Czech University of Life Sciences

Faculty of Environmental Sciences
Department of Soil Science and Soil Protection

Assessment of the potentially toxic elements sources in forest soils of the Czech Republic using isotopic ratios

DIPLOMA THESIS

Supervisor: RNDr. Václav Tejnecký, Ph.D.
Author: Hana Hurychová

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Author’s declaration:

I hereby declare that I wrote this diploma thesis independently, under the direction of RNDr. Václav Tejnecký, Ph.D. I have listed all literature and publications from which I have acquired my information.

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Abstract:

Lead is an element which serves no known purpose in living organisms and may be a cause of severe poisoning in humans, especially young children. Lead can be introduced to the environment from both natural and anthropogenic sources and distinguishing between them is often an arduous task. Lead isotope analyses can serve as a solid base for recognizing the leading sources of pollution in an area if all possible inputs are known.

The purpose of this thesis is to evaluate possible sources of lead in forest soils of the Czech Republic which are not directly affected by industrial activities or urban areas. The focus was on finding differences in isotope ratios across different regions, vegetation compositions, and altitudes.

120 sites were sampled across the area of Czech Republic, digested using aqua regia and analyzed using ICP-MS for lead isotope ratios. All sites showed an impact of coal burning and the use of leaded gasoline and a generally uniform pollution signature most likely stemming from a mixture of atmospheric pollution and local sources. Fluvisols showed an increased ^{206}Pb/^{207}Pb ratio, which could be connected to chemical processes in soils and a larger scale of possible pollution sources. In full soil profiles, the ^{206}Pb/^{207}Pb ratio increased with increasing depth due to greater effect of bedrock.

Key words: Forest soil, vegetation levels, lead isotopes, ICP-MS, aqua regia

Abstrakt:

Olovo je prvek, který nemá žádnou známou funkci v živých organismech a může být příčinou vážných otrav u lidí, hlavně u malých dětí. Olovo v životním prostředí může pocházet z přírodních i antropogenních zdrojů, rozlišit je ovšem může být velmi náročné. Analýza izotopů olova může sloužit jako dobrý základ pro rozlišování hlavních zdrojů znečištění, pokud jsou možné zdroje známé.

Cílem této práce bylo vyhodnotit možné zdroje olova v lesních půdách České republiky, které nebyly přímo ovlivněny průmyslovými zdroji znečištění či urbanizovanými oblastmi. Práce byla zaměřena na hledání rozdílů v izotopových poměrech mezi jednotlivými regiony, různými vegetačními porosty a místy s rozdílnou nadmořskou výškou.

Po celé České republice bylo odebráno 120 vzorků, které byly rozloženy lučavkou královskou a analyzovány pomocí ICP-MS. Všechny lokality ukazují dopad pálení uhlí, olovnatého benzinu a relativně jednotvárné znaky atmosférického znečištění a místních zdrojů. Fluvisoly vykazovaly zvýšený poměr ^{206}Pb/^{207}Pb, což může být spojeno s chemickými procesy v půdě a větší množství možných zdrojů znečištění. Při analýze celých profilů byl vypozorován trend zvyšujícího se poměru ^{206}Pb/^{207}Pb s větší hloubkou kvůli většímu vlivu podloží.

Klíčová slova: Lesní půda, vegetační stupně, izotopy olova, ICP-MS, lučavka královská

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1. Introduction

Lead is a metal with long history of usage by humans and has been mined and smelted for millennia. The wide industrial use of lead has caused it to be present in almost all atmospheric emissions, which allows for transport of lead on a global scale. Current urbanized areas have lead concentrations which are several orders of magnitude higher than levels in pre-industrial times (Patte & Pain 2003).

The World Health Organization lists lead as a major public health concern due to its adverse effects, particularly for children and pregnant women, as it affects nervous system and may cause anaemia, paralysis, damage to liver and kidneys, malformations of the fetus and stillbirth (WHO 2010). In plants, lead reduces the productivity of crops, may cause stunted growth and decrease the rate of photosynthesis, which is mainly due to enzyme inhibition (Sharma & Dubey 2005).

The soils in the Czech Republic have been affected by many industries including ore mining, smelting, burning of coal and the use of leaded gasoline which have all made an impact on the lead composition in the country (Novák et al. 2003; Tlustoš et al. 2006). The negative impact lead may have on both people and the nature around them is the reason why lead sources still require the attention of the scientific community.

1.1 Objectives and hypothesis

The purpose of this thesis is to assess the lead isotopic ratios in forest soils across different regions, altitudes, and vegetation compositions. Samples from 120 locations will be digested and measured for isotopic ratios to determine major sources of lead in forests not directly affected by large roads or settlements. The hypotheses are as follows:

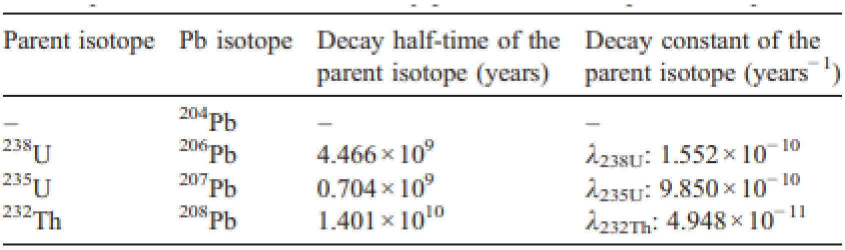
Lead in Czech soils will have ratios influenced by Czech coals.
Different regions will have specific isotopic ratios.
Different forest vegetation zones will have specific isotopic ratios.

2. Properties and utilization of lead

Lead (Pb) is an element belonging to Group 14 in the periodic table of elements with an atomic number 207.2. It is a soft, grey metal with low melting temperature of 327.46 °C, with average concentration of 0.016 g.kg^{-1} of soil in the Earth's crust. It can be found in both organic and inorganic compounds, with inorganic compounds making the bulk of the global lead cycle (Greenwood & Earnshaw 1984; Pattee & Pain 2003; Lide 2005).

There are four stable isotopes of lead occuring in nature: ^{204}Pb ^{206}Pb, ^{207}Pb, ^{208}Pb (Dickin 2005) out of which ^{208}Pb is the most abundant, comprising 52% of total mass of lead on Earth (Salminen et al. 2005). The proportions of the respective isotopes are 1:17:15:37 in nature (Hopper et al. 1991). ^{204}Pb is the only non-radiogenic isotope, while the others are the product of radioactive decay of ^{238}U, ^{235}U and ^{232}Th respectively (Dickin 2005), with specific half-lives and decay constants (see Table 1). As the only primordial isotope, ^{204}Pb is not very abundant and requires very precise and specialized instrumentation for detecting, which makes analysis difficult, therefore the radiogenic isotopes are more frequently used in isotope studies (Reimann et al. 2012). Apart from its stable isotopes, 43 other lead isotopes are recognized, and all of them are radioactive (Lide 2005).

Table 1: Stable isotopes of lead and the half-lives of their parent materials (Komárek et al. 2008)



Parent isotope	Pb isotope	Decay half-time of the parent isotope (years)	Decay constant of the parent isotope (years^{-1})
–	^{204}Pb	–	–
^{238}U	^{206}Pb	4.466×10^{9}	λ_{238U}: 1.552×10^{-10}
^{235}U	^{207}Pb	0.704×10^{9}	λ_{235U}: 9.850×10^{-10}
^{232}Th	^{208}Pb	1.401×10^{10}	λ_{232Th}: 4.948×10^{-11}

Lead is an easy-to-mine element and has been sought after for over 7000 years (Pattee & Pain 2003), finding use in a variety of fields throughout history, for instance in pottery glazing in ancient Egypt or water pipes in Roman times. Due to its high resistance to corrosion, it is being used in containers holding corrosives such as sulphuric acid. Lead has a wide industrial utilization - it is used in alloys, for example with antimony in car batteries, as rust inhibitors in iron and steel paints or in a wide range of mechanical applications such as ballast or ammunition. Its importance in the recent past was also in the production of leaded gasoline (Greenwood & Earnshaw 1984; Lide 2005).

3. Importance of lead in the environment

Despite its natural occurrence, lead has no physiological function in living organisms (Tiwari et al. 2013). It can be highly toxic to both animal and plant life and poses a particular risk due to its tendency to accumulate in individual organisms as well as in food chains, making lead pollution a significant global threat (Salminen et al. 2005). Lead is considered a poison as it inhibits protein synthesis and causes anaemia, brain damage and damage to the nervous system (Greenwood & Earnshaw 1984).

In nature, lead occurs both as a trace metal in minerals (K-feldspars, micas, plagioclases) as well as their major component (galena, cerussite, anglesite), the weathering of said elements may result in mobilisation of lead, increasing its concentration in stream waters, especially in mining areas (Salminen et al. 2005). Almost all forms of soil lead pollution can be transformed through soil microorganismal and chemical processes into adsorbed lead. With the decrease in particle size, the concentration of lead in soils increases, allowing movement of lead-rich dust into households. This property of soil lead is particularly dangerous to small children whose mouthing behaviours make them susceptible to ingesting significant amounts of lead and lead enriched dust plays more of an important role in absorption of lead by humans than airborne particles (Chaney & Mielke 1989).

A study conducted by Cikrt et al. 1997 showed that in industrial hotspots such as smelters, both the aerial contamination and soil lead are responsible for the increase of blood lead in children, but in areas more distant from the point-source soil contaminated through other means (such as leaded gasoline) is a more important source. Although industrial activity can be indicative of possible risks of increased blood lead, the risk is posed not only by contemporary activity but also by industrial processes from the past (Cikrt et al. 1997).

Lead-based paint used to be considered the main source of lead intake in children, however both soil lead and lead-based paint can be the cause of severe lead poisoning. The reduction of soil lead has been shown to have greater effect on lowering blood lead levels in children than the reduction of lead-based paint, which stresses the importance of identifying the correct cause of the problem and increases pressure on reducing soil pollution (Mielke & Reagan 1998).

4. Lead and other trace elements in soils

Soils play an essential part in the functioning of global terrestrial ecosystem, serving as a storage, filtration and buffering medium. They are composed of a vast array of organic and mineral compounds, oxides, clay minerals and a wide range of soluble substances and their properties vary depending on the soil’s pH, redox conditions and activity of soil organisms and plant roots. As such, soils are an important factor in the determination of toxicity, mobility and bioavailability of trace elements in the environment (Kabata-Pendias 1993).

Assessment of soil contamination is generally a complicated process. The variability of soil conditions and the associated differences in soil activity create an environment that is hard to evaluate without proper reference materials. Reference materials obtained off-site tend to be less sensitive towards contamination and may not identify any at all especially in weakly contaminated areas (Desaules 2012). However, it is always important to take into account the scale and specific location as natural background levels of some elements can vary so much within a particular area that the amount of anthropogenic contamination will become extremely difficult to identify (Reimann & Garret 2005).

The primary source of trace elements in soil is the parent material and with progressive weathering the amount of trace elements in soil usually increases. Depending on the stability of its primary minerals, the distribution of trace elements also changes, although there are many other factors influencing the spatial differences in element concentrations. Topsoil minerals are often enriched in copper and chromium compared to the minerals of the bedrock, while cobalt and nickel show higher concentrations in parent materials, which may point at a higher mobility of copper and chromium under weathering conditions (Kabata-Pendias 1993). Lead is one of the trace elements whose anthropogenic fraction inclines towards accumulation in the topsoil layers, mainly due to the high affinity of lead to organic carbon. Topsoil layers also usually contain higher exchangeable fraction of lead compared to subsoil layers (Borůvka et al. 2005).

Some trace elements (copper, zinc, manganese etc.) are important micronutrients required for successful plant growth, but still may be toxic to organisms at higher concentrations. Their deficiency in soils can pose a problem though, especially in agricultural production. Other elements are non-essential (cadmium, lead, nickel etc.) with adverse effects on the biosphere and are considered pollutants. While it can be easy to identify simple point sources of pollution, other sources may pollute soils in a wide area which makes them harder to amend and identify (He et al. 2005).

Over the course of the past three hundred years the amount of lead in the environment has increased rapidly as a result of human activities and is posing a significant threat to various groups of the population, including young children, pregnant women, people with kidney diseases and people affected by malnutrition (ATSDR 2007). As was mentioned earlier, human activity has become the greatest driving force in global trace element cycles, supplying large amounts of trace elements into air, water and soil environments. In most cases, trace metals are supplied to soils mainly from industrial waste, where ash residues from the combustion of coal and commercial products tend to be the major sources (Nriagu & Pacyna 1988).

In 1988 Nriagu & Pacyna published a paper which estimated the amount of lead released in 1983 into the biosphere through burning of fuels in stationary sources to be 10 577 tons per year on a worldwide scale. The amount of emissions in 1995 was even higher at 11, 690 tons per year (Pacyna & Pacyna 2001). Considering all the factors involved, lead should be addressed as an important pollutant whose origin should be carefully tracked and its release into the environment prevented.

5. Lead bioavailability and mobility in soils

In the past, the total bioavailability of soil metals has been based on the total metal concentration. The true value of metals in the soil would include even lattice-bound elements in minerals that may not always be released even with strong extractants, but mostly the total value includes both exchangeable ions as well as metals that would normally remain within solid phases and therefore unavailable for uptake by organisms (Rieuwerts et al. 1998). Trace metals (including lead) in soils can generally be divided into five categories: exchangeable, bound to carbonates, bound to Fe and Mn oxides, bound to organic fraction and residual fraction. These fractions can be selectively extracted and provide information about the speciation of trace metals under different conditions (Tessier et al. 1979).

Lead is considered the least mobile element among potentially hazardous elements (Kabata-Pendias & Pendias 2001). The most important components in lead adsorption in soils are organic matter, clay minerals and iron oxides. Lead has a strong affinity towards soil organic matter which thus strongly influences the distribution of lead in the soil profile. Clay minerals may also play an important role in lead retention as they contain a high amount of lead adsorbents (e.g.: calcium) and the effect is especially strong in swelling clay minerals (Sipós et al. 2005).

The transition of metals between available and unavailable forms is influenced by chemical conditions in the soil (Rieuwerts et al. 1998). The mobility and availability of lead and many other soil pollutants increases with low pH of the soil solution but unlike other, more mobile metals (cadmium, zinc), lead tends to be bound within silicates, usually remaining in the residual fraction (Kabata-Pendias 1993).

6. Lead deposition and its records

Virtually every industry is responsible for releasing one or more trace metals into the environment, whether it is oil combustion, ore roasting and smelting or refuse incineration. Assessing the sources and pathways through which contaminants enter the environment is critical for the evaluation of possible environmental threats and also a way to create policies which reduce the introduction of these contaminants before any damage is done (Pacyna & Pacyna 2001).

While creating a good global record of lead emissions, it is important to draw data from local or national emissions experts as they usually have more detailed information on industrial activities, exact types of raw materials used and the industrial processes commonly applied in their respective region (Pacyna & Pacyna 2001). In a review by Markus & Mcbratney (2001), a number of soil lead pollution studies were compared to assess the amount of lead in urban, agricultural and industrial areas. The common goal of the studies was to map the spatial distribution of lead and identify background and anomalous values. The problem with comparison of these studies is that they largely differ in their approach - the inconsistency in methodology, extraction and sampling design make any comparison between different studies very difficult.

A unified approach towards sampling and sample treating is necessary for a proper assessment on a larger scale. This idea was implemented by the IUGS/IAGC Global Geochemical Baselines Programme which sampled soils and stream waters across Europe to create geochemical maps with element distributions in different layers of soil and provides good reference materials and geochemical baselines created with unified methodology (Salminen et al. 2005).

While looking for historical sources of lead, a good record of pollution can be found in peat bogs which are capable of immobilising and preserving the metal. Samples from peat bogs support the evidence for human induced pollution as recent bogs have up to hundred times higher lead content than those from pre-anthropogenic pollution (Kabata-Pendias 1993). Isotopic analyses have also proven that vertical migration of lead in peat bogs is absent, therefore they faithfully reflect the specific conditions of the past (Shotyk et al. 1996). Other useful sources for dating lead pollution can be lake sediments with annual lamination (Renberg et al. 2002) ice cores (Bourton et al. 1995) or tree bark pockets (Satake et al. 1996).

7. Possibilities of amendments and remediation

The risks associated with increased levels of lead in the environment (as mentioned earlier) increase the pressure on development of remediation techniques. Unlike organic contaminants, trace elements can't be simply destroyed, but must be either relocated or prevented from organismal uptake (Kumpiene et al. 2008). Most common techniques include capping of contaminated soils or their excavation and replacement with fresh soil. Both of these techniques, however, are costly, disruptive and often ineffective in fulfilling their primary objective (Hettiarachchi & Pierzynski 2004; Kumpiene et al. 2008).

7.1 Soil washing

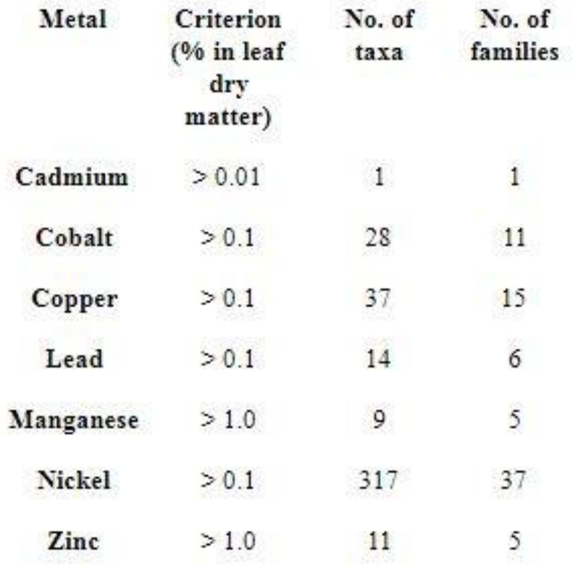
Lead contaminated soils may be treated by soil washing. The affected soil is extracted and washed with a washing solution before being returned to the original site. The washing solution can be water but also an acid or a chelating agent (e.g. EDTA) depending on the site and exact nature of contamination. Water is a better agent for removal of organic pollutants compared to EDTA, which had better results for metallic fractions, however, the removal of EDTA from the soil is a more difficult and significantly more expensive process (USEPA 1991).

