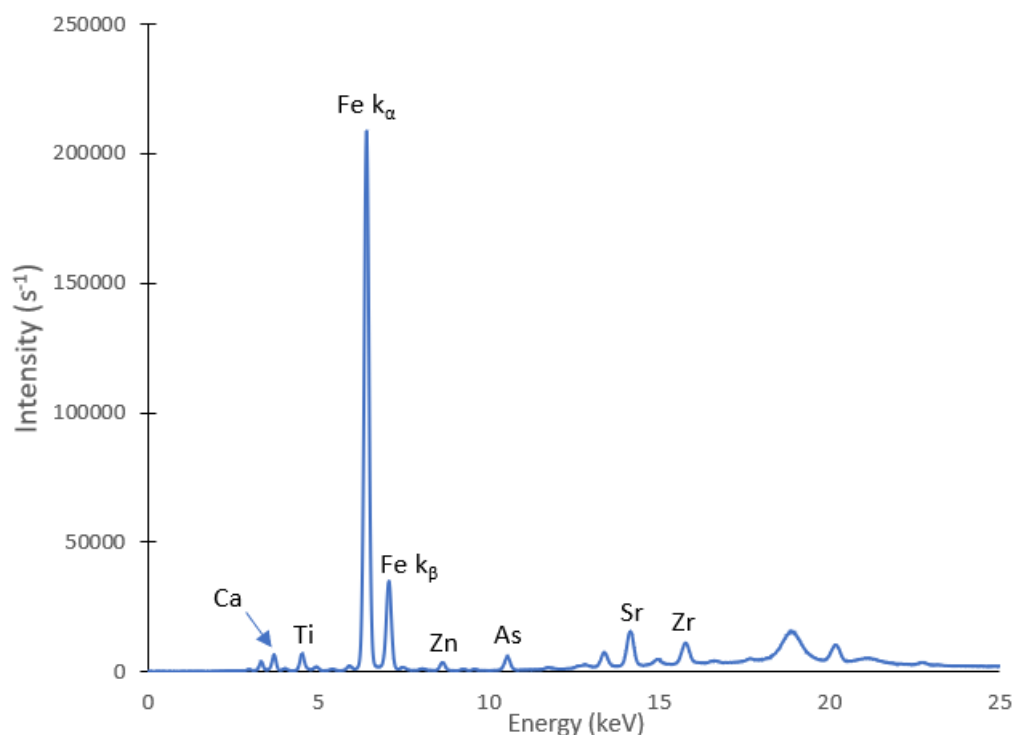


Figure 10 XRF spectrum of waste sample from the heat plant

As shown in Figure 10, the waste sample contains different heavy metals and one metalloid. From the metals present, Fe was found in abundance. Other elements included in the waste sample were Zr, Sr, Ca, Ti, Zn, and As and compared with the fly ash sample, the waste sample showed similar element composition.

10.5.2 Metal content in the waste sample

The metal content of the waste sample was determined by flame AAS, and the results are shown in figure 11. During the analysis of waste samples, both methods showed a high content of Iron in the waste sample up to 3000 mg.kg⁻¹. However, the digested sample had a much more Iron content than the 2M HNO₃ leached sample. The second most abundant element in the sample was Manganese and Zinc, which were present in a low amount than Fe however in a high amount compared to Cu, Cd, Pb, and Co. As a result, the digestion method was more efficient in extraction than 2M HNO₃ method.

