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Apportionment of sources of industrial contamination by isotope composition analysis - case study in Ostrava, Czech Republic

Diploma thesis

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DIPLOMA THESIS ASSIGNMENT

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Thesis title

Identification of sources of Pb in soil by isotope composition analysis – case study in Ostrava, Czech Republic

Objectives of thesis

The isotope composition of metals in the environment reflects the mixing of their sources, and source apportionment can be quantified in cases where all potential sources are characterized and have specific ratios. Metal isotope studies thus provide a convenient approach for studying and tracing the sources of pollution in different environmental compartments.

The aim of the study is to determine Pb concentration and Pb isotope composition in soil profiles from different sampling site in Ostrava (Czech Republic) and evaluate the input of each source to the environment.

Methodology

Soil profiles from 6 sites in the Ostrava region will be decomposed in a mixture of acid (HNO₃, HCl and HF) and analysed for metal(loid) (Cr, Cd, Ni, Zn, Pb, As, Cu) content. Subsequently the upper soil horizons will be analysed for Pb isotope composition in order to identify sources of Pb in the local environment.

The proposed extent of the thesis

60

Keywords

soil, industrial contamination, lead, isotopes

Recommended information sources

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Declaration

I **Daniel C. Anyamene**, hereby declare that I'm the author of this diploma thesis. The content herein was independently compiled by me from different sources that are relevant to the subject of this research in addition to my own view of the research outcome. I have listed all data sources, literature and publications from which I acquired the necessary information for the completion of this study.

Signature and date: Daniel C. Anyamene 18/04/2017.

Abstract

Industrial contamination in Ostrava region of Czech Republic has left enormous pollution related to the disposal site for mining and smelting waste (tailings, slags) and to the continuous deposition of stack particulates containing metals in the environment. Identifying the sources and pathways of contaminant like Pb is important because its toxicity is known to have adverse effects on human health. Previous studies showed that soils in specific sites around the region had elevated amount of Hg, Cd, Pb, Zn, As and Cu but concentration data alone might not be an efficient tool in ascertaining the main input source of these pollutant. This study aims to compare the isotopic and trace metal concentration data of similar studies in conjunction with metal concentration of selected soil samples around Ostrava in assessing the input of each potential source of contaminant to the environment while taking into account the role of soil mineral and organic matter content in contaminants distribution within the respective soil profiles.

Keywords: metals, industrial contamination, source, isotopes, Ostrava

Shrnutí

Průmyslová kontaminace Ostravského regionu v České Republice za sebou nechala obrovské znečištění související se skládkami pro důlní a výrobní odpad (těžební, škváry) a nepřetržité emise částic obsahujících kovy v životním prostředí. Rozpoznávání původu a cest škodlivin jako Pb je důležité kvůli jeho toxicitě a negativnímu vlivu na lidské zdraví. Dřívější studie ukázaly, že půda v určitých místech regionu měla vysoký obsah Hg, Cd, Pb, Zn, As a Cu, ale koncentrační analýzy samotné nejsou účinný nástroj pro zjištění hlavních vstupních zdrojů těchto škodlivin. Tato studie se zaměřuje na porovnání koncentračních a izotopových dat o kovech, zejména pak Pb, z podobných studií a koncentrací kovů u vybraných půdních vzorků kolem Ostravy a zjištěných v rámci této studie. Je zhodnocen každý potenciální zdroj kovů, navíc s přihlédnutím k funkci půdních minerálů a organické hmoty na distribuci a mobilitu těchto škodlivých látek uvnitř příslušných půdních vrstev.

Klíčová slova: kovy, průmyslová kontaminace, zdroje znečištění, izotopy, Ostrava

Table of contents

1. Introduction.....	1
2. Aims of the study.....	2
3. Literature review.....	3
3.1. Causes of industrial contamination.....	3-4
3.2. Industrial contaminants in different environmental media.....	4-9
3.3. Bioavailability, speciation and mobility of Pb in the environment.....	9-13
3.4. Techniques of Isotope fingerprinting.....	13-15
4. Research Methods	16
4.1. Sampling area	16-17
4.2. Sample collection.....	17-18
5. Results	19-27
6. Discussion	28-30
Conclusions.....	31
Sources.....	32-41

1. Introduction

According to Song et al. (2015), urban dust and upper soil horizons are good designators of the spreading of metals and metalloids from human activities. Both are mobile and can be easily suspended by wind or transported in storm water runoff. Dangerous contaminants buildup in soils mainly due to atmospheric deposition from sundry sources and the most significant emanates from industrial activities (mining, chemical, metallurgy, building and electronics industry), fuel burning and transport. Consequently, this fact leads to various distributions of metals in the urban environment as a result of the rapid growth of industries (Madarang and Kang, 2014).