The results obtained from washing soils with acids depends on the type of acid used - hydrochloric acid has proven to be a good agent for the removal of lead as well as other metal contaminants, while sulphuric acid was rather ineffectual with respect to lead (Moutsatsou et al. 2006). The success of this method is also dependent on the amount of fine fraction in the treated soil as it has a high adsorption capacity and may need further treatment (USEPA 1991).

7.2 Phytoextraction

Phytoremediation is a cost-effective, in-situ treatment that allows for a non-disruptive amendment of metal contaminated soil. Plants have an innate ability to take up and store specific nutrients, depending on their needs and their environment, with some capable of accumulating large amounts of both essential nutrients and non-essential metals (Lasat 1999), however, lead hyperaccumulation is rather rare as seen in Table 2 (Baker et al. 2000).

Table 2: Number of taxa and families of hyperaccumulator plants (Baker et al. 2000)

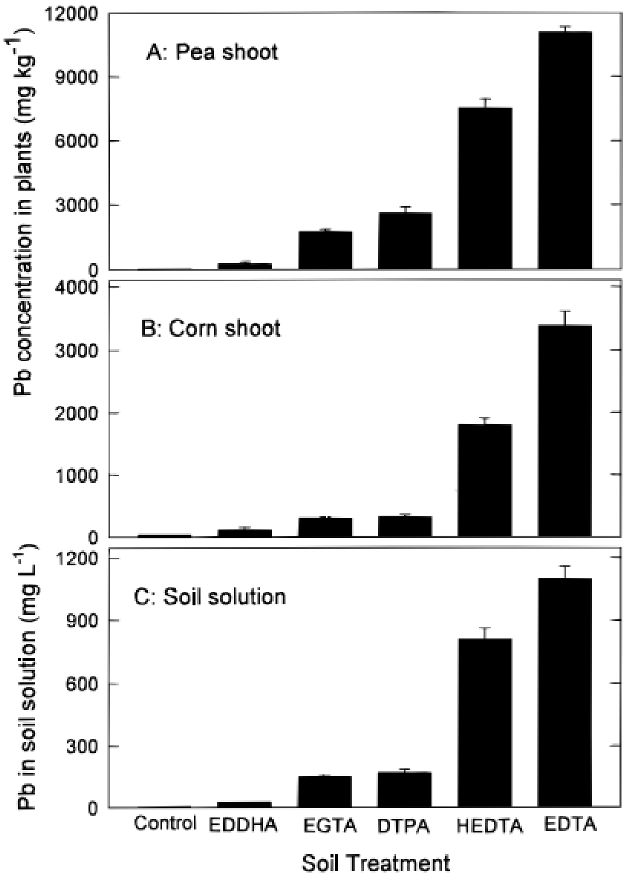


Metal	Criterion (% in leaf dry matter)	No. of taxa	No. of families
Cadmium	> 0.01	1	1
Cobalt	> 0.1	28	11
Copper	> 0.1	37	15
Lead	> 0.1	14	6
Manganese	> 1.0	9	5
Nickel	> 0.1	317	37
Zinc	> 1.0	11	5

Some plants - such as the round-leaved pennycress - have exhibited a remarkable ability for lead uptake, with lead making up to 82% of their dried leaf biomass. Despite the high lead uptake and ability to thrive on contaminated soils, its slow growth and low biomass do not allow for its use as a phytoremediation species (Reeves & Brooks 1983). Successful phytoextraction requires growth of plants with high harvestable biomass which can be difficult to achieve on metal contaminated sites as they usually do not support quality agricultural conditions (Blaylock et al. 1997). The low solubility and therefore bioavailability can hinder the plant uptake of lead, which can be eliminated by the use of synthetic chelating agents such as EDTA (Blaylock et al. 1997; Meers et al. 2009).

Huang et al. (1997) tested the efficiency of different chelating agents on plant lead uptake and the translocation of lead from roots to shoots in several plant species. The more effective the chelate was in releasing lead to the soil solution, the more lead was absorbed by the plants, with EDTA being the most effective (see Figure 1). The difference in the efficiency of different chelates highlights the importance of finding a lead-specific one which would allow for smaller amounts of chelates being added to soils for a successful phytoextraction.

Figure 1: The relative efficiency of different chelate treatments (Huang et al., 1997)



7.3 Phosphorus application

In contaminant remediation, the focus is often placed on converting a substance into a highly insoluble form, reducing its bioavailability. Porter et al. (2004) suggests three forms of lead as possible candidates - galena, wulfenite and chloropyromorphite. While galena - one of the most common forms of lead in nature - is rather insoluble, it can easily be oxidised to form anglesite, which is be much easier to dissolve. Wulfenite requires the presence of molybdates, which may effectively do more harm than good, leaving only chloropyromorphite as a solution to lead contamination. The key to a successful remediation is thus finding a proper end-product that will not result in further release of the contaminant into the environment.

In lead polluted soils, the application of phosphorus and phosphate rocks is quite a common *in situ* amendment (e.g. Hettiarachchi & Pierzynski 2001; Raicevic et al. 2005). Arnich et al. 2003 demonstrated the potential of hydroxyapatite to form insoluble compounds with lead, which could be used for safe treatment of drinking water and possibly also sewage sludge. Phosphate rock is an effective medium for sorption of other metals (copper, zinc) as well, however it shows greatest affinity towards phosphorus. The majority of immobilized lead can be attributed to the dissolution of the phosphate rock and subsequent precipitation of pyromorphites (Cao et al. 2004).

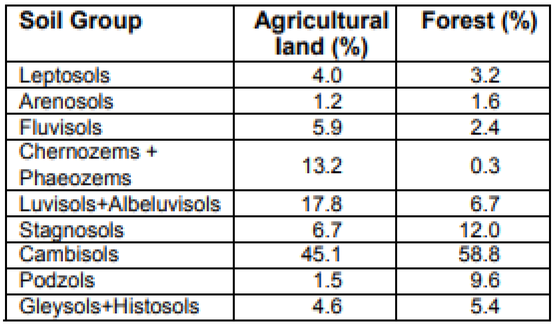
Since phosphorus is an element used as a fertiliser in agriculture and is naturally found in living cells, it doesn't pose a risk to the environment on its own, however phosphorus application still requires caution. Depending on the type of phosphorus compound added, there can be several negative factors affecting the soil such as pH changes (phosphoric acid), excessive increase of specific elements (sodium salts) or irreversible changes to soil structure (apatite formation) (Porter et al. 2004). Phosphorus is also the most common reason for the eutrophication of freshwater and estuarine systems (Correl 1998).

8. Soils in the Czech Republic

The soils in Czech Republic are mainly represented by cambisols, which cover about 45% of the country. Cambisols originate from a wide variety of bedrocks, their common feature being a dark, cambic subsurface horizon. The release of Fe and Al in its upper horizons can cause non significant colour changes due to accumulation of organic matter (Šarapatka 2014). As of 2018, non-agricultural soil took 46.70% of the total area of Czech Republic, out of which 33.90% were forested areas (Český úřad zeměměřický a katastrální 2019).

As seen in Table 3, the majority of forested areas in Czech Republic are over cambisols, followed by stagnosols and podzols (Jones et al. 2005). According to Sánchez-Camazano et al. (1998), more developed soils - cambisols included - tend to have lower amounts of trace elements such as cadmium or lead. This could also be attributed to higher carbonate contents and higher amounts of organic matter of less developed soils which both contribute to lead retention (Sánchez-Camazano et al. 1998). Total amount of a particular element in soil doesn’t however indicate the risk of toxicity to organisms as there are various factors influencing its actual bioavailability (Finzgar et al 2007).

Table 3: Distribution of soils in agricultural and forest areas (Jones et al. 2005)



Soil Group	Agricultural land (%)	Forest (%)
Leptosols	4.0	3.2
Arenosols	1.2	1.6
Fluvisols	5.9	2.4
Chernozems + Phaeozems	13.2	0.3
Luvisols+Albeluvisols	17.8	6.7
Stagnosols	6.7	12.0
Cambisols	45.1	58.8
Podzols	1.5	9.6
Gleysols+Histosols	4.6	5.4

There are several areas of Czech Republic where the contaminant values are exceeding limits deemed safe for agricultural production (Tlustoš et al. 2006). Czech legislative sets the limits differently for regular soils and for sand, loamy sand and sandy loams as seen in Table 4.

Table 4: Concentration limits for hazardous elements in Czech Republic (Ministerstvo Životního Prostředí 2016)

Concentration limits for elements extracted by aqua regia in dry soil (mg.kg-1)											
	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**	**Be**	**Co**	**V**
Regular soils	20	0,5	90	60	0,3	50	60	120	2	30	130
Light soils	15	0,4	55	45	0,3	45	55	105	1,5	20	120

These areas are usually those affected by the weathering of products from the mining of ores (e.g. Kutná Hora), atmospheric deposition from mining (Příbram) and mining and burning of coal (Northern Bohemia). Contamination is also caused by acid mine drainages as well as waters infiltrating mine tailings (Tlustoš et al. 2006).

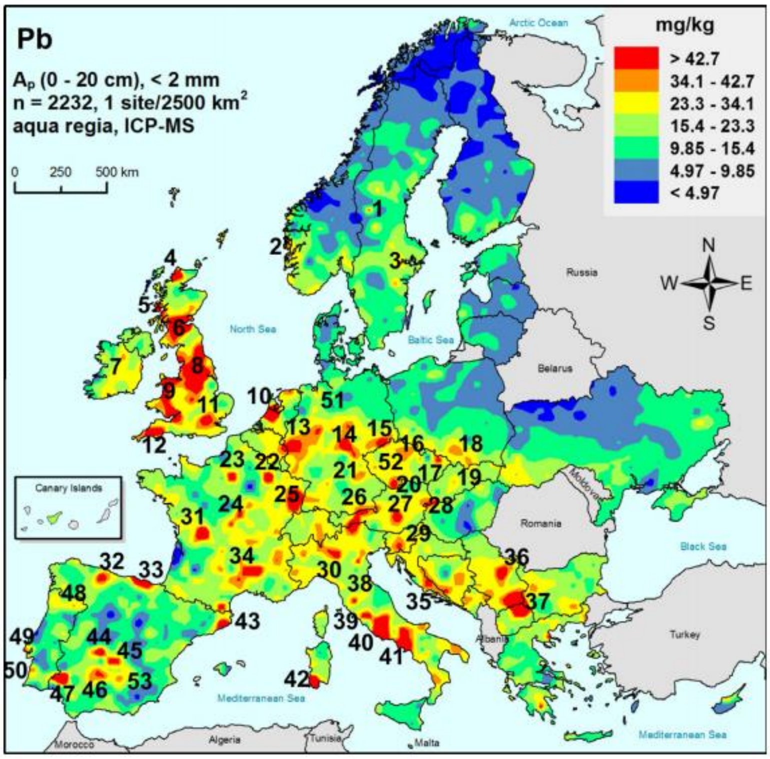
9. Lead industry and pollution

9.1 European perspective

Lead pollution has a long history in Europe and in order to understand modern pollution, it is important to take into account lead deposition from as far as 3000 years ago (Branwall et al. 1999). The earliest increase in atmospheric lead deposition can be tracked through sediments in peat bogs from 6000 years ago and is associated with the increase in agricultural activities and soil dust (Weiss et al. 1999).

The total amount of lead in soils is the sum of both anthropogenic and geogenic lead, which - as stated earlier - can be influenced by many factors. European soil lead concentrations differ greatly between the soils north and south of the European Trans Suture Zone and correlate well with the extent of the last glaciation (Reimann et al. 2012). Czech Republic was situated in the periglacial zone between the north-european continental glacier and the Alpine ice sheet, with only sporadic glacial occurrence (Kachlík 2003), thus displaying lead soil concentrations similar to the rest of Europe not affected by glaciation during the last ice age (Figure 2).

Figure 2: European agricultural soil lead contents (numbers represent the occurrence of local anomalies) (Reimann et al. 2012)



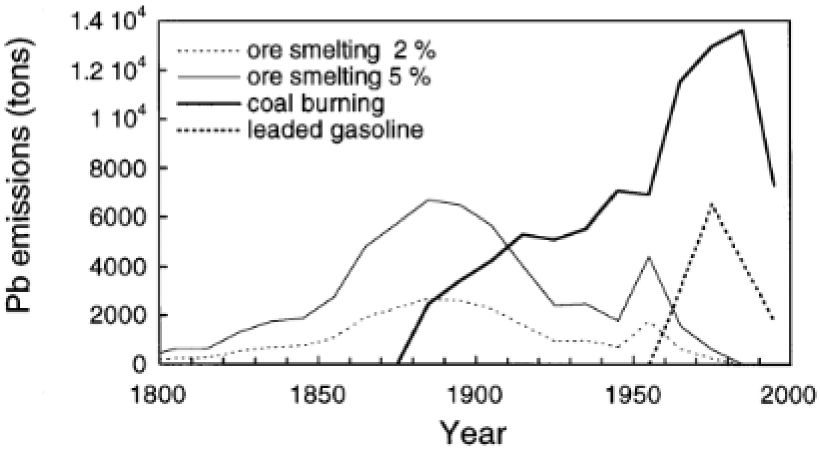
Until the introduction of leaded gasoline in the twentieth century, ore processing along with smelting was responsible for the majority of lead pollution in Europe. From analyzed peat samples, lake sediments and ice cores, three significant peaks of lead emissions can be identified - Roman era (100 BC to 200 AD), Medieval era (1000 to 1200 AD) and Modern era (1970 AD to present), although these time spans may not be relevant for all areas. Not enough studies have been carried out to determine long term pollution and many of the existing rely on a limited number of data (Renberg et al. 2001).

The major rise in lead emissions in Europe can be traced to the 1970s when the industrial sector started to thrive, but the measures to contain the resulting pollution were yet to be implemented. The subsequent drop in lead emissions can be accounted to the installation of controlling equipment and the reduction of leaded gasoline use. Further decrease between the years 1990 and 1995 are attributed to a decline in industrial production of Central and Eastern Europe (Steenblik & Coroyannakis 1995).

9.2 Lead pollution in the Czech Republic

The oldest datable record of lead deposition from the Czech Republic comes from a peat bog and can be dated between 1780-1825. As no gasoline and almost no coal was burned in the area in these days, the most likely source of the lead trace is ore smelting. In the following years the major lead supply to the environment changed to coal burning and the use of leaded gasoline, which both peaked during the country’s communist era (see Graph 1) (Novák et al. 2003). The rise of industry in Czech lands was also reflected in employment, as large industrial complexes became the lead source of employment opportunities (Paul Dana 2000).

Graph 1: Lead pollution in the Czech Republic (Novák et al. 2003)



While many countries have started investing into environmental protection measures to cope with the consequences of coal burning and mining, the Central European market in 1980s was isolated and the rising costs of coal mining have been largely compensated by skipping pollution prevention. This resulted in the creation of an extremely polluted environment with land disturbances and high concentrations of atmospheric dust and acidifying substances (Steenblik & Coroyannakis 1995).

9.2.1 Coal industry

About 80% of all coal in Czech Republic is mined and burned in Northern Bohemia (Tlustoš et al. 2006) and although it's cheap to obtain from surface mines, its quality is poor as it is high in ash and sulphur contents. Especially in the past the quality of burned coal often resulted in contamination of the environment with sulphur oxides and particulate matter. Subsequent production of ash from coal burning required the construction of ash ponds which often leaked metals into its vicinity, causing further ecological problems (Schnoor 1993). The map of Czech Republic's major coal basins can be seen in Figure 3.

Figure 3: Coal basins of the Czech Republic and their production (Novák et al. 2003)

9.2.2 Leaded gasoline

The use of leaded gasoline in the Czech Republic ceased in 2000. Between the years 1960 and 1983, the contents of lead in gasoline amounted to around 0.6 g.L^{-1}, later decreasing to 0.4 g.L^{-1} and 0.15 g.L^{-1} in 1984 and 1989 respectively, complying with regulations set in Western Europe at that time. The majority of lead additives found in Czech leaded gasoline (and Central European gasoline in general) comes from a deposit at Broken Hill in Australia, with inputs from local and Russian ores as well. The coal production and use of leaded gasoline in Czech Republic peaked at about the same time as is reflected in Graph 1. (Novák et al. 2003).

10. Identifying sources of pollution

Isotope analysis has proven to be a useful tool in various fields, for instance in tracing of migratory wildlife (Hobson 1999), determining trophic positions of organisms (Cabana & Rasmussen 1994) or in determination of stratigraphic boundaries (Walker et al. 2009), mostly depending on isotope fractionation. Hoefs (1997) defines fractionation as “the partitioning of isotopes between two substances or two phases of the same substance with different isotope ratios”.

The isotope fractionation of specific element is dependent on the isotope mass and is therefore more pronounced in light elements. Lead has a high mass and the relative differences between its isotopes is thus fairly small, causing only insignificant changes in isotope composition during smelting and refining (Shiel et al. 2010).

Since the isotopic composition of lead doesn't significantly change during different processes, they can be used as fingerprints of lead pollution in the environment. Successful determination of pollution source, however, depends on the characteristics of lead used by the specific sources. The overall composition of lead isotopes in soil is the combination of inputs of various origins and if the isotope signatures are very similar, it's difficult to distinguish between them. Still, if all sources of lead contamination are known and have specific isotope ratios, they can be used to determine the original sources (Komárek et al. 2008).