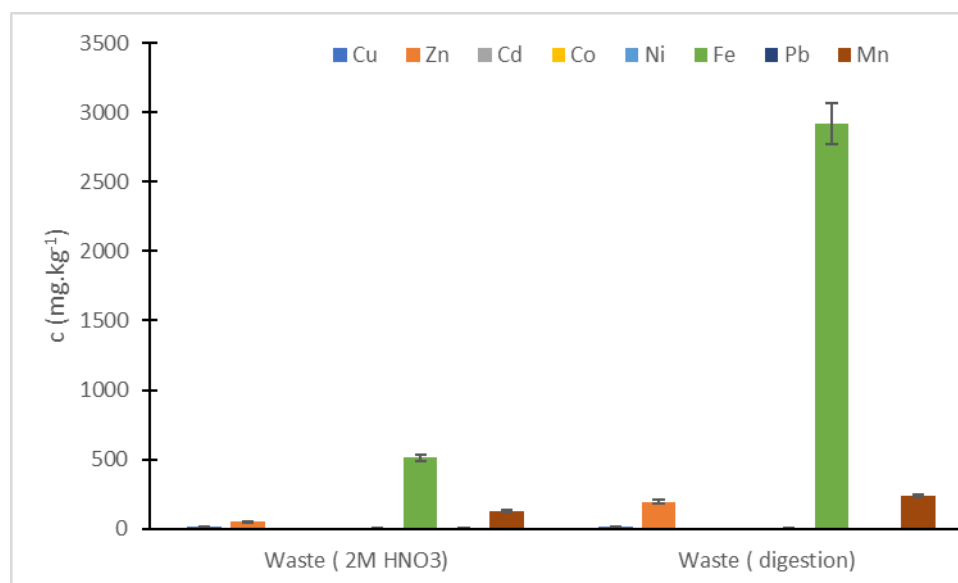


Figure 11 metal content in waste sample from heat plant

Other metals and metalloids present in the waste sample were Hg and As. The concentration of Mercury and arsenic from the leached samples were determined by AMA 254 and GFAAS, respectively. The results are shown in table 14.

In both distilled water and acetic acid leached samples, the arsenic was found in a relatively high concentration for acetic acid leachate, 29.02 mg.kg⁻¹ and distilled water leachate, 18.75 mg.kg⁻¹. The arsenic concentration for the waste sample from heat plant was 37.21 mg.kg⁻¹. when compared with European standard for waste landfill limits for arsenic, which is 25 mg.kg⁻¹ for hazardous and 2 mg.kg⁻¹ for non-hazardous wastes, the result is above the limit. (European commission 2003)

Furthermore, the mercury concentration of waste samples showed a very low result in both leaching methods. It was even lower than the limit for the European standards, which is 2 mg.kg⁻¹, and the Universal treatment standard (UTS), which was 0.025 mg.kg⁻¹. (US EPA 2016)

Table 14 As and Hg concentration of a leached waste sample

Sample	As concentration [mg.kg ⁻¹]	Hg concentration [μg.kg ⁻¹]
Fly ash (Acetic acid leachate)	29.02 (2.185)	0.026 (0.0025)
Fly ash (Distilled water leachate)	18.75 (2.821)	0.0423 (0.0005)
Waste [mg.kg ⁻¹]		
	37.21 (3.2)	0.48 (0.11)

10.5.3 Stabilization and solidification results

The waste sample was stabilized and solidified by using Portland cement. Seven ratios of cement and waste were used. After solidification of the samples, they were leached with distilled water and acetic acid. The measured values of the stabilized and solidified samples are shown in table 15 and table 16.

Table 15 Hg concentration in stabilized and solidified samples

Cement, waste ratio	Hg Concentration [mg.kg ⁻¹]	
	Distilled water leachate	Acetic acid leachate
20/80	Not detected	0.0812
30/70	Not detected	Not detected
40/60	Not detected	Not detected
50/50	Not detected	Not detected
60/40	Not detected	Not detected
70/30	Not detected	Not detected
Raw waste		
	18.75	29.02

As shown in table 15, the mercury concentration was only determined in the test solidified sample in which the waste content was 80 %wt. and the pH of the leachate was close to 3. The concentration of mercury was 0.0812 mg.kg⁻¹, which was below the UTS limit set to 0.025 mg.kg⁻¹ (US EPA 2016). Thus, the stabilizing material used (portland cement) proved to be efficient in reducing the mercury content in the solidified test solids in the whole range of waste content. Furthermore, the mobility and insolubility of mercury in the waste sample were significantly decreased.