Human contact to metal pollutants through inhalation, direct ingestion and skin contact can negatively affect human health and most metals will harm human internal organs if the safe dose levels are exceeded but this is particularly the case for some poisonous metals such as lead (Pb), chromium (Cr), and cadmium (Cd), which are often referred to as “chemical time explosives”. Detecting the origins of metals in the contaminated environment is important to understanding their behavior and to control the dangers of exposure (Zibret, 2012). Origins of metals in urban environments are numerous and often difficult to ascertain and statistical analysis were commonly used to identify the sources and pathways of a metal, these methods usually provide only general evidence on the origins but isotopic fingerprinting which is centered on the ratios of stable and radiogenic isotopes using spectrometry is a more in-depth technique used to designate the sources of various pollutants. Stable and radiogenic isotopes of Zn, Ni, Cu, Pb, and other metals have often been employed to designate the origins of contaminants (Gao et al., 2013).

Certain research have determined Pb isotope (^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb) composition for various environmental means including organisms, atmospheric aerosol, soil, urban dust, sediment (Hu et al., 2015b). At the same time, the metal isotope composition of pollution sources such as coal burning, mining, industrial emissions, vehicle exhaust were also examined (Hu et al., 2014).

2. Aims of study

To analyze the metal contents of contaminants and their spatial distributions in the environment and apportion contaminants contribution from different industrial-related sources by comparing it with similar studies that employed metal isotope ratios using soil samples from heavily industrialized Ostrava region of Czech Republic. This will give environmental investigators a better understanding of how to tackle continuous occurrence or in employing remediation technique that is deemed fit for the particular metal contaminant source

3. Literature review

Most of the environmental pollution can be traced back to industries of some kind. As a matter of fact, the issue of industrial pollution has taken on grave significance for agencies trying to combat against environmental degradation. Nations facing rapid growth of such industries are finding it to be a grave problem which has to be brought under control immediately

3.1. Causes of Industrial Contamination

3.1.1. Lack of effective Policies to Control Pollution

Lack of effective policies and poor enforcement drive allowed many industries to bypass laws made by pollution control board which results into massive scale pollution that affects the lives of many people.

3.1.2. Rapid Industrial Growth

In most industrial townships, unplanned growth took place wherein those companies ignored rules and pollutes the environment with both air and soil contaminants.

3.1.3. Use of Outdated Technologies

Some industries still use old technologies to produce products that generate large amount of waste. To evade high cost and expenditure, many companies still make use of these techniques in producing high end products.

3.1.4. Presence of Large Number of Small Scale Industries

Small scale industries and factories that don't have enough capital and still rely on government grants to run their day-to-day businesses will most likely escape environment regulations by improperly disposing their regular wastes that are toxic.

3.2 Industrial contaminants in different environmental media

Though the main focus of this research is on contaminants in soil, it will be incomplete to skip the discussion of the fate of these contaminants in other environmental media which are directly or indirectly linked to soil.

3.2.1. Soil

Soils are contaminated by metals and metalloids through emissions from the industrial areas, mine tailings, disposal of high metal wastes, paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, burning of coal residues, spillage of petrochemicals, and atmospheric deposition (Zhang et al., 2010). Metals and metalloids most typically found at polluted areas are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) (GWRTAC USA, 1997) and soils are the most important deposits for these contaminants. There are contrasting difference of metals when compared to organic contaminants, which are oxidized to carbon (IV) oxide by microbial action, most metal(loid)s do not undergo microbial or chemical breakdown (Kirpichtchikova et al., 2006), and their whole concentration in soils remains for a long time after introduction (Adriano, 2003). Variations in their chemical forms (speciation) and bioavailability are nevertheless possible.

In the terrestrial ecosystem, soils play an important role in element environmental cycling and accumulate metals in amount orders of degree higher than in water and air (Cottenie and Verloo, 1984). Overall metal content in soils is a valuable evidence for several geochemical applications but frequently, the speciation (bioavailability) of these metals is an added interest in terms of what is biologically extractable (Cottenie et al. 1980). Speciation is the form or phase in which an element occurs (Tack and Verloo, 1995) and is basically a function of the mineralogy and chemistry of soil (Tessier et al., 1979). In terms of bioavailability, sundry species of metals like Pb, Cu, Mn, Cr are more biologically accessible in the ecosystem, bioavailability and the mobility of metals are also linked to each other. Greater concentration of mobile poisonous metals in the soil

column does upsurges the possibility for plant uptake, and animal/human consumption (Ratuzny et al., 2009)

Metals play a role in biogeochemical cycles and are not always fixed in soils; consequently, assessment of their circulation in soils is a key topic in many environmental studies (Salim et al. 1993). Metals are involved in soil minerals as well as bound to different stages of soil particles by ranges of mechanisms, mainly absorption, ion exchange, co-precipitation and complexation. Besides, soil properties for example contents of organic matter, carbonates, oxides as well as soil structure and profile development affects metal movement (Kabata and Pendias, 2001). The evidence of the binding of metals with the different soil phases and constituents is of important interest to determine the links with other living and non-living elements of the environment (Hirner, 1992). However, Cabral and Lefebvre (1998) showed that metal speciation is a more intricate tasks that assessment of total metal contents.