11. Lead isotope signatures

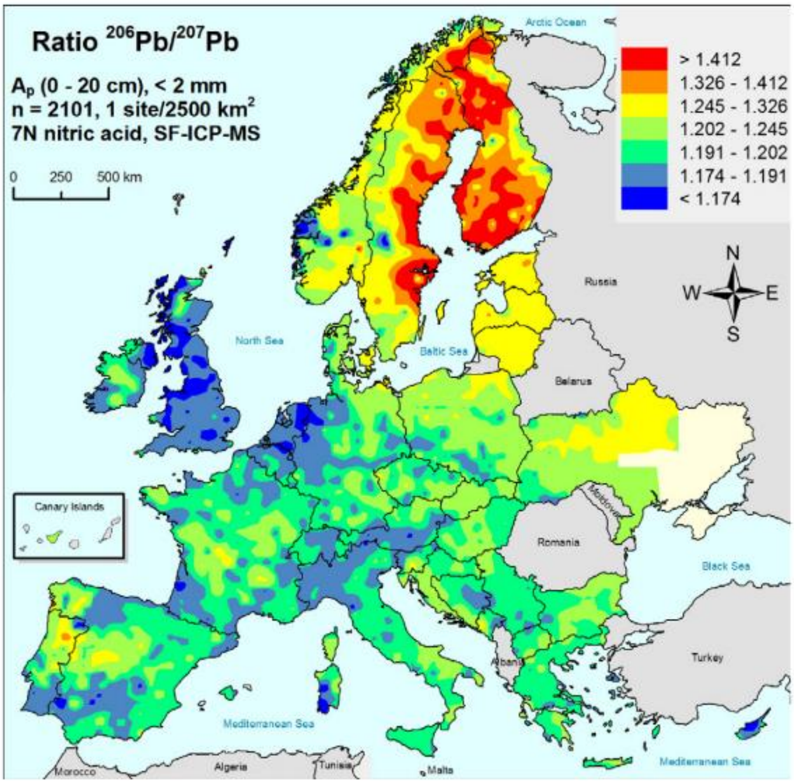
In geochemical analyses, the composition of lead isotopes is usually represented by isotope ratios, most commonly as $^{206}Pb/^{204}Pb$, $^{206}Pb/^{207}Pb$ or $^{208}Pb/^{206}Pb$. $^{206}Pb/^{207}Pb$ tends to be the preferred as both of the isotopes are relatively abundant, and their analytical determination can be very precise (Komárek et al. 2008). The ratios differ among deposits, allowing for a rather reliable way to distinguish between ores coming from different locations.

Globally, five main types of lead deposits can be distinguished: sedimentary, volcanogenic sedimentary, metasomatic, contact metamorphic, and vein deposits (Starý et al., 2005), but it has not yet been established whether these different types of deposits also have distinct lead isotope signatures (Sangster et al. 2000). The isotope ratios of lead ores are highly dependent on the contents of thorium and uranium in the parent rock.

Rocks with higher contents of thorium will have higher $^{208}Pb/^{207}Pb$ contents. While ^{238}U has a longer half-life than ^{235}U, there is more ^{206}Pb produced due to a greater abundance of ^{238}U. The increase in the $^{206}Pb/^{207}Pb$ ratio can therefore be observed with time. This shows that since isotope ratios also rely on time, different ores will have different signatures based on the time of their formation, with old ores having lower $^{206}Pb/^{207}Pb$ signatures than newly formed ones (Böllhofer 2003). Lead pollution derived from coal can often be distinguished from that caused by leaded gasoline through isotope ratios, as coal tends to have more radiogenic signature (Dickin 2005).

Reimann et al. (2012) provide maps of Europe with lead soil concentrations and lead isotope ratios for agricultural soils, showing the differences between its regions. The trend across Europe is an increasing amount of lead in soils from north to south, the median in north being 10 mg.kg^{-1} while in south it reaches 20 mg.kg^{-1} (the European median is 15.7 mg.kg^{-1}). This reflects not only the difference in bedrock across Europe, but also the amount of weathering it has been subjected to. The isotope ratios also follow a gradient from north to south, with the ^{206}Pb/^{207}Pb ratio decreasing in this direction as seen in Figure 4 which suggests different ages of formation of various parts of Europe.

Figure 4: The ^{206}Pb/^{207}Pb ratio in agricultural soils of Europe (Reimann et al. 2012)

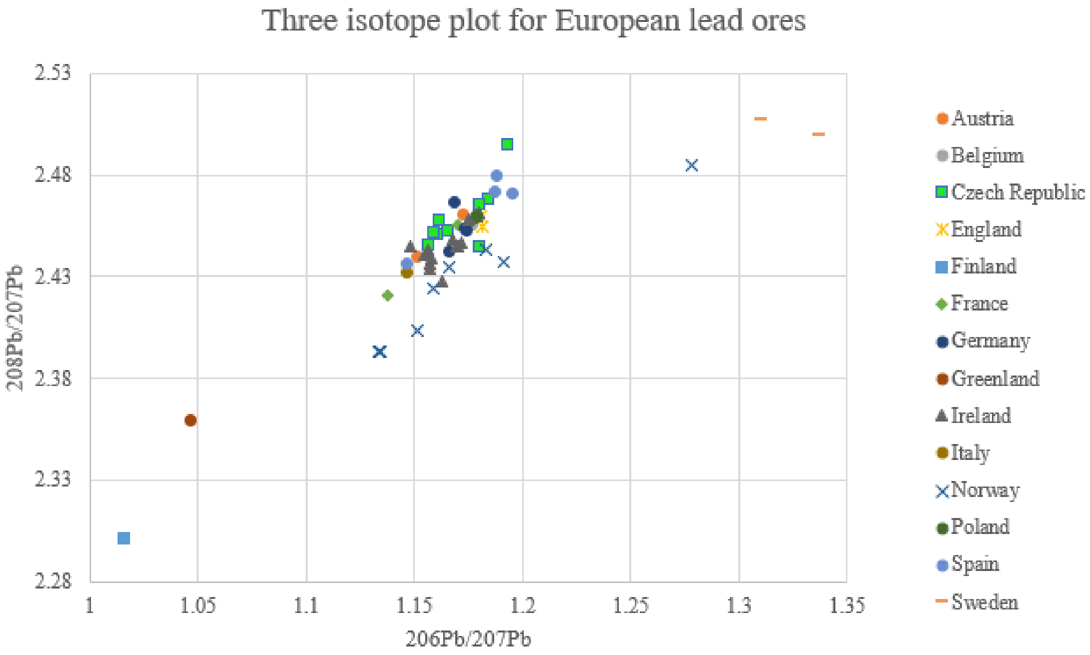


The majority of ores used in Czech Republic in medieval ages came from hydrothermal polymetallic veins, which are commonly found in the Bohemian Massif. Notable locations include Příbram, Kutná Hora, Oloví, Stříbro or Jihlava. Volcanogenic sediments dated to Devonian can be found in Northern Moravia, namely Horní Benešov, Horní Město or Zlaté Hory (Starý et al. 2005). The isotope ratios recorded in some of the more significant deposits in Czech Republic can be found in Table 5 while Graph 2 shows the differences between various European ores.

Table 5: Isotope ratios of important lead ores in the Czech Republic (Novák et al. 2003)

Isotope ratio:	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$
Location:		
Horní Benešov	1.180	2.445
Jáchymov	1.184	2.468
Jihlava	1.165	2.453
Kutná Hora	1.160	2.451
Oloví	1.180	2.466
Příbram	1.159	2.452
Ratibořské hory	1.156	2.446
Rudolfov	1.161	2.458
Stříbro	1.193	2.495

Graph 2: Comparison of isotope ratios of various lead ores in Europe (data for Europe Sangster et al. 2000; data for the Czech Republic Novák et al. 2003)



The geological origin of lead in leaded gasoline is often hard to identify and may not always correspond with local sources (Hopper et al. 1991). West European leaded gasoline, produced mainly by a British company Associated Octel and its branches around Europe, contained Precambrian ore from Australia and Canada (Monna et al. 1997; Bölhoffer & Rosman 2001), where the percentage of Australian ore ranged between 50% in 1980 and 80% in 1994 (Véron et al. 1999).

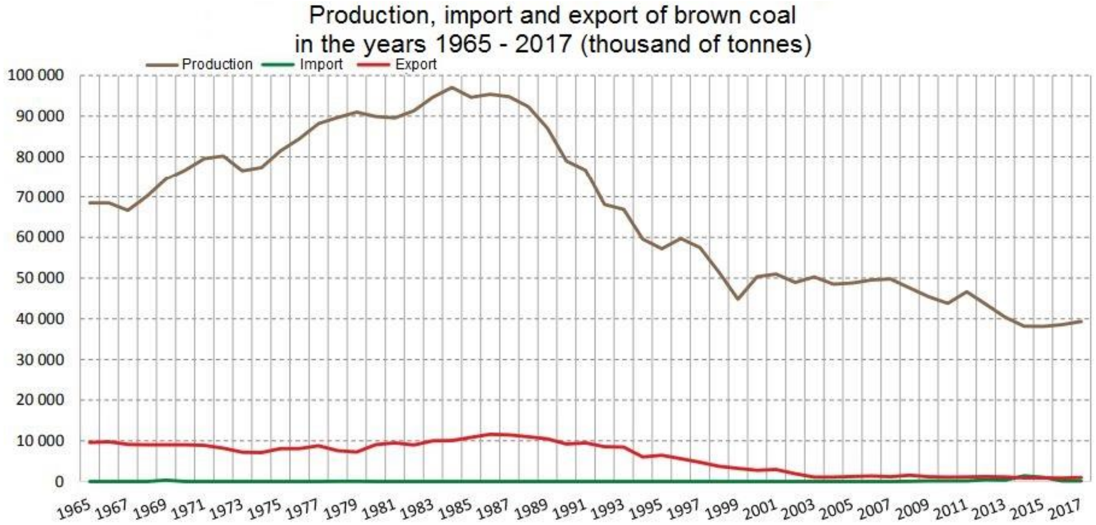
These ores exhibit a typically low isotopic signature, with Broken Hill - one of the largest lead producers worldwide - having a $^{206}Pb/^{207}Pb$ ratio of 1.0407 and Sullivan in Canada having $^{206}Pb/^{207}Pb$ ratio 1.0679. For comparison, the main ore used for primary production of lead in North America comes from the Mississippi valley and shows a significantly more radiogenic signature of 1.4060 $^{206}Pb/^{207}Pb$ (Sangster et al. 2000).

Novák et al. (2003) measured isotope composition of leaded gasoline in Czech Republic, obtaining mean value of 1.11 for $^{206}Pb/^{207}Pb$ and 2.38 for $^{208}Pb/^{207}Pb$. These results are similar not only to values obtained in Western Europe but also those from Eastern Germany, which had a different alkyl lead manufacturer. East German $^{206}Pb/^{207}Pb$ values for leaded gasoline were 1.10 as a result of mixing Australian ores with ore from local source in Freiberg. The similarly low $^{206}Pb/^{207}Pb$ values indicate that Australian ores comprised a significant part of lead used in leaded gasoline in the Czech Republic as well.

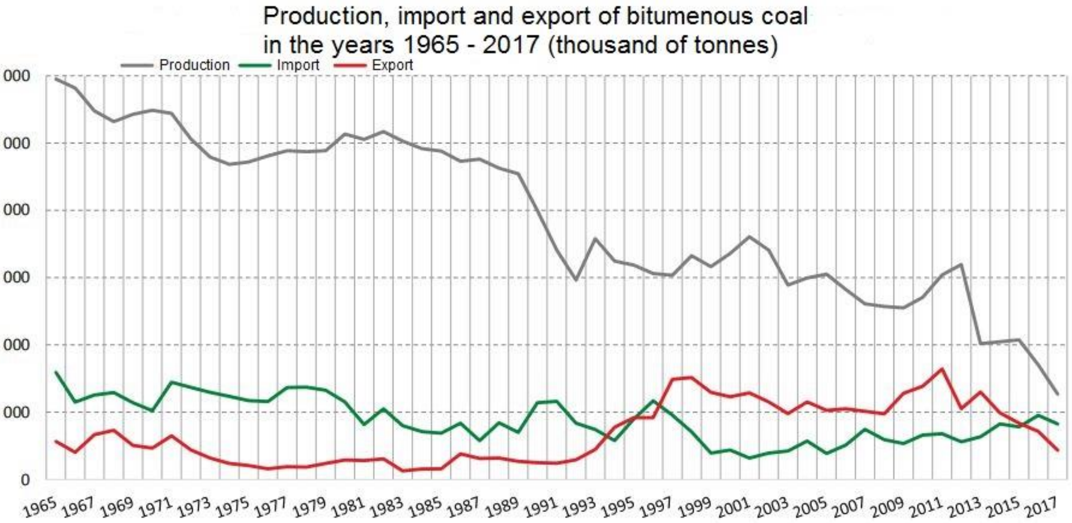
The values for lead ratios in coal across Europe also vary. Some coals in the United Kingdom show values of $^{206}Pb/^{207}Pb$ as low as 1.159 ($^{208}Pb/^{207}Pb$ 2.089) (Highhouse colliery, Scotland) but the mean values for Scotland are 1.181 and 1.184 for England and Wales (Farmer et al. 1999). Belgian coal has a slightly lower $^{206}Pb/^{207}Pb$ ratio of 1.176 (Walraven et al. 1997), similar to polish and german coals with $^{206}Pb/^{207}Pb$ ratio of 1.177 and 1.174 respectively (Farmer et al. 1999). Novák et al. (2003) reported Czech bituminous coal to have a higher $^{206}Pb/^{207}Pb$ ratio of 1.190 and 2.465 for $^{208}Pb/^{207}Pb$, but the range of $^{206}Pb/^{207}Pb$ around coal fired power plants was between 1.17 and 1.19. A more recent study by Mihaljevič et al. (2009) shows the ranges of coals as 1.167– 1.234 $^{206}Pb/^{207}Pb$ for bituminous and 1.172–1.24 $^{206}Pb/^{207}Pb$ for brown coals.

During the era of communism, Czech Republic has been one of only two countries (along with Poland) to produce coal surplus in the Eastern Bloc and has been largely self-sufficient in coal production, producing 1.3% of global total calorific equivalent (Anderson 1995). Since very little coal was imported - as seen in Graphs 3 and 4 - and majority of the coal burned in Czech Republic came from local sources, it is safe to assume the isotope signatures from coal burning will correspond with local coal values.

Graph 3: The production, import and export of brown coal in the Czech Republic (Bufka & Veverková 2018)



Graph 4: The production, import and export of bituminous coal in the Czech Republic (Bufka & Veverková 2018)



12. Types of isotope analysis

In general, different types of mass spectrometry are used in soil isotope analyses (e.g. Hansmann & Köppel 2000; Prohaska et al. 2000; Ettler et al. 2004) and in a variety of other fields such as forensics, food industry and archaeology. This is mainly due to its high sensitivity, efficiency and reliability in element detection (Ammann 2007).

Mass spectrometers do not measure solely the mass of the ions but rather their mass-to-charge ratio and may use different means of analysis. Mass analyzers can separate ions based on various properties, such as the stability of trajectory in oscillating electric field (quadrupoles), momentum or kinetic energy (magnetic and electric sector fields) or velocity (time-of-flight) (de Hoffmann & Stroobant 2007).

12.1 Ion Sources

Before samples can be analyzed by the mass analyzer, ionization of the analyte is necessary. A common method for the analysis of inorganic compounds is the thermal ionisation mass spectrometry (TIMS) (de Hoffmann & Stroobant 2007). For several decades, TIMS has been considered the only technique capable of analyzing heavier elements such as lead (Vanhaecke & Moens 2004). The ionization involves heating of the sample under vacuum, however, it requires an extraction of the required sample from the sample matrix. This problem has been resolved through the use of inductively coupled plasma source (ICP). Since ICP doesn’t require extensive sample purification, it is possible to analyze some samples with sufficient concentration of the target element directly *in situ* through the means of laser ablation. Nevertheless, compared to TIMS, ICP is still more expensive to both build and operate (Dickin 2005).

12.2 Quadrupole mass analyzers

Quadrupole mass analyzers (QMS) are the most common ICP MS instruments used (Becker 2002). They provide quick measurements and are suitable for quantitative analyses, although their precision is limited, usually to 0.1 - 0.5%, which is mainly due to plasma instability (Platzner et al., 1999). ICP QMS also usually have lower precision as the incoming ion masses aren’t being detected at the same time

(Komárek 2008), but with proper control of possible instrumental bias, it can be a sufficient tool for lead isotope analysis (Marguí et al. 2007).

12.3 Sector field mass spectrometry

In the late 1980s, first sector field mass spectrometry (SMS) instruments became commercially available, offering high resolution up to 10 000, eliminating major number of spectral interferences (Moldovan et al. 2004). Their operations has initially been hindered by high purchase costs and has been largely limited to the semi-conductor industry, which requires high purity of reagents.

At low resolution, SMS instruments can have detection limits in the range of $fg.ml^{-1}$, which - however - deteriorates with increasing resolution. In multicollector devices, where several elements can be detected simultaneously, precision ranging in 10^{-3}% of relative standard deviation can be achieved (Jakubowski et al. 1998). The ICP SMS method is precise and accurate enough to allow for distinguishing between anthropogenic and geogenic lead in soil and is thus suitable for use in environmental sciences (Prohaska et al. 2000).

12.4 Time-of-Flight

Similar to SMS analyzers, the Time-of-Flight (TOF) analyzers use an electric field to separate ions. These are sorted according to their velocities, and mass to charge ratio is calculated based on the time of travel between their source and the detector (de Hoffmann & Stroobant 2007). In measurement of lead isotopes, TOF mass spectroscopy can yield similar results to SMS in terms of precision and accuracy, however its poor sensitivity may require sample pre-treatment (Barbaste et al. 2001).

13. Isotope ratios in forest soils of the Czech Republic

13.1 Sampling sites

The soil samples used in this study were taken from the KOLEP project which started in 2011 and whose goal was to create objective methods and criteria for evaluating forest soil contamination with hazardous elements and persistent organic pollutants. In total, 120 sites were selected through a mathematical model and divided into eight groups. The criteria for selection of sampling sites and their group division were their altitude, composition of vegetation species, soil type, distance from large settlements and industrial areas and the distance from the edge of forested areas. The details of soil sampling methods are described in Borůvka et al. (2012).

For each of the 120 sites, four depths were sampled - F+H horizon, A horizon (0-2 cm), 2-10 cm and 10-20 cm. For the purpose of this thesis, all A horizons and one full soil profile from each of the eight groups were analyzed. The rationale behind this choice is the enrichment of upper soil levels in anthropogenic lead fraction and distinguishing natural lead levels and signatures from the anthropogenic ones.