Table 16 As concentration in stabilised and solidified samples

cement, waste ratio	As Concentration [mg.kg^{-1}]	
	Distilled water leachate	Acetic acid leachate
20/80	0.2	16.6
30/70	0.2	10.3
40/60	0.1	5.3
50/50	0.1	11.2
60/40	0.1	12.9
70/30	0.1	7.9

As shown in table 16, the arsenic concentration of stabilized and solidified samples leached with distilled water was in the range of $0.1 - 0.2 \text{ mg.kg}^{-1}$, which was below UTS limits.(US EPA 2016). In the case of the acetic acid leachate, the arsenic concentration was in a range $5.3 - 16.6 \text{ mg.kg}^{-1}$, which was above the European limit for non-hazardous waste and below the limit for hazardous wastes. (European commission 2003). A study carried out on fly ash from different power plants showed an average arsenic concentration of 38.46 mg.kg^{-1} .(Shen et al. 2022)As a result, the stabilization and solidification of waste sample using Portland cement has shown an efficient result.

11 CONCLUSION

The main aim of this Master's thesis was to determine mercury in environmental samples. Determination was carried out in soil and water samples. Three water samples, five soil samples, and waste sample from a heat plant were used for the analysis. Sampling was performed during winter and spring seasons in order to compare effects on the environment. To determine leachable elements concentrations at different experiment conditions in all samples, the 2M HNO₃ leachate, distilled water leachate, acetic acid leachate and mineralization were used as an extraction method.

The XRF results showed that the most abundant element found in the soil samples was Iron . It was present in all five samples. Apart from Iron, the fly ash sample contains Calcium and Sulfur. Other metals present in all the soil samples include Zr, Sr, Rb, Zn, which were found in a trace amount. Moreover, Arsenic was also detected in a small content.

In the three water samples, the mercury concentration was in the range of 0.1 – 0.2 µg.L⁻¹ during winter, whereas the mercury concentration in spring showed a range of 0.6 - 0.9 µg.L⁻¹. All the results showed a lower value when compared with the mercury concentration limit for drinking water, which was 0.002 mg.kg⁻¹ as per EPA limits. For mercury concentration in soils, the fly ash sample was the one that showed a higher concentration than the other samples during both seasons, with an average mercury concentration of 0.395 mg.kg⁻¹ in winter and 0.763 mg.kg⁻¹ in spring.

Another result also showed that arsenic was also found in the soil. From all the soil samples tested, during winter, the arsenic concentration in the fly ash sample using 2M HNO₃ leachate was 3.2 mg.kg⁻¹, which was the highest of all, whereas, in spring samples, the highest concentration was 17 mg.kg⁻¹. In the case of distilled water leachate, the highest arsenic concentration determined was 0.9 mg.kg⁻¹, whereas, for acetic acid leachate, the concentration was 71.7 mg.kg⁻¹.

In addition, the stabilization and solidification of waste samples from heat plant was also performed. Seven cement-waste ratios were used. The mercury concentration in both leaching methods was measured and the result was found only for the leaching with acetic acid in a 20:80 cement-waste ratio, which was 0.0812 mg.kg⁻¹. However, the determination of arsenic using both leaching methods showed a concentration range of 0.1 – 0.2 mg.kg⁻¹ and 5.3 – 16.6 mg.kg⁻¹ concentration. A successful stabilization and solidification result was found in a 40:60 cement waste ratio with a concentration of 0.1 mg.kg⁻¹ for distilled water

leachate, whereas in the case of acetic acid leachate, an efficient result was determined at 40:60 cement-waste ratio with the arsenic concentration of 5.3 mg.kg^{-1} . Most results, in which the concentration was the highest were obtained by the mineralization method using HNO_3 and H_2O_2 .

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LIST OF ABBREVIATIONS

AMA Advanced mercury analyzer

AAS Atomic absorption spectrometry

XRF X-ray fluorescence

ORP oxidation-reduction potential

GFAAS Graphite furnace atomic absorption spectroscopy

UTS Universal treatment standards

TCLP Toxicity Characteristic Leaching Procedure

EN European norm

WHO World Health Organization

EPA Environmental protection agency

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APPENDICES

Appendix P I: Appendix title

Appendix P II: Appendix title

APPENDIX P I: APPENDIX TITLE