It is extensively documented that to determine the environmental effect of soil contamination, the assessment of the basic physico-chemical characteristics in addition to metal speciation will give more evidence about the possibility for discharge of contaminants and additional derived processes of movement and toxicity (Usero et al., 1998). Hence, in geo-environmental studies of risk determination, chemical segregation among the numerous geochemical phases is more helpful than measurements of total metals contents (Quevauviller et al., 1996). Among the processes to ascertain element speciation, those based on sequential extraction are the most commonly used (Rauret et al., 1988).

Preceding studies in Ostrava presented row concentration data of Hg, Cd, Pb, Zn, Cu, V and Mn in soil and pH (Table 1, Yaroshevsky, 2006). The soil samples were taken in the industrial site of the metallurgical company and from the middle of Ostrava with high traffic concentration; the data showed wide arrays connected to alterations in different contamination degrees of sampling sites.

The determination of metal pollution by means of specific indexes confirmed that urban soils of Ostrava are predominantly moderate to high pollution by Hg, Cd, Pb, Zn, Cu, V

and Mn. Major Component Analysis had confirmed the human sources of metals except manganese, which can originate also from non-anthropogenic sources as a high level contribution factor. This study clearly points out the immediate need to make a concerted effort to tame industrial emissions and to rehabilitate heavily contaminated urban soils alongside with other monitoring of metal levels in urban soils.

According to Table 1 the arithmetic mean and median data of metals have cumulative character in the order Hg < Cd < Cu < Pb < V < Zn < Mn. The average content of metals in the Earth crust was surpassed in all instances of ascertained level

Table 1.

Descriptive statistics of Hg, Cd, Pb, Zn, Cu, V, Mn and V in soil samples of Ostrava. N=153. Unit: mg/kg (Yaroshevsky, 2006).

Statistical parameters	Hg	Cd	Pb	Zn	Cu	V	Mn	pH
Minimum	0.08	0.05	11.09	60.91	9.76	43.46	263.72	6.93
Maximum	0.25	0.43	174.03	393.08	98.83	181.80	2368.31	7.86

Consequently, high concentration signals the anthropogenic source of the metals contamination in study area, the metallurgical industry and urban dense traffic are common feature for this area. To be precise, Pb and Cu seem to be dominantly associated with traffic, coal combustion (Van Bohemen and Van de Laak, 2003). Other origins of these metals in urban environments can be waste incinerators, pipes, cables, paints, and colors. The soils also accumulate Cu, Pb, Cd, and Hg from atmospheric deposition, irrigation water, applications of fertilizers, pesticides, manures, sewage sludge which can be applied in parks, grass, gardens (Wong et al., 2006). Generally speaking, the industrial origins of metal pollution in Ostrava are majorly from plumes of coal power plants, slags and fly ash of mines and metal smelting plants.

3.2.2. Atmosphere

Dust particles in the air can have a significant consequence on human health. The degree of their influence is linked not only with particle size dispersal but also with the tendency to absorb poisonous and carcinogenic compounds (Chung et al., 2008). Particulate matter (PM) is one of the most important transport conduits of contaminants in the atmosphere. The fundamental origins of PM are anthropogenic and sources can be defined as;

- i. long-distance origins (e.g., particles transported by wind)
- ii. short-distance origins (e.g., re-suspension of road deposited sediments)
- iii. traffic linked sources and other general origins with low impact