13.2 Laboratory methods

The samples were processed according to the ICP Forest manual (Cools & De Vos 2016) From each of the dried, homogenized samples, 1 g of soil was weighed on a scale with accuracy to 0.001 g into a clean and dry teflon vessel. Subsequently aqua regia was added into the vessel (2.3 ml of HCl and 7 ml of HNO_3), a lid was placed onto the container (but not tightened) and left to stand overnight at room temperature under a fume hood, for approximately 16 hours. The vessels were then tightly closed and heated on a hot plate for two hours at 200 °C.

After the samples cooled down, they were poured into a 50 ml volumetric flask using a funnel. The residue from the container was washed out into the flask with deionized water. The sample volume was adjusted to 50 ml with deionized water and filtered using a funnel and filtration paper into plastic bottles and closed. The samples were processed over the course of several months in batches of 10-15 samples due to a lack of laboratory equipment.

After all samples were digested and filtered, they were analyzed for isotopic ratios with ICP MS (ICP MS, X Series 2, Thermoscientific) at Charles University in Prague by Prof. Dr. Martin Mihaljevič. The mass bias was corrected using NIST Standard Reference Material 981.

13.3 Analysis

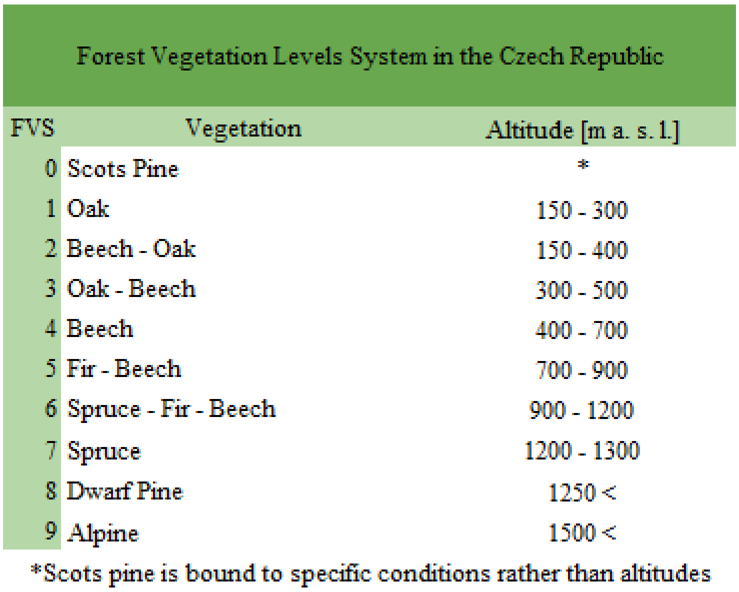
Analyses conducted in this thesis were one-way ANOVA and Tukey's honestly significant difference (HDS) test, which have been done through functions included in Microsoft Excel's Analysis ToolPak and Real Statistics Resource Pack.

The ^{206}Pb/^{207}Pb ratio was chosen as the primary analyzed ratio since the abundance of both of these isotopes is relatively significant, they can be precisely analyzed and vary significantly among reservoirs (Komárek et al. 2006; Komárek et al. 2008). ^{208}Pb/^{207}Pb and ^{208}Pb/^{206}Pb, two other ratios largely used in environmental studies, will be used for three isotope graphs to better represent the individual signatures

13.4 Sample categorization

The KOLEP project divides samples into eight groups based on forest vegetation levels (FVL), a classification system frequently used in the Czech Republic. The system recognizes the following levels:

Table 6: Forest vegetation levels (Kusbach et al. 2003; Divíšek et al. 2010)



Forest Vegetation Levels System in the Czech Republic

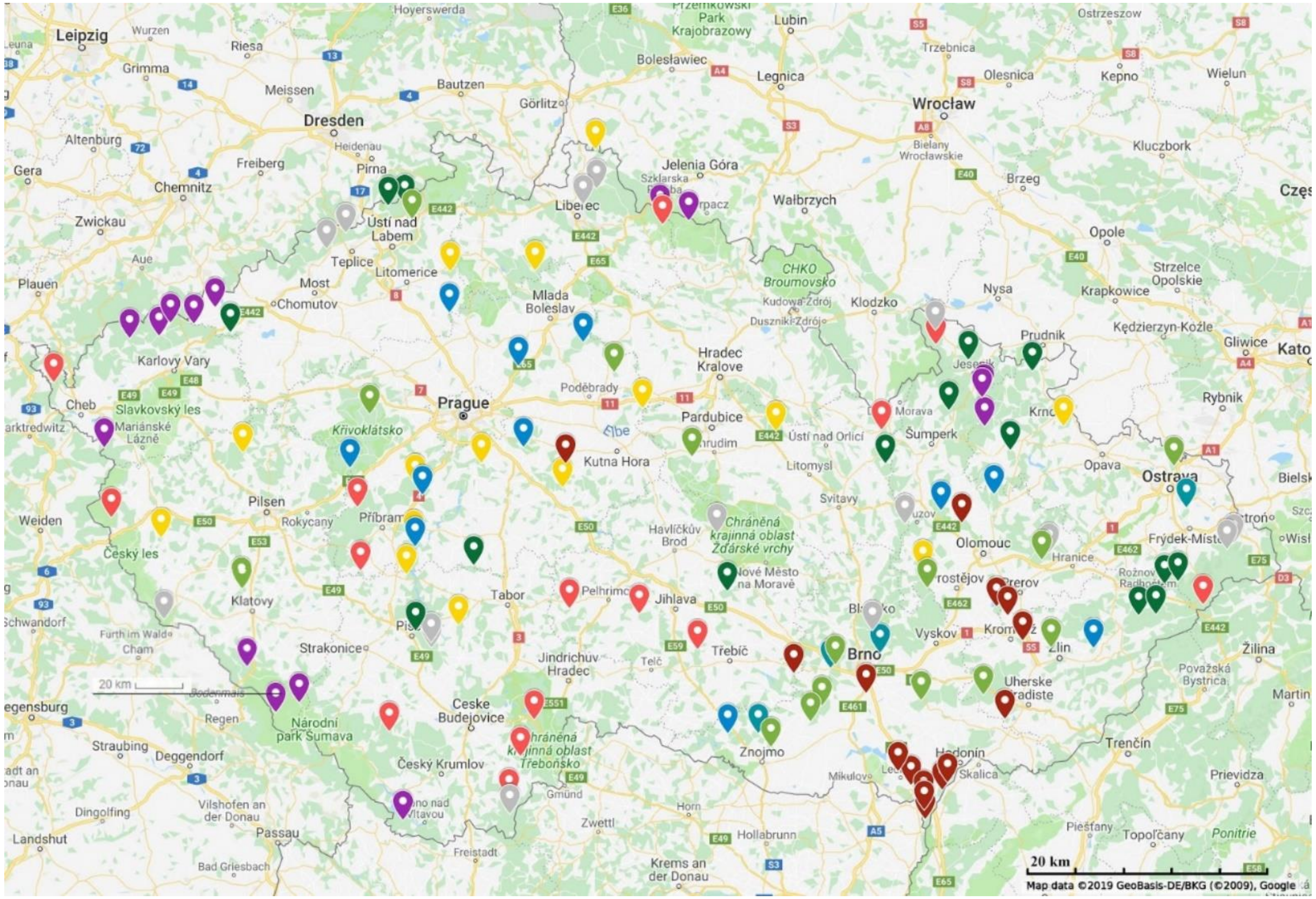
FVS	Vegetation	Altitude [m a. s. l.]
0	Scots Pine	*
1	Oak	150 - 300
2	Beech - Oak	150 - 400
3	Oak - Beech	300 - 500
4	Beech	400 - 700
5	Fir - Beech	700 - 900
6	Spruce - Fir - Beech	900 - 1200
7	Spruce	1200 - 1300
8	Dwarf Pine	1250 <
9	Alpine	1500 <

*Scots pine is bound to specific conditions rather than altitudes

For the purpose of this thesis, the KOLEP project categories were labelled A to H for clarity and easier referencing to the respective category. The descriptions of these categories are given as follows:

A - Fluvisols in all altitudes, mainly broad-leaf floodplain forests
B - 1.-3. FVL, forests with needle-leaf tree dominance
C - 1.-3. FVL, forests with broad-leaf tree dominance
D - 1.-3. FVL, mixed forests
E - 4.-6. FVL, forests with needle-leaf tree dominance
F - 4.-6. FVL, forests with broad-leaf tree dominance
G - 4.-6. FVL, mixed forests
H - 7.-9. FVL

Figure 5: Locations of sampled sites based on category. A - red, B - yellow, C - light green, D - blue, E - pink, F - gray, G - dark green, H - purple. (Google Maps 2019)



Map data ©2019 GeoBasis-DE/BKG (©2009), Google

14. Results

14.1 Individual samples

14.1.1 Categories

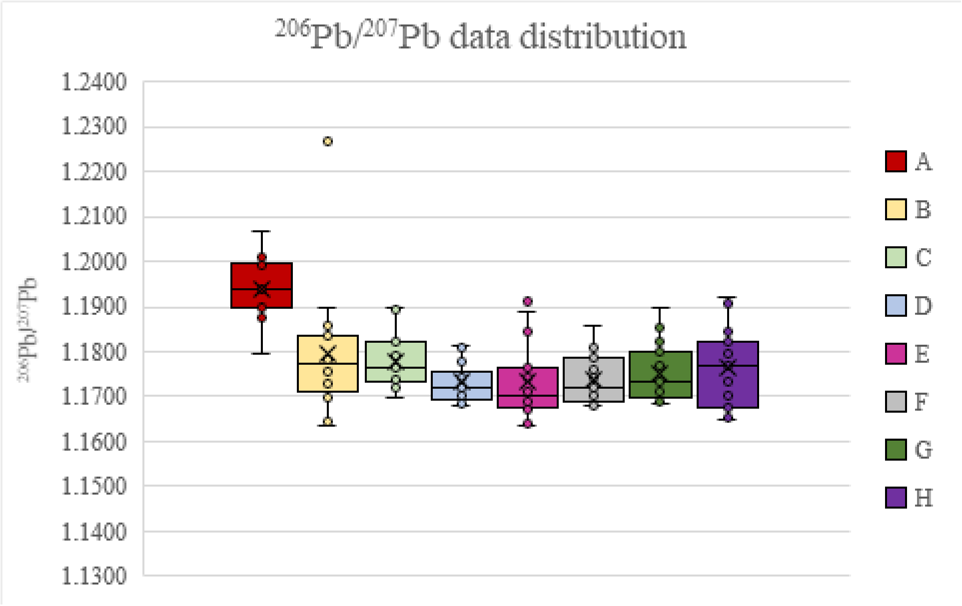
Enclosures 1-4 listed in the chapter Enclosures show the total data for isotope ratios obtained from the individual sampling sites. They are divided based on the system mentioned above. Table 7 below shows the minima, maxima and averages for different categories and their respective ratios.

Table 7: Maxima, minima and averages for recorded categories (n=120)

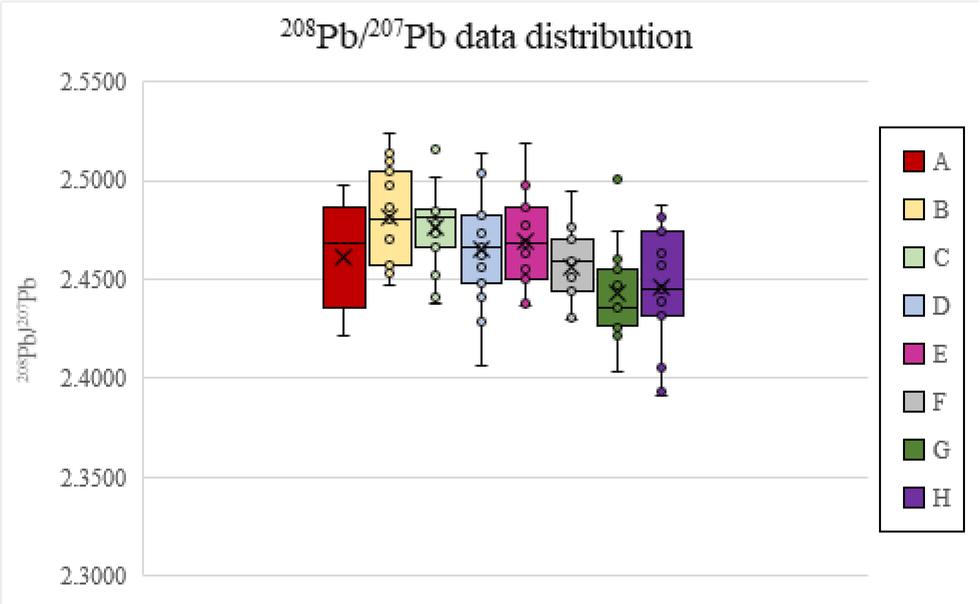
	$^{206}Pb/^{207}Pb$			$^{208}Pb/^{207}Pb$			$^{208}Pb/^{206}Pb$		
	Min	Max	Average	Min	Max	Average	Min	Max	Average
A	1.1794	1.2067	1.1939	2.4214	2.4980	2.4610	2.0205	2.1072	2.0614
B	1.1635	1.2269	1.1794	2.4473	2.5235	2.4813	2.0411	2.1318	2.1040
C	1.1696	1.1897	1.1777	2.4380	2.5160	2.4762	2.0783	2.1316	2.1026
D	1.1681	1.1812	1.1731	2.4063	2.5140	2.4648	2.0546	2.1362	2.1010
E	1.1636	1.1911	1.1735	2.4371	2.5192	2.4697	2.0502	2.1456	2.1047
F	1.1678	1.1859	1.1740	2.4299	2.4941	2.4565	2.0666	2.1133	2.0925
G	1.1684	1.1900	1.1751	2.4033	2.5010	2.4434	2.0470	2.1248	2.0793
H	1.1650	1.1919	1.1763	2.3918	2.4874	2.4463	2.0497	2.1326	2.0797

The ratios of the sampled sites fall within the range of 1.1635-1.2269 for $^{206}Pb/^{207}Pb$, 2.4290-2.5239 for $^{208}Pb/^{207}Pb$ and 2.025-2.1456 for $^{208}Pb/^{206}Pb$. The following boxplot graphs (Graphs 5-7) show the distribution of data within their respective categories and isotope ratios.

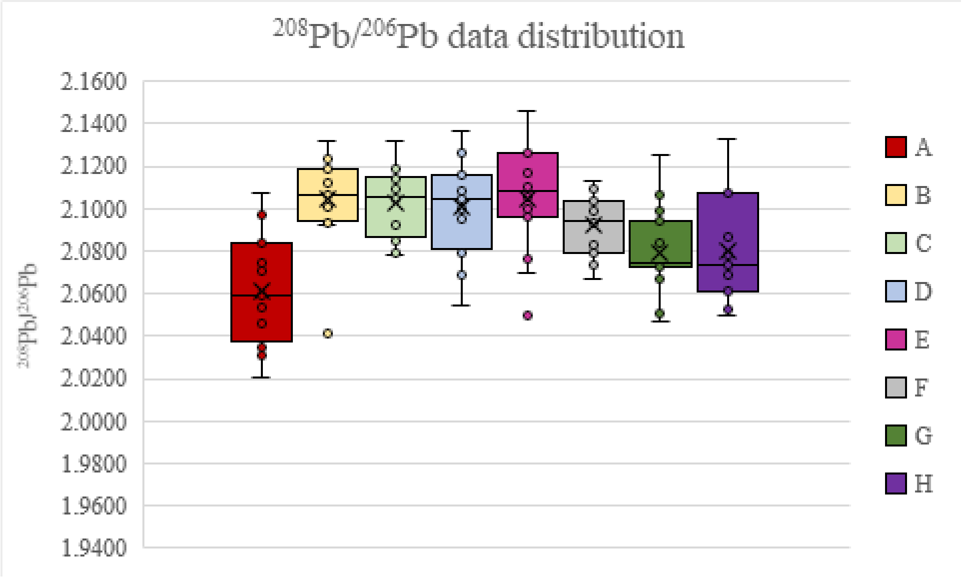
Graph 5: Boxplot - data distribution for $^{206}Pb/^{207}Pb$ (n=120)



Graph 6: Boxplot - data distribution for $^{208}Pb/^{207}Pb$ (n=120)



Graph 7: Boxplot - data distribution for $^{208}Pb/^{206}Pb$ (n=120)



A one-way ANOVA in Table 8 has shown there is a significant difference between categories (p=<0.0001). However, using the Tukey's post-hoc test (see results in Appendix 1), it was shown that statistical difference was only found between category A and other categories. Categories B-H are not significantly different from each other.

Table 8: One-way ANOVA for $^{206}Pb/^{207}Pb$ in categories

Summary		Categories		
Groups	*Count*	*Sum*	*Average*	*Variance*
A	15	17.9083	1.1939	<0.0001
B	15	17.6908	1.1794	0.0002
C	15	17.6655	1.1777	<0.0001
D	15	17.5972	1.1731	<0.0001
E	15	17.6024	1.1735	0.0001
F	15	17.6097	1.1740	<0.0001
G	15	17.6265	1.1751	<0.0001
H	15	17.6448	1.1763	0.0001

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between groups	0.0049	7	0.0007	10.1783	<0.0001	2.0924
Within groups	0.0077	112	0.0001			
Total	0.0126	119				

One-way ANOVA was also performed for the ratios $^{208}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ (Tables 9 and 10) and significant difference was found in both of them. $^{208}Pb/^{206}Pb$ largely follows the trend of $^{206}Pb/^{207}Pb$, finding significant difference between category A and categories B-F, however significant difference was also found between categories B and G, E and G or E and H (see Appendix 5). The $^{208}Pb/^{207}Pb$ ratio has only been found significantly different for four pairs of categories, B and G, B and H, C and G, C and H (see Appendix 6).

Table 9: One-way ANOVA for $^{208}Pb/^{207}Pb$ in categories

Summary	Categories			
Groups	*Count*	*Sum*	*Average*	*Variance*
A	15	36.9145	2.4610	0.0007
B	15	37.2189	2.4813	0.0006
C	15	37.1427	2.4762	0.0004
D	15	36.9718	2.4648	0.0008
E	15	37.0460	2.4697	0.0005
F	15	36.8478	2.4565	0.0003
G	15	36.6506	2.4434	0.0006
H	15	36.6944	2.4463	0.0009

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between groups	0.0189	7	0.0027	4.4871	0.0002	2.0924
Within groups	0.0676	112	0.0006			
Total	0.0865	119				

Table 10: One-way ANOVA for $^{208}Pb/^{206}Pb$ in categories

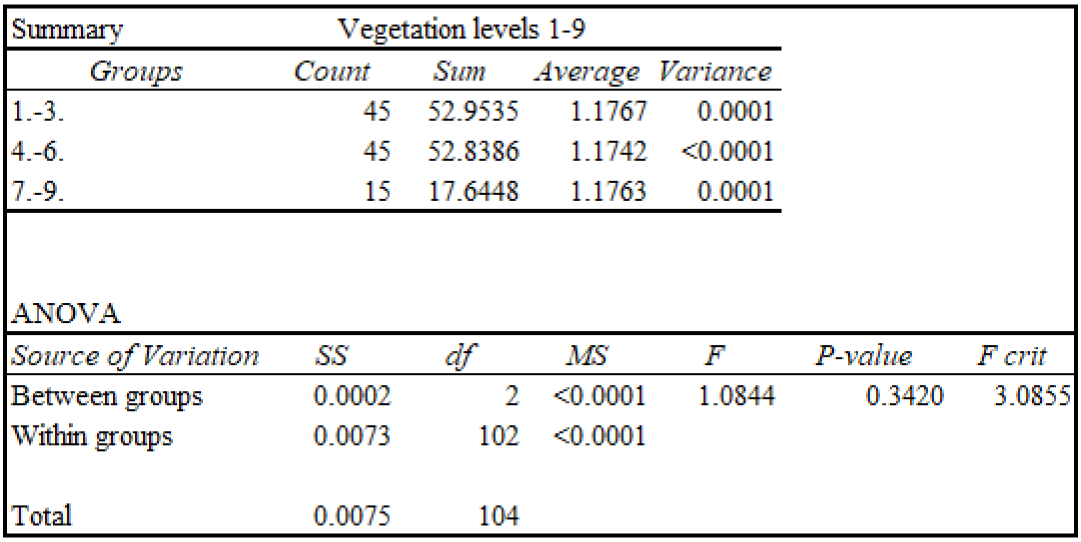
Summary	Categories			
Groups	*Count*	*Sum*	*Average*	*Variance*
A	15	30.9210	2.0614	0.0007
B	15	31.5603	2.1040	0.0004
C	15	31.5383	2.1026	0.0003
D	15	31.5152	2.1010	0.0005
E	15	31.5708	2.1047	0.0006
F	15	31.3869	2.0925	0.0002
G	15	31.1893	2.0793	0.0004
H	15	31.1948	2.0797	0.0006

ANOVA						
Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between groups	0.0260	7	0.0037	7.9252	<0.0001	2.0924
Within groups	0.0525	112	0.0005			
Total	0.0786	119				

14.1.2 Forest vegetation levels and altitude

A one-way ANOVA was conducted to find the effect of vegetation level on lead isotope ratios. The categories were divided into three groups: levels 1-3 (categories B, C and D), levels 4-6 (categories E, F and G) and levels 7-9 (category H). Category A was not included as it is bound to soil type rather than altitude and vegetation. Based on the results presented in Table 11 it can be stated that there is no significant difference between these groups.

Table 11: One-way ANOVA for $^{206}Pb/^{207}Pb$ in forest vegetation levels



Summary	Vegetation levels 1-9			
Groups	*Count*	*Sum*	*Average*	*Variance*
1.-3.	45	52.9535	1.1767	0.0001
4.-6.	45	52.8386	1.1742	<0.0001
7.-9.	15	17.6448	1.1763	0.0001

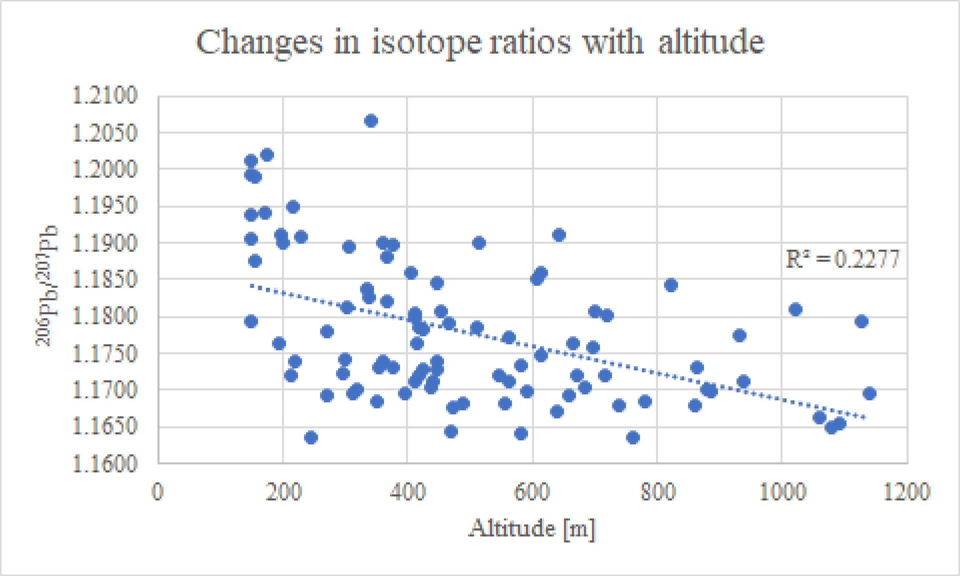
ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between groups	0.0002	2	<0.0001	1.0844	0.3420	3.0855
Within groups	0.0073	102	<0.0001			
Total	0.0075	104				

As vegetation levels do not always mean a difference between altitudes - since the levels may overlap in this aspect - another analysis was conducted for altitudinal changes. Data about altitude were collected from the KOLEP project and ranged between 150 - 1140 m above sea level, however, this type of data was not available for all collected samples.

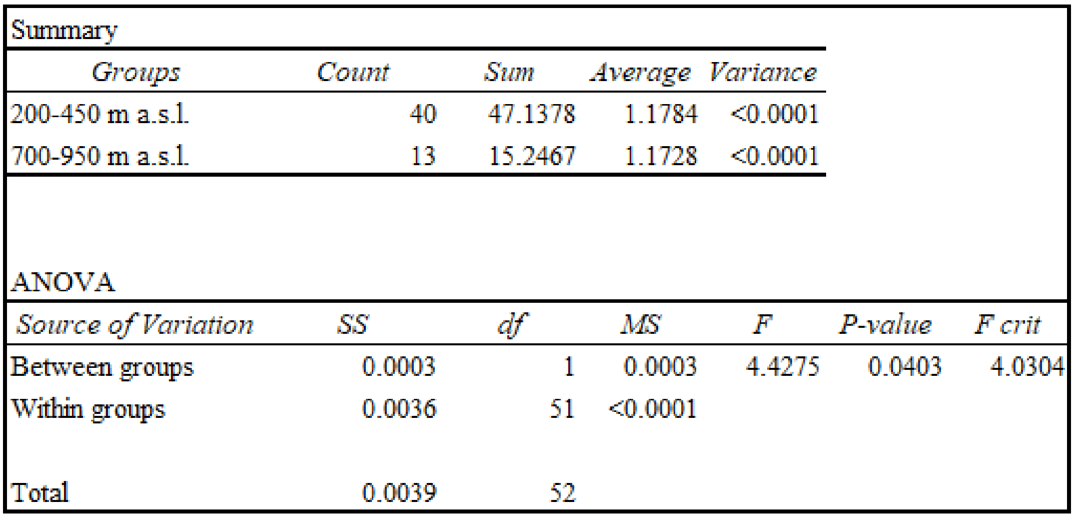
Graph 8 shows the existence of an altitudinal gradient of the $^{206}Pb/^{207}Pb$ ratio, which increases with decreasing altitude. This relationship could be better established if more data were collected for this specific purpose, as the majority of data for altitude were collected for altitudes under 600 m a.s.l.

Graph 8: Relationship between altitude and ^{206}Pb/^{207}Pb isotope ratio.



Results from one-way ANOVA (Table 12) show a significant difference between isotope ratios of profiles in the range of 200-450 m a.s.l. and 700-950 m a.s.l. These ranges were selected to include more categories, as altitudes below 200 m a.s.l. were primarily samples from category A and samples from altitudes above 950 m a.s.l. were primarily category H.

Table 12: One-way ANOVA for ^{206}Pb/^{207}Pb for altitude



Summary

Groups	*Count*	*Sum*	*Average*	*Variance*
200-450 m a.s.l.	40	47.1378	1.1784	<0.0001
700-950 m a.s.l.	13	15.2467	1.1728	<0.0001

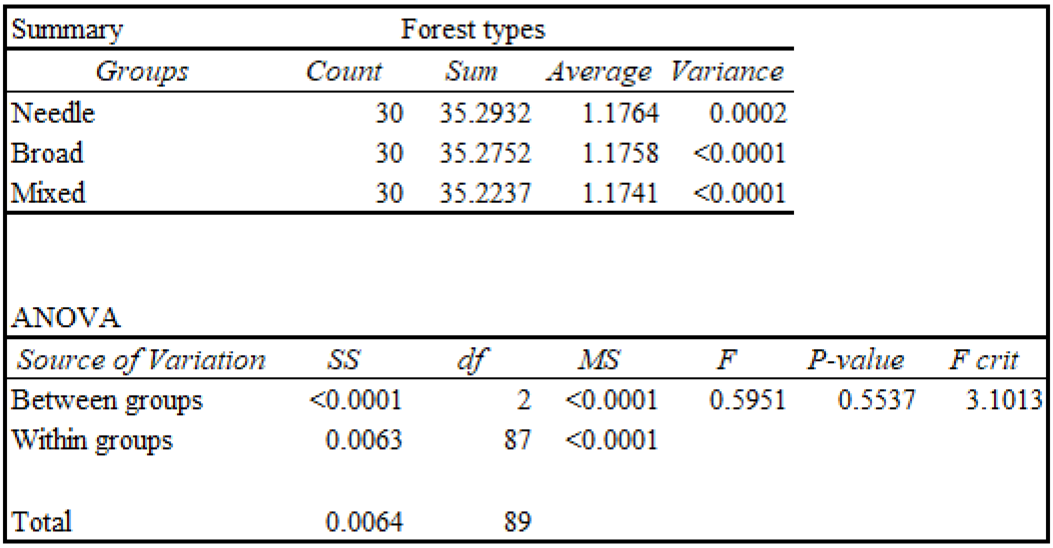
ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between groups	0.0003	1	0.0003	4.4275	0.0403	4.0304
Within groups	0.0036	51	<0.0001			
Total	0.0039	52				

14.1.3 Vegetation type

The effect of vegetation type has been also analyzed. The data were grouped based on their forest type - categories B and E for broad leaved forests, C and F for needle leaved forests and D and G for mixed forests, however no significant difference was found through the one-way ANOVA as seen in Table 13.

Table 13: One-way ANOVA for different forest types



Summary	Forest types			
Groups	*Count*	*Sum*	*Average*	*Variance*
Needle	30	35.2932	1.1764	0.0002
Broad	30	35.2752	1.1758	<0.0001
Mixed	30	35.2237	1.1741	<0.0001

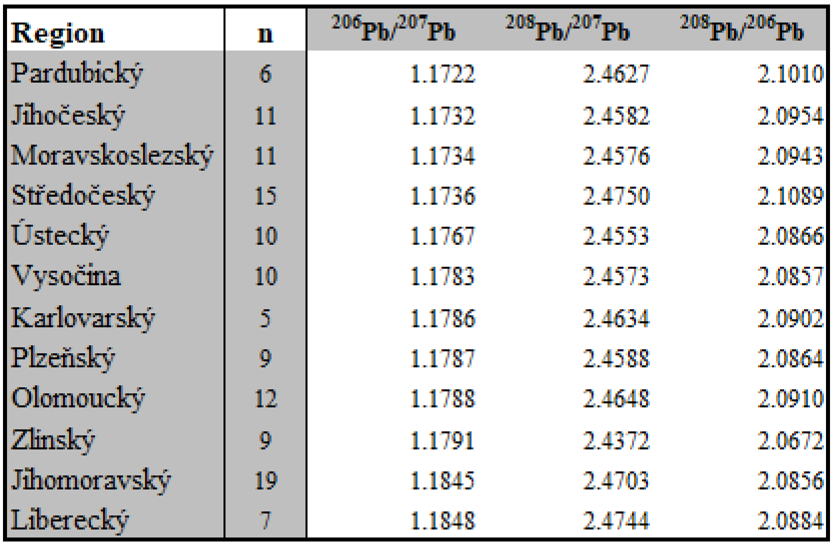
ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between groups	<0.0001	2	<0.0001	0.5951	0.5537	3.1013
Within groups	0.0063	87	<0.0001			
Total	0.0064	89				

14.1.4 Regions

Samples were further divided by regions - all regions were sampled except Prague, which wouldn’t comply with the KOLEP projects objectives. Since only one sample was taken in Královéhradecký region, it was assigned to Liberecký region, whose border lies about 7 kilometres away from the sampling site. Table 14 shows average values for the respective regions in order of increasing ^{206}Pb/^{207}Pb ratio.

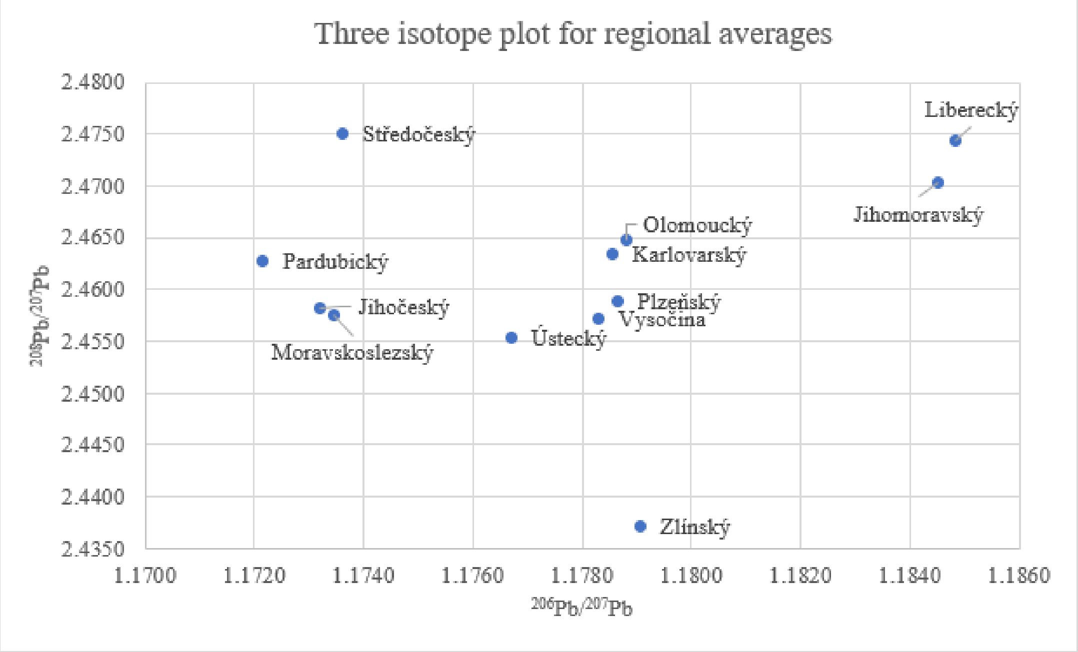
Table 14: Regional averages



Region	**n**	**^{206}Pb/^{207}Pb**	**^{208}Pb/^{207}Pb**	**^{208}Pb/^{206}Pb**
Pardubický	6	1.1722	2.4627	2.1010
Jihočeský	11	1.1732	2.4582	2.0954
Moravskoslezský	11	1.1734	2.4576	2.0943
Středočeský	15	1.1736	2.4750	2.1089
Ústecký	10	1.1767	2.4553	2.0866
Vysočina	10	1.1783	2.4573	2.0857
Karlovarský	5	1.1786	2.4634	2.0902
Plzeňský	9	1.1787	2.4588	2.0864
Olomoucký	12	1.1788	2.4648	2.0910
Zlinský	9	1.1791	2.4372	2.0672
Jihomoravský	19	1.1845	2.4703	2.0856
Liberecký	7	1.1848	2.4744	2.0884

Graphs 9 and 10 show the three isotope plots for average regional isotope signatures. Pardubický region has the lowest and Liberecký region the highest $^{206}Pb/^{207}Pb$ ratio, Zlínský region exhibits a notably low ratio of $^{208}Pb/^{207}Pb$. While the ratios vary within regions, based on the one-way ANOVA in Table 15 there is no significant difference between regions.

Graph 9: Three isotope plot for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ in regional averages



Graph 10: Three isotope plot for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ in regional averages

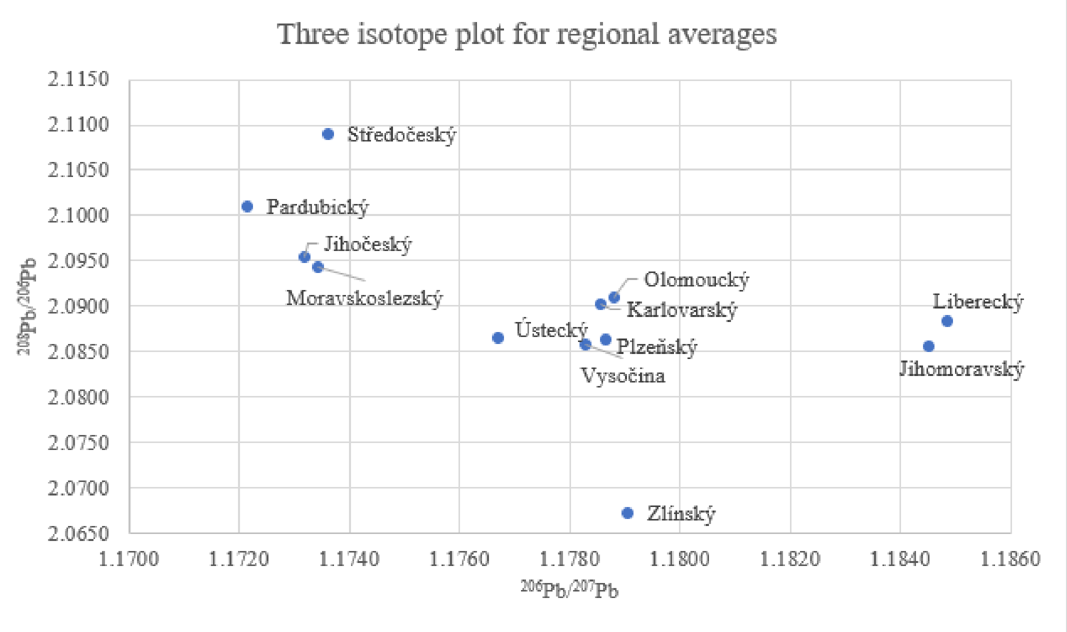


Table 15: One-way ANOVA for ^{206}Pb/^{207}Pb in regions

Summary — Regions

Groups	*Count*	*Sum*	*Average*	*Variance*
Jihočeský	11	23.0490	2.0954	0.0008
Jihomoravský	18	37.5323	2.0851	0.0010
Karlovarský	5	10.4511	2.0902	0.0003
Liberecký	7	14.6187	2.0884	0.0004
Moravskoslezský	11	23.0372	2.0943	0.0004
Olomoucký	12	25.0919	2.0910	0.0003
Pardubický	6	12.6060	2.1010	0.0001
Plzeňský	9	18.7775	2.0864	0.0013
Středočeský	15	31.6337	2.1089	0.0002
Ústecký	10	20.8660	2.0866	0.0004
Vysočina	6	12.5141	2.0857	0.0011
Zlinský	9	18.6046	2.0672	0.0007

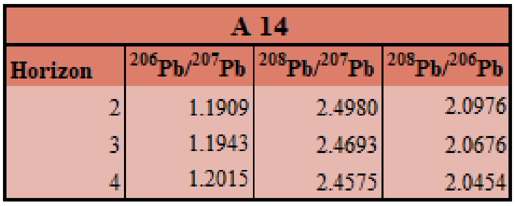
ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between groups	0.0121	11	0.0011	1.7642	0.0693	1.8792
Within groups	0.0665	107	0.0006			
Total	0.0785	118				

14.2 Full profiles

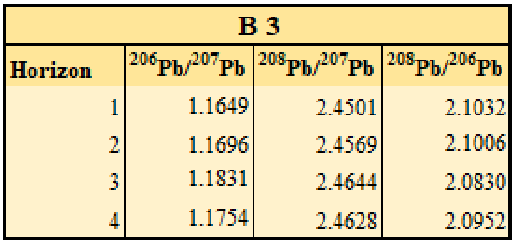
One profile from each category has been selected based on sample availability at the time and analyzed for isotope ratios. The results are presented in Tables 16 - 23 below.

Table 16: Isotopic composition of site A 14



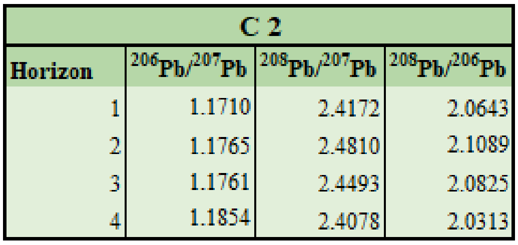
A 14			
Horizon	**^{206}Pb/^{207}Pb**	**^{208}Pb/^{207}Pb**	**^{208}Pb/^{206}Pb**
2	1.1909	2.4980	2.0976
3	1.1943	2.4693	2.0676
4	1.2015	2.4575	2.0454

Table 17: Isotopic composition of site B 3



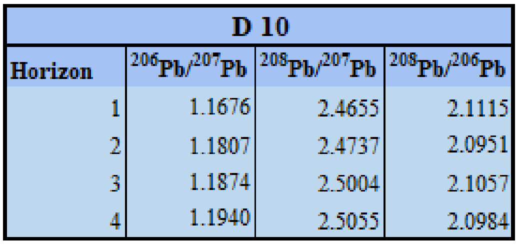
B 3			
Horizon	**^{206}Pb/^{207}Pb**	**^{208}Pb/^{207}Pb**	**^{208}Pb/^{206}Pb**
1	1.1649	2.4501	2.1032
2	1.1696	2.4569	2.1006
3	1.1831	2.4644	2.0830
4	1.1754	2.4628	2.0952

Table 18: Isotopic composition of site C 2



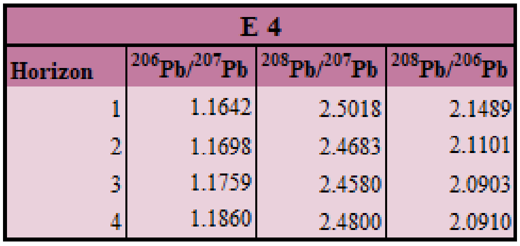
C 2			
Horizon	**^{206}Pb/^{207}Pb**	**^{208}Pb/^{207}Pb**	**^{208}Pb/^{206}Pb**
1	1.1710	2.4172	2.0643
2	1.1765	2.4810	2.1089
3	1.1761	2.4493	2.0825
4	1.1854	2.4078	2.0313

Table 19: Isotopic composition of site D 10



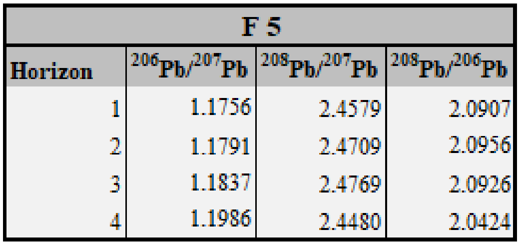
D 10			
Horizon	**^{206}Pb/^{207}Pb**	**^{208}Pb/^{207}Pb**	**^{208}Pb/^{206}Pb**
1	1.1676	2.4655	2.1115
2	1.1807	2.4737	2.0951
3	1.1874	2.5004	2.1057
4	1.1940	2.5055	2.0984

Table 20: Isotopic composition of site E 4



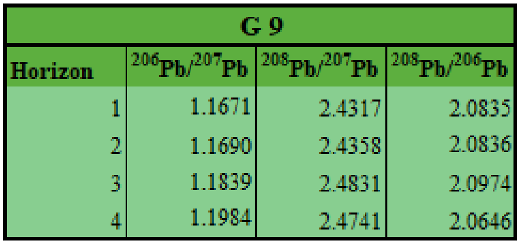
E 4			
Horizon	**^{206}Pb/^{207}Pb**	**^{208}Pb/^{207}Pb**	**^{208}Pb/^{206}Pb**
1	1.1642	2.5018	2.1489
2	1.1698	2.4683	2.1101
3	1.1759	2.4580	2.0903
4	1.1860	2.4800	2.0910

Table 21: Isotopic composition of site F 5



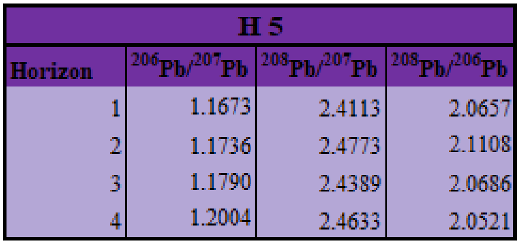
F 5			
Horizon	**^{206}Pb/^{207}Pb**	**^{208}Pb/^{207}Pb**	**^{208}Pb/^{206}Pb**
1	1.1756	2.4579	2.0907
2	1.1791	2.4709	2.0956
3	1.1837	2.4769	2.0926
4	1.1986	2.4480	2.0424

Table 22: Isotopic composition of site G 9



G 9			
Horizon	**^{206}Pb/^{207}Pb**	**^{208}Pb/^{207}Pb**	**^{208}Pb/^{206}Pb**
1	1.1671	2.4317	2.0835
2	1.1690	2.4358	2.0836
3	1.1839	2.4831	2.0974
4	1.1984	2.4741	2.0646

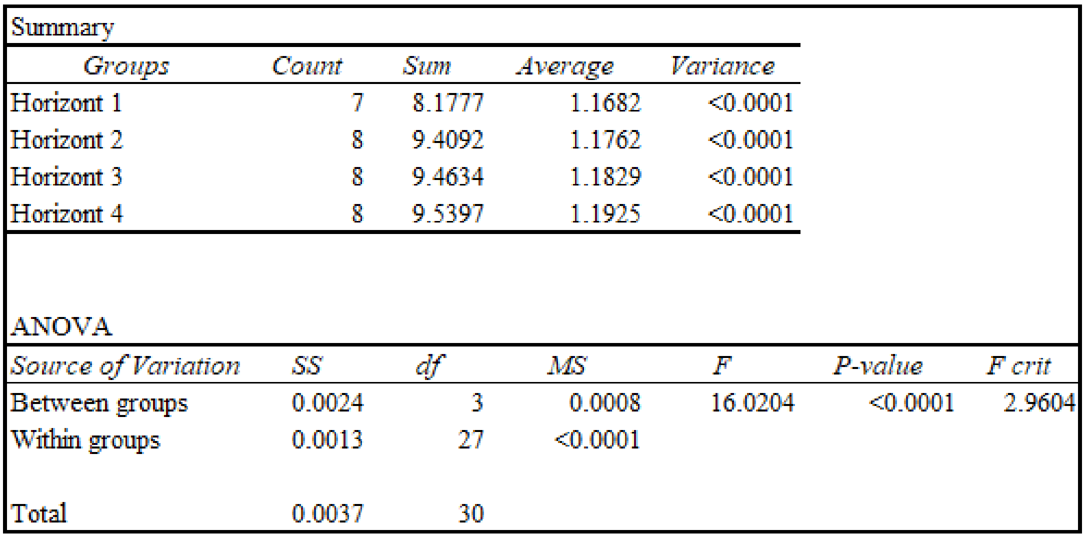
Table 23: Isotopic composition of site H 5



H 5			
Horizon	**^{206}Pb/^{207}Pb**	**^{208}Pb/^{207}Pb**	**^{208}Pb/^{206}Pb**
1	1.1673	2.4113	2.0657
2	1.1736	2.4773	2.1108
3	1.1790	2.4389	2.0686
4	1.2004	2.4633	2.0521

A change in the isotopic composition between different horizons was expected. The one-way ANOVA in Table 24 confirms a significant difference between horizons of the full-profile samples along with increasing mean value of ^{206}Pb/^{207}Pb in a downward direction.

Table 24: One-way ANOVA for ^{206}Pb/^{207}Pb in soil horizons



Summary

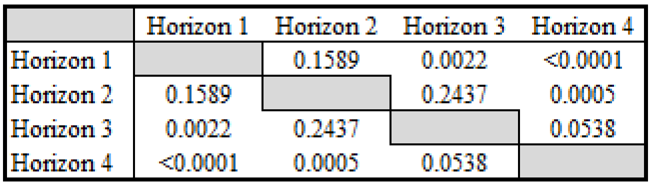
Groups	*Count*	*Sum*	*Average*	*Variance*
Horizont 1	7	8.1777	1.1682	<0.0001
Horizont 2	8	9.4092	1.1762	<0.0001
Horizont 3	8	9.4634	1.1829	<0.0001
Horizont 4	8	9.5397	1.1925	<0.0001

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between groups	0.0024	3	0.0008	16.0204	<0.0001	2.9604
Within groups	0.0013	27	<0.0001			
Total	0.0037	30				

Tukey's HSD test in Table 25 reveals significant difference between the ^{206}Pb/^{207}Pb ratio for soil horizons not directly adjacent to each other, showing greater difference with increasing distance. Neighbouring horizons are not significantly different.

Table 25: Tukey's HSD test for $^{206}Pb/^{207}Pb$ in soil horizons



	Horizon 1	Horizon 2	Horizon 3	Horizon 4
Horizon 1		0.1589	0.0022	<0.0001
Horizon 2	0.1589		0.2437	0.0005
Horizon 3	0.0022	0.2437		0.0538
Horizon 4	<0.0001	0.0005	0.0538	

15. Discussion

The isotopic composition of lead in an area is the combination of all sources which affect it, making it difficult to find the individual inputs even if ratios of all potential contaminants are known. Lower $^{206}Pb/^{207}Pb$ ratios in upper soil horizons (see Averages in Table 24), which point to anthropogenic pollution, can be observed even in areas that should not be largely affected by human activity (Komárek et al. 2006). The atmospheric mixture observed over Central Europe can mainly be attributed to the burning of coal and leaded petrol combustion and yields a $^{206}Pb/^{207}Pb$ ratio of 1.131-1.156, a value obtained from European glaciers (Weiss et al. 1999).

Atmospheric deposition of this industrial mixture is likely the cause of the low values of $^{206}Pb/^{207}Pb$ ratios in the A horizons of the sampled soils. However, while the $^{206}Pb/^{207}Pb$ values detected may first bring up the idea of large influence of leaded gasoline, whose isotopic signature in Czech Republic tends to be low in $^{206}Pb/^{207}Pb$ ratio due to the influence of Broken Hill ore (see Chapter 11), the number of emissions from coal and gasoline were not equal and coal burning emissions greatly exceeded emissions from leaded gasoline (Novák et al. 2003). The solution to this problem may lie in particle sizes from coal burning and gasoline emissions.

Coal combustion produces a significant amount of emissions but only about 4-7% of particulate matter in them reaches the size of less than 2.5 µm in diameter (Linak et al. 2011). The particle size in gasoline tends to be smaller and usually ranges between 0.04-0.08 µm in diameter (Harris & Maricq 2001). Lead is primarily concentrated in the submicron fraction of emissions (Samara & Voutsa 2005; Pan et al. 2015) which has a longer residence time in the atmosphere and as such can travel greater distances (Anastastio & Martin 2001). As such it is possible that despite smaller total emissions, leaded gasoline can be a significant factor influencing the isotopic ratios of Czech soils.

Reimann et al. (2012) measured the majority of Czech agricultural soils to be within the range of 1.191 - 1.245 for ^{206}Pb/^{207}Pb, which is a higher number than the averages we measured in forest soils (see Table 7). This effect might be caused by several factors. Ettler et al. (2005) reports the concentration of lead in heavily polluted areas to be an order of magnitude higher in forest soils compared to agricultural soils caused by ploughing and harvest of crops. The mixing of soil through ploughing may affect the total isotope composition since this changes with depth (see Chapter 14.2) and lead may also be taken up by plants and redeposited. The composition of lead in forest soils is also more influenced by the atmospheric lead composition due to the interception of forest canopy (Gandois et al. 2010).

The shifting of the ^{206}Pb/^{207}Pb ratio towards higher values with increasing depth can be attributed to a greater effect of the bedrock, which - in the Czech Republic - tends to have values around 1.20 but may reach up to 1.60 in extreme conditions (leucocratic granite) (Novák et al. 2010). Under ideal conditions, bedrock itself should be sampled to rule out the possibility of local anomalies and gain more precise data about the sampled location. As was already mentioned in Chapter 4, generalization of data may lead to erroneous assumptions about the actual scale of anthropogenic pollution in an area.

When comparing the isotope composition of different forest vegetation levels, the majority of levels in the Czech Republic were not significantly different from each other (Tables 8-10), most likely due to the reasons mentioned above. Since the sites were sampled so that they wouldn't be in a close vicinity of large contamination sources such as cities or industrial complexes, their isotopic signature similarity could have been expected, though as observed in Appendices 6 and 7, some categories exhibit differences in ^{208}Pb/^{207}Pb and ^{208}Pb/^{206}Pb ratios, indicating input from other, likely local sources.

The altitudinal gradient observed in Graph 8 shows the increasing ^{206}Pb/^{207} ratio with decreasing altitude. Differences in isotopic composition in higher altitudes can be caused by thermal inversions, which prevent pollutants from reaching higher altitudes (Anquetin et al. 1999; Rosman et al. 2000). The only exception to the similarity of signatures are the fluvisols (category A), which display a much higher ^{206}Pb/^{207}Pb and generally lower ^{208}Pb/^{206}Pb ratio than other categories.

Rivers and floodplains are frequently highly polluted and may provide records of pollution from both recent and early industrial activities (Matys Grygar et al. 2016). Due to their soil characteristics, which allows for water storage, filtration etc. floodplains can serve as buffer areas during flood events as well as a retention barrier for pollutants (Haase 2003). As seen in Figure 5, the majority of fluvisol samples in this thesis were taken from the vicinity of Morava and Dyje rivers where especially Morava has been extensively studied for pollution (Kadlec et al. 2009; Matys Grygar et al. 2012; Famera et al. 2013).

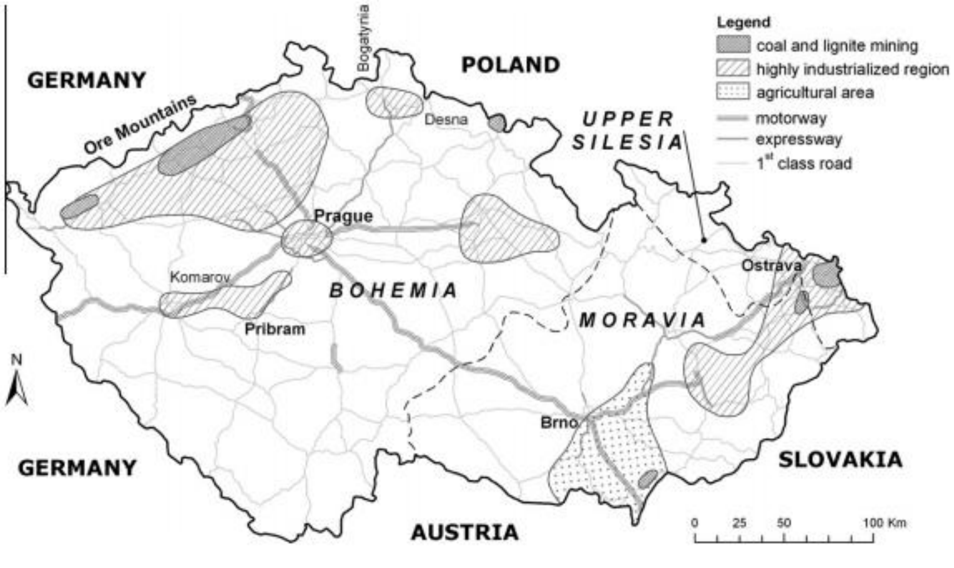
Grygar et al. (2010) sampled the sediments of the Morava river floodplains, measuring isotope ratios of ^{206}Pb/^{207}Pb between 1.188 and 1.191 which were attributed mainly to coal burning. The average value recorded in this thesis for floodplains is higher at 1.1939, the measured range lies between 1.1794 and 1.2067. The reason for this could be the specific conditions in flooded soils, such as the fixation of lead and other trace metals during prolonged flooding (Charlatchka & Cambier 2000) or the large combination of pollution inputs present, for example surface runoff, pollution from agriculture (pesticides), pollution from urban paved areas or sewer overflows. Erosion and weathering of sediments are also a notable source of lead in river streams (Thonon 2006) which could greatly contribute to the isotopic composition of lead in floodplains.

Although in general there was no significant difference between regions, some notable locations should be commented upon. Graph 9 shows the average isotopic signature of lead in different regions, out of which the Zlínský region stands out the most with its low ^{208}Pb/^{207}Pb. Sucharová et al. (2014) reported low ^{208}Pb/^{207}Pb (as well as low ^{206}Pb/^{207}Pb) ratio found in mosses in the area around the city of Hodonín, the vicinity of the city of Zlín however shows high ^{208}Pb/^{207}Pb ratios. The total isotope composition in the Zlín area is likely influenced by local metallurgical and glass industry.

The problem with comparison of regions in this thesis is the small amount of samples available for certain regions - while there were 15 sampled sites in Středočeský and 19 in Jihomoravský regions, Karlovarský and Vysočina regions only had 5 and 6 samples respectively (see Table 14). Sucharová et al. (2011) conducted a study on the spatial distribution of lead isotopes with over 250 samples spaced evenly across the whole country, finding specific signatures for local leads and industries. Unlike this study, Sucharová et al. (2011) did not exclude industrial locations (see Figure 6), however it remains possible that just because no significant difference was found between regions in this study, it doesn't mean it was caused by a lack of isotope signature diversity, but rather by the lack of samples.

One of the issues with comparing lead pollution of forest soils in relatively unpolluted areas of the Czech Republic is the lack of comparative studies. While many studies focus on soils in areas affected by large pollution sources such as mining or smelting activity (Kapička et al. 1999; Ettler et al. 2006; Francová et al. 2017 and others) targeting specifically unpolluted areas has received notably less attention on the territory of this country. While it can be assumed that areas not directly under the influence of pollution sources such as big cities or industrial complexes will have a generally uniform signature of a broad range of sources (Renberg et al. 2001; Matys Grygar et al. 2012), this study shows that differences can be found even across unpolluted sites depending on their altitude and forest vegetation zones.

Figure 6: Major emission areas in the Czech Republic (Sucharová et al. 2011)



16. Conclusion

The aim of this thesis was to assess isotope ratios of forest soils on the territory of Czech Republic and find sources of their contamination.

One of the hypotheses of this thesis was that the isotope ratio of soils will be influenced by Czech coals. While coal is definitely influencing the composition of lead in forest soils, other factors such as leaded gasoline or the general mixture of atmospheric lead are also strong factors that shouldn’t be left out. A further exploration of the influence of local sources such as metallurgical industries could also shed light on the total compositions of lead in specific areas.

Regional isotope ratios were not found to be significantly different, disproving the second hypothesis of this thesis. This could be in part due to the sampling of areas without direct sources of pollution but also due to the unequal and insufficient sampling throughout the regions.

Among different forest vegetation levels significant difference was observed in fluvisols compared to other levels. Fluvisols are often highly polluted soils with specific chemistry and multiple inputs contributing to the total lead isotope composition and as such should be closely monitored for pollution. Although the remaining vegetation levels were similar, an altitudinal gradient was observed, suggesting the influence of atmospheric processes.

This thesis stresses out the necessity of good environmental air pollution controls and monitoring. It also accentuates the importance of pollution studies in areas without obvious contamination sources such as national parks and natural reservations, which could help limit and prevent the destruction of sensitive habitats.

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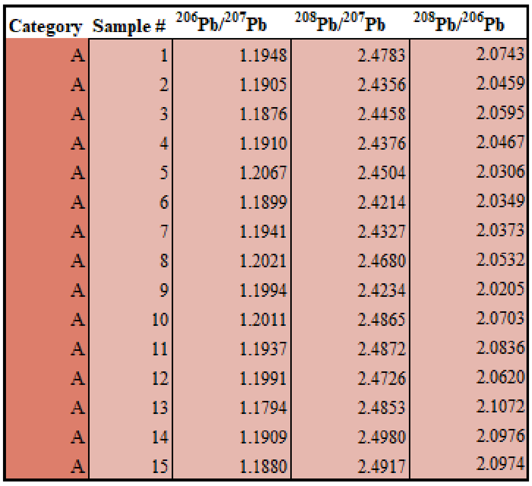
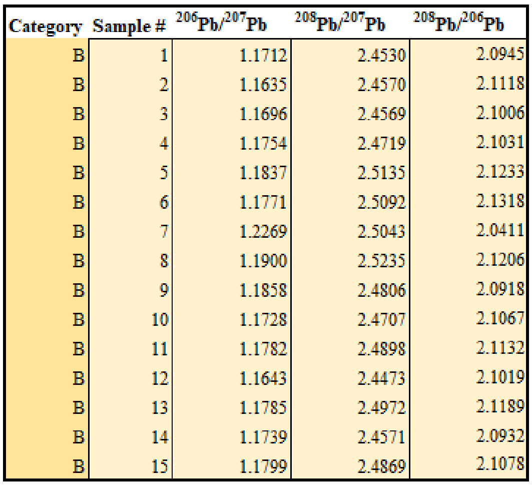
18. List of figures, tables, graphs and appendices

19. Appendix

Appendix 1: Isotope ratios for categories A and B

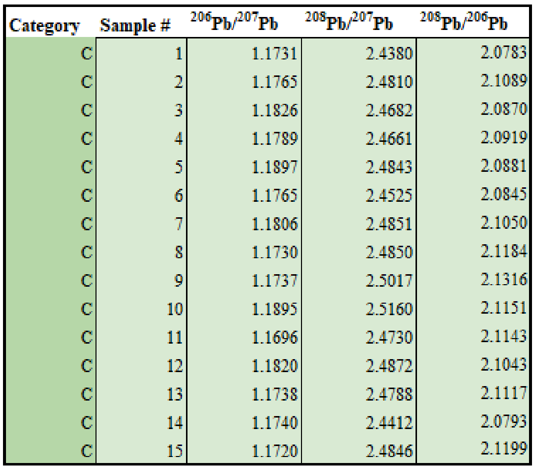


Category	Sample #	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb	^{208}Pb/^{206}Pb
A	1	1.1948	2.4783	2.0743
A	2	1.1905	2.4356	2.0459
A	3	1.1876	2.4458	2.0595
A	4	1.1910	2.4376	2.0467
A	5	1.2067	2.4504	2.0306
A	6	1.1899	2.4214	2.0349
A	7	1.1941	2.4327	2.0373
A	8	1.2021	2.4680	2.0532
A	9	1.1994	2.4234	2.0205
A	10	1.2011	2.4865	2.0703
A	11	1.1937	2.4872	2.0836
A	12	1.1991	2.4726	2.0620
A	13	1.1794	2.4853	2.1072
A	14	1.1909	2.4980	2.0976
A	15	1.1880	2.4917	2.0974

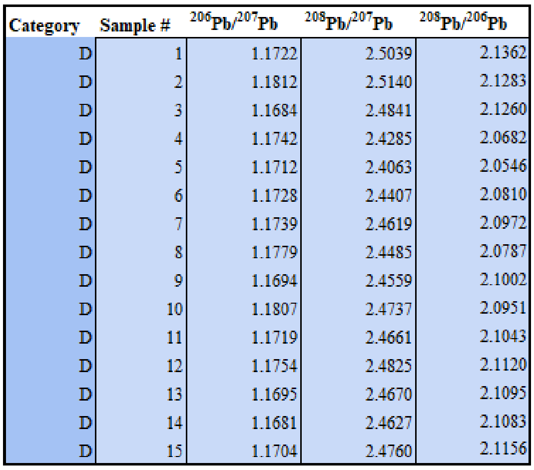


Category	Sample #	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb	^{208}Pb/^{206}Pb
B	1	1.1712	2.4530	2.0945
B	2	1.1635	2.4570	2.1118
B	3	1.1696	2.4569	2.1006
B	4	1.1754	2.4719	2.1031
B	5	1.1837	2.5135	2.1233
B	6	1.1771	2.5092	2.1318
B	7	1.2269	2.5043	2.0411
B	8	1.1900	2.5235	2.1206
B	9	1.1858	2.4806	2.0918
B	10	1.1728	2.4707	2.1067
B	11	1.1782	2.4898	2.1132
B	12	1.1643	2.4473	2.1019
B	13	1.1785	2.4972	2.1189
B	14	1.1739	2.4571	2.0932
B	15	1.1799	2.4869	2.1078

Appendix 2: Isotope ratios for categories C and D

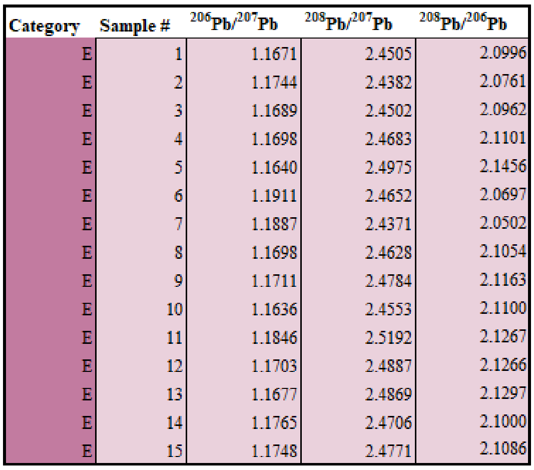


Category	Sample #	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb	^{208}Pb/^{206}Pb
C	1	1.1731	2.4380	2.0783
C	2	1.1765	2.4810	2.1089
C	3	1.1826	2.4682	2.0870
C	4	1.1789	2.4661	2.0919
C	5	1.1897	2.4843	2.0881
C	6	1.1765	2.4525	2.0845
C	7	1.1806	2.4851	2.1050
C	8	1.1730	2.4850	2.1184
C	9	1.1737	2.5017	2.1316
C	10	1.1895	2.5160	2.1151
C	11	1.1696	2.4730	2.1143
C	12	1.1820	2.4872	2.1043
C	13	1.1738	2.4788	2.1117
C	14	1.1740	2.4412	2.0793
C	15	1.1720	2.4846	2.1199

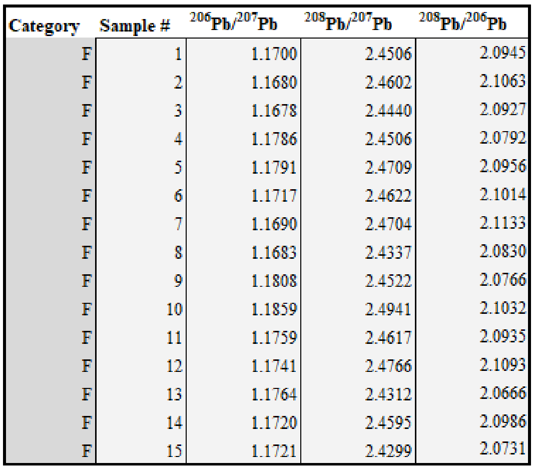


Category	Sample #	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb	^{208}Pb/^{206}Pb
D	1	1.1722	2.5039	2.1362
D	2	1.1812	2.5140	2.1283
D	3	1.1684	2.4841	2.1260
D	4	1.1742	2.4285	2.0682
D	5	1.1712	2.4063	2.0546
D	6	1.1728	2.4407	2.0810
D	7	1.1739	2.4619	2.0972
D	8	1.1779	2.4485	2.0787
D	9	1.1694	2.4559	2.1002
D	10	1.1807	2.4737	2.0951
D	11	1.1719	2.4661	2.1043
D	12	1.1754	2.4825	2.1120
D	13	1.1695	2.4670	2.1095
D	14	1.1681	2.4627	2.1083
D	15	1.1704	2.4760	2.1156

Appendix 3: Isotope ratios for categories E and F

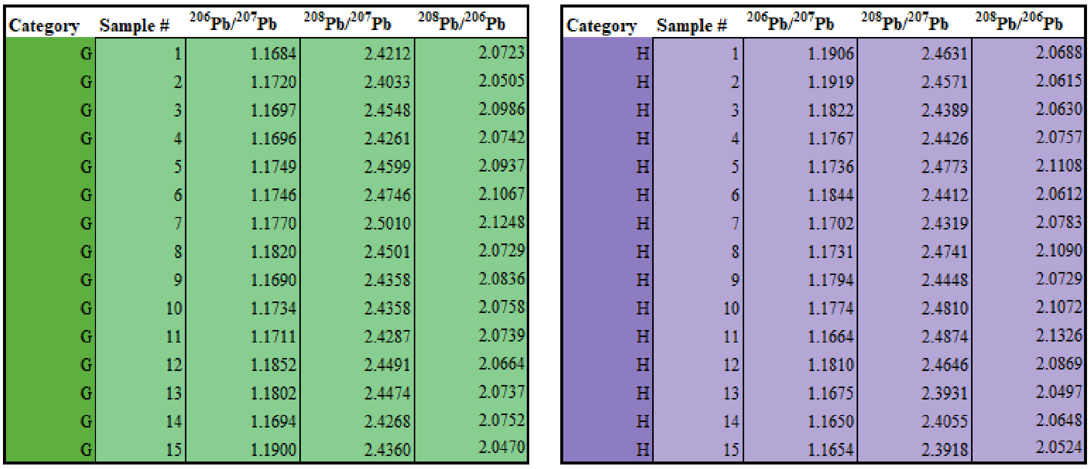


Category	Sample #	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb	^{208}Pb/^{206}Pb
E	1	1.1671	2.4505	2.0996
E	2	1.1744	2.4382	2.0761
E	3	1.1689	2.4502	2.0962
E	4	1.1698	2.4683	2.1101
E	5	1.1640	2.4975	2.1456
E	6	1.1911	2.4652	2.0697
E	7	1.1887	2.4371	2.0502
E	8	1.1698	2.4628	2.1054
E	9	1.1711	2.4784	2.1163
E	10	1.1636	2.4553	2.1100
E	11	1.1846	2.5192	2.1267
E	12	1.1703	2.4887	2.1266
E	13	1.1677	2.4869	2.1297
E	14	1.1765	2.4706	2.1000
E	15	1.1748	2.4771	2.1086



Category	Sample #	^{206}Pb/^{207}Pb	^{208}Pb/^{207}Pb	^{208}Pb/^{206}Pb
F	1	1.1700	2.4506	2.0945
F	2	1.1680	2.4602	2.1063
F	3	1.1678	2.4440	2.0927
F	4	1.1786	2.4506	2.0792
F	5	1.1791	2.4709	2.0956
F	6	1.1717	2.4622	2.1014
F	7	1.1690	2.4704	2.1133
F	8	1.1683	2.4337	2.0830
F	9	1.1808	2.4522	2.0766
F	10	1.1859	2.4941	2.1032
F	11	1.1759	2.4617	2.0935
F	12	1.1741	2.4766	2.1093
F	13	1.1764	2.4312	2.0666
F	14	1.1720	2.4595	2.0986
F	15	1.1721	2.4299	2.0731

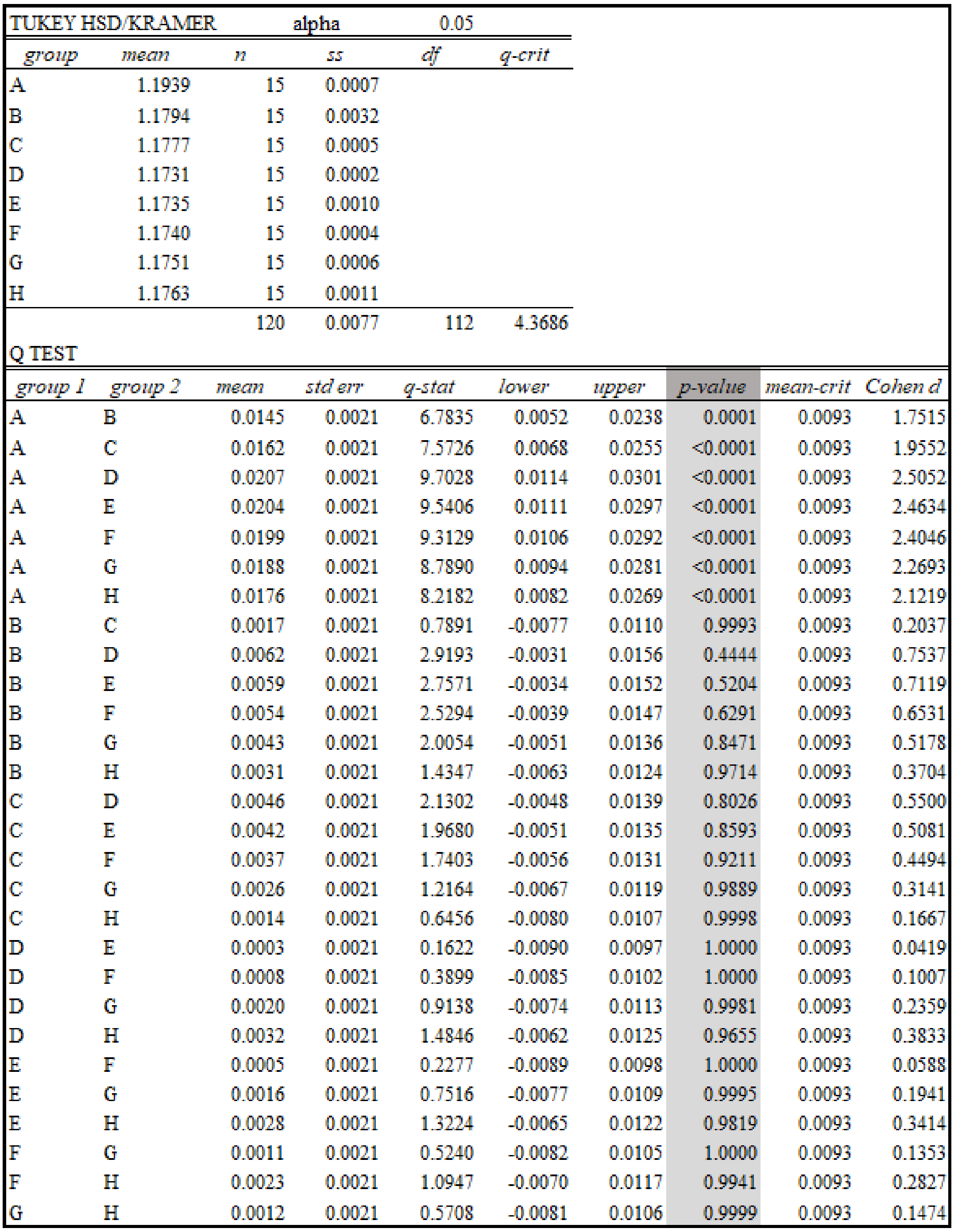
Appendix 4: Isotope ratios for categories G and H



Category	Sample #	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$
G	1	1.1684	2.4212	2.0723
G	2	1.1720	2.4033	2.0505
G	3	1.1697	2.4548	2.0986
G	4	1.1696	2.4261	2.0742
G	5	1.1749	2.4599	2.0937
G	6	1.1746	2.4746	2.1067
G	7	1.1770	2.5010	2.1248
G	8	1.1820	2.4501	2.0729
G	9	1.1690	2.4358	2.0836
G	10	1.1734	2.4358	2.0758
G	11	1.1711	2.4287	2.0739
G	12	1.1852	2.4491	2.0664
G	13	1.1802	2.4474	2.0737
G	14	1.1694	2.4268	2.0752
G	15	1.1900	2.4360	2.0470

Category	Sample #	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$
H	1	1.1906	2.4631	2.0688
H	2	1.1919	2.4571	2.0615
H	3	1.1822	2.4389	2.0630
H	4	1.1767	2.4426	2.0757
H	5	1.1736	2.4773	2.1108
H	6	1.1844	2.4412	2.0612
H	7	1.1702	2.4319	2.0783
H	8	1.1731	2.4741	2.1090
H	9	1.1794	2.4448	2.0729
H	10	1.1774	2.4810	2.1072
H	11	1.1664	2.4874	2.1326
H	12	1.1810	2.4646	2.0869
H	13	1.1675	2.3931	2.0497
H	14	1.1650	2.4055	2.0648
H	15	1.1654	2.3918	2.0524

Appendix 5: Tukey's HSD for $^{206}Pb/^{207}Pb$



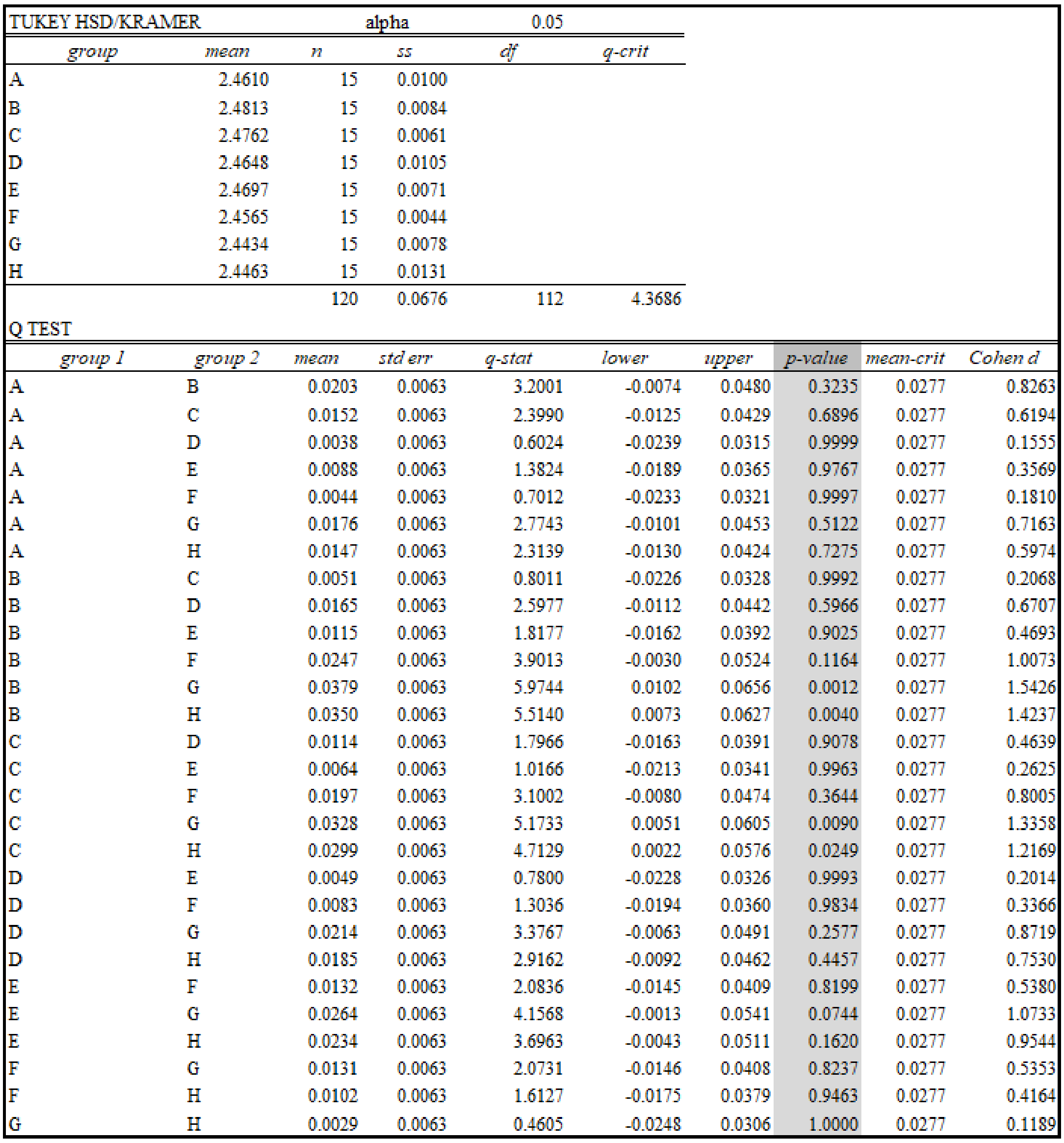
TUKEY HSD/KRAMER alpha 0.05

group	*mean*	*n*	*ss*	*df*	*q-crit*
A	1.1939	15	0.0007		
B	1.1794	15	0.0032		
C	1.1777	15	0.0005		
D	1.1731	15	0.0002		
E	1.1735	15	0.0010		
F	1.1740	15	0.0004		
G	1.1751	15	0.0006		
H	1.1763	15	0.0011		
		120	0.0077	112	4.3686

Q TEST

group 1	*group 2*	*mean*	*std err*	*q-stat*	*lower*	*upper*	*p-value*	*mean-crit*	*Cohen d*
A	B	0.0145	0.0021	6.7835	0.0052	0.0238	0.0001	0.0093	1.7515
A	C	0.0162	0.0021	7.5726	0.0068	0.0255	<0.0001	0.0093	1.9552
A	D	0.0207	0.0021	9.7028	0.0114	0.0301	<0.0001	0.0093	2.5052
A	E	0.0204	0.0021	9.5406	0.0111	0.0297	<0.0001	0.0093	2.4634
A	F	0.0199	0.0021	9.3129	0.0106	0.0292	<0.0001	0.0093	2.4046
A	G	0.0188	0.0021	8.7890	0.0094	0.0281	<0.0001	0.0093	2.2693
A	H	0.0176	0.0021	8.2182	0.0082	0.0269	<0.0001	0.0093	2.1219
B	C	0.0017	0.0021	0.7891	-0.0077	0.0110	0.9993	0.0093	0.2037
B	D	0.0062	0.0021	2.9193	-0.0031	0.0156	0.4444	0.0093	0.7537
B	E	0.0059	0.0021	2.7571	-0.0034	0.0152	0.5204	0.0093	0.7119
B	F	0.0054	0.0021	2.5294	-0.0039	0.0147	0.6291	0.0093	0.6531
B	G	0.0043	0.0021	2.0054	-0.0051	0.0136	0.8471	0.0093	0.5178
B	H	0.0031	0.0021	1.4347	-0.0063	0.0124	0.9714	0.0093	0.3704
C	D	0.0046	0.0021	2.1302	-0.0048	0.0139	0.8026	0.0093	0.5500
C	E	0.0042	0.0021	1.9680	-0.0051	0.0135	0.8593	0.0093	0.5081
C	F	0.0037	0.0021	1.7403	-0.0056	0.0131	0.9211	0.0093	0.4494
C	G	0.0026	0.0021	1.2164	-0.0067	0.0119	0.9889	0.0093	0.3141
C	H	0.0014	0.0021	0.6456	-0.0080	0.0107	0.9998	0.0093	0.1667
D	E	0.0003	0.0021	0.1622	-0.0090	0.0097	1.0000	0.0093	0.0419
D	F	0.0008	0.0021	0.3899	-0.0085	0.0102	1.0000	0.0093	0.1007
D	G	0.0020	0.0021	0.9138	-0.0074	0.0113	0.9981	0.0093	0.2359
D	H	0.0032	0.0021	1.4846	-0.0062	0.0125	0.9655	0.0093	0.3833
E	F	0.0005	0.0021	0.2277	-0.0089	0.0098	1.0000	0.0093	0.0588
E	G	0.0016	0.0021	0.7516	-0.0077	0.0109	0.9995	0.0093	0.1941
E	H	0.0028	0.0021	1.3224	-0.0065	0.0122	0.9819	0.0093	0.3414
F	G	0.0011	0.0021	0.5240	-0.0082	0.0105	1.0000	0.0093	0.1353
F	H	0.0023	0.0021	1.0947	-0.0070	0.0117	0.9941	0.0093	0.2827
G	H	0.0012	0.0021	0.5708	-0.0081	0.0106	0.9999	0.0093	0.1474

Appendix 6: Tukey's HSD for $^{208}\text{Pb}/^{207}\text{Pb}$



TUKEY HSD/KRAMER		alpha		0.05	
group	*mean*	*n*	*ss*	*df*	*q-crit*
A	2.4610	15	0.0100		
B	2.4813	15	0.0084		
C	2.4762	15	0.0061		
D	2.4648	15	0.0105		
E	2.4697	15	0.0071		
F	2.4565	15	0.0044		
G	2.4434	15	0.0078		
H	2.4463	15	0.0131		
		120	0.0676	112	4.3686

Q TEST

group 1	*group 2*	*mean*	*std err*	*q-stat*	*lower*	*upper*	*p-value*	*mean-crit*	*Cohen d*
A	B	0.0203	0.0063	3.2001	-0.0074	0.0480	0.3235	0.0277	0.8263
A	C	0.0152	0.0063	2.3990	-0.0125	0.0429	0.6896	0.0277	0.6194
A	D	0.0038	0.0063	0.6024	-0.0239	0.0315	0.9999	0.0277	0.1555
A	E	0.0088	0.0063	1.3824	-0.0189	0.0365	0.9767	0.0277	0.3569
A	F	0.0044	0.0063	0.7012	-0.0233	0.0321	0.9997	0.0277	0.1810
A	G	0.0176	0.0063	2.7743	-0.0101	0.0453	0.5122	0.0277	0.7163
A	H	0.0147	0.0063	2.3139	-0.0130	0.0424	0.7275	0.0277	0.5974
B	C	0.0051	0.0063	0.8011	-0.0226	0.0328	0.9992	0.0277	0.2068
B	D	0.0165	0.0063	2.5977	-0.0112	0.0442	0.5966	0.0277	0.6707
B	E	0.0115	0.0063	1.8177	-0.0162	0.0392	0.9025	0.0277	0.4693
B	F	0.0247	0.0063	3.9013	-0.0030	0.0524	0.1164	0.0277	1.0073
B	G	0.0379	0.0063	5.9744	0.0102	0.0656	0.0012	0.0277	1.5426
B	H	0.0350	0.0063	5.5140	0.0073	0.0627	0.0040	0.0277	1.4237
C	D	0.0114	0.0063	1.7966	-0.0163	0.0391	0.9078	0.0277	0.4639
C	E	0.0064	0.0063	1.0166	-0.0213	0.0341	0.9963	0.0277	0.2625
C	F	0.0197	0.0063	3.1002	-0.0080	0.0474	0.3644	0.0277	0.8005
C	G	0.0328	0.0063	5.1733	0.0051	0.0605	0.0090	0.0277	1.3358
C	H	0.0299	0.0063	4.7129	0.0022	0.0576	0.0249	0.0277	1.2169
D	E	0.0049	0.0063	0.7800	-0.0228	0.0326	0.9993	0.0277	0.2014
D	F	0.0083	0.0063	1.3036	-0.0194	0.0360	0.9834	0.0277	0.3366
D	G	0.0214	0.0063	3.3767	-0.0063	0.0491	0.2577	0.0277	0.8719
D	H	0.0185	0.0063	2.9162	-0.0092	0.0462	0.4457	0.0277	0.7530
E	F	0.0132	0.0063	2.0836	-0.0145	0.0409	0.8199	0.0277	0.5380
E	G	0.0264	0.0063	4.1568	-0.0013	0.0541	0.0744	0.0277	1.0733
E	H	0.0234	0.0063	3.6963	-0.0043	0.0511	0.1620	0.0277	0.9544
F	G	0.0131	0.0063	2.0731	-0.0146	0.0408	0.8237	0.0277	0.5353
F	H	0.0102	0.0063	1.6127	-0.0175	0.0379	0.9463	0.0277	0.4164
G	H	0.0029	0.0063	0.4605	-0.0248	0.0306	1.0000	0.0277	0.1189

Appendix 7: Tukey's HSD for $^{208}Pb/^{206}Pb$

TUKEY HSD/KRAMER			*alpha*	*0.05*	
group	*mean*	*n*	*ss*	*df*	*q-crit*
A	2.0614	15	0.0099		
B	2.1040	15	0.0061		
C	2.1026	15	0.0038		
D	2.1010	15	0.0073		
E	2.1047	15	0.0086		
F	2.0925	15	0.0027		
G	2.0793	15	0.0057		
H	2.0797	15	0.0084		
		120	0.0525	112	4.3686

Q TEST

group 1	*group 2*	*mean*	*std err*	*q-stat*	*lower*	*upper*	*p-value*	*mean-crit*	*Cohen d*
A	B	0.0426	0.0056	7.6218	0.0182	0.0670	<0.0001	0.0244	1.9679
A	C	0.0412	0.0056	7.3595	0.0167	0.0656	<0.0001	0.0244	1.9002
A	D	0.0396	0.0056	7.0841	0.0152	0.0640	0.0001	0.0244	1.8291
A	E	0.0433	0.0056	7.7469	0.0189	0.0677	<0.0001	0.0244	2.0003
A	F	0.0311	0.0056	5.5545	0.0066	0.0555	0.0036	0.0244	1.4342
A	G	0.0179	0.0056	3.1987	-0.0065	0.0423	0.3240	0.0244	0.8259
A	H	0.0183	0.0056	3.2643	-0.0062	0.0427	0.2985	0.0244	0.8428
B	C	0.0015	0.0056	0.2623	-0.0230	0.0259	1.0000	0.0244	0.0677
B	D	0.0030	0.0056	0.5377	-0.0214	0.0274	0.9999	0.0244	0.1388
B	E	0.0007	0.0056	0.1252	-0.0237	0.0251	1.0000	0.0244	0.0323
B	F	0.0116	0.0056	2.0673	-0.0129	0.0360	0.8258	0.0244	0.5338
B	G	0.0247	0.0056	4.4231	0.0003	0.0492	0.0450	0.0244	1.1420
B	H	0.0244	0.0056	4.3575	-0.0001	0.0488	0.0511	0.0244	1.1251
C	D	0.0015	0.0056	0.2754	-0.0229	0.0260	1.0000	0.0244	0.0711
C	E	0.0022	0.0056	0.3875	-0.0223	0.0266	1.0000	0.0244	0.1000
C	F	0.0101	0.0056	1.8050	-0.0143	0.0345	0.9057	0.0244	0.4660
C	G	0.0233	0.0056	4.1608	-0.0012	0.0477	0.0739	0.0244	1.0743
C	H	0.0229	0.0056	4.0952	-0.0015	0.0473	0.0832	0.0244	1.0574
D	E	0.0037	0.0056	0.6629	-0.0207	0.0281	0.9998	0.0244	0.1712
D	F	0.0086	0.0056	1.5296	-0.0159	0.0330	0.9594	0.0244	0.3949
D	G	0.0217	0.0056	3.8854	-0.0027	0.0462	0.1195	0.0244	1.0032
D	H	0.0214	0.0056	3.8198	-0.0031	0.0458	0.1332	0.0244	0.9863
E	F	0.0123	0.0056	2.1925	-0.0122	0.0367	0.7783	0.0244	0.5661
E	G	0.0254	0.0056	4.5483	0.0010	0.0499	0.0350	0.0244	1.1744
E	H	0.0251	0.0056	4.4827	0.0006	0.0495	0.0400	0.0244	1.1574
F	G	0.0132	0.0056	2.3558	-0.0113	0.0376	0.7090	0.0244	0.6083
F	H	0.0128	0.0056	2.2902	-0.0116	0.0372	0.7377	0.0244	0.5913
G	H	0.0004	0.0056	0.0656	-0.0241	0.0248	1.0000	0.0244	0.0169