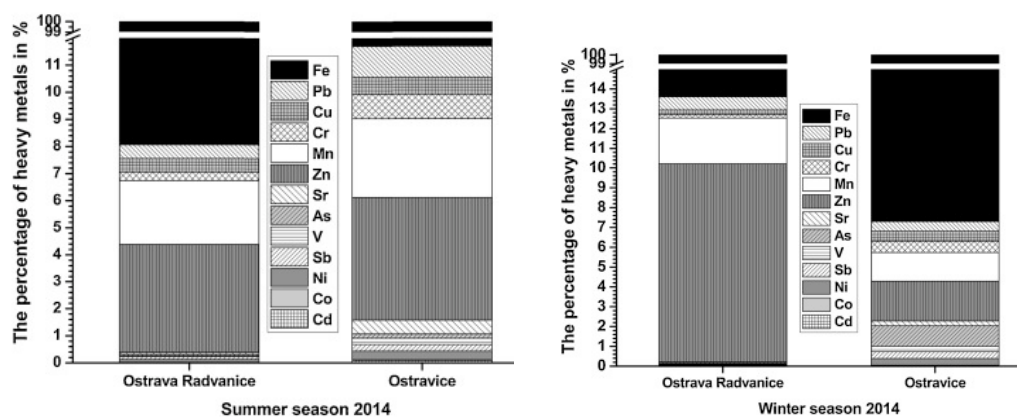
PM can also be grouped according to size into; super coarse ($>10\ \mu\text{m}$), coarse (2.5–10 μm), belonging to the accumulation mode (0.1–2.5 μm), ultrafine Aitken mode (10–100 nm) and nucleation mode (15–40 nm) (Hsieh et al., 2009). The coarse particles are formed primarily by re-suspension of dust, demolition and construction works, burnings in local heaters and biogenic origins. Ultrafine particles originate mostly in combustion high-temperature processes and atmospheric reactions (Amann et al., 2006). Particles in the atmosphere are formed by secondary minerals through physical and chemical reactions (gypsum, halite and lecontite) (Song et al., 2014). Particles from metallurgy contain minerals formed during metallurgical processes and minerals used as input raw materials for metallurgical processes (hematite, magnetite), and components from metallurgical manufacture (graphite, akermanite, mayenite, spinel) (Journet et al., 2014).

Metals are present in negligible amount in fossil fuels and biomass and they also can be present in PM. The processing of mineral resources at high temperatures, such as the burning of coal and oils in electric power stations, industrial plants, ore roasting and smelting of non-ferrous metal, melting operations in ferrous foundries, refuse incineration and kiln operations in cement plants results in the release of unstable compounds into the atmosphere. During burning, unstable species in the coal vaporize from the boiler and re-condense as sub-micrometer aerosol particles or on the exteriors of ash particles as the flue gas cools in the convective units. Among the unstable

pollutants, arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg) are widely studied because of the health concern related with them. The emissions of these elements by the above processes changes their biogeochemical cycles in the entire human surroundings and to determine these perturbations, wide emission records are essential. In the last years, the mounting interest in this field has been documented in the literature, emission strengths of As, Cd, Pb and Hg was assessed by several international and national groups and agencies. The concentrations of As, Cd and Pb increase noticeably with decreasing particle size from bottom ash through fly ash from control devices to stack fly ash (stack dust) emitted into the atmosphere and seemingly, more than 90% of mercury in coal is released as vapor (Pacyna, 1980). Combustion temperature in the boiler is one of the important factors affecting the extents of metals released, the higher the temperature in a boiler, the larger the releases of unstable elements. Large amounts of As, Cd and Pb are emitted into the atmosphere from usually fired boiler systems burning fuel at temperatures higher than 1650 K.

Research Outcomes from earlier studies show that the total amount of dust particles (PM₁₀) during summer at Ostrava region varied between 11.5 and 30.2 µg/m³ depending on the sampling site (Barbora et al. 2015). The two figures below show percentages of metals in the sum of all evaluated metals.

Figure 1 Varying concentration of metals in Ostrava localities during different seasons of the year in PM₁₀ (Barbora et al., 2015)



Percentages of metals in the sum of metals, summer season.

Percentages of metals in the sum of metals, winter season.

3.2.3. Water

Pollution of aquatic environment by inorganic chemicals has been deliberated as a major threat to the aquatic organisms as well as fishes. The agricultural drainage water containing pesticides, fertilizers and discharges of industrial activities supply the water bodies and sediment with enormous amounts of inorganic anions and metals (ECDG, 2002). Majority inorganic contaminants in water quickly change from aqueous phase to solid phase under physical precipitation and chemical adsorption and are deposited in river's sediment. Nevertheless they can be released again if environmental conditions changes triggering secondary pollution (Zhou et al., 2005)

Metal ions can be assimilated into food chains and bio-accumulates in aquatic organisms to a level that affects their physiological state. Of the effective pollutants are metals which have drastic hostile environmental effect on all organisms, however trace metals such as Zn, Cu and Fe play a biochemical role in the life processes of all aquatic plants and animals; therefore they are still necessary in the aquatic environment in little amounts. Study of metals contents in Odra River, of which 84.9% lies in Poland, 10.4% in Germany and 4.7% in the Czech Republic, showed high levels of Zn, Pb, Cr, Cu and other metals. The environmental problems at the Odra River are initiated by geology and geomorphology, terrain shape, agricultural and industrial activity and localization of major industrial centers, which are: mining (coal, copper), metallurgy (non-ferrous), electroplating plants, pigments production, pesticides, anticorrosive materials, and **power** industry (Adamiec and Rybicka, 2002). Overall, there are about **1700 sources** of pollutions at the Odra River catchment area, out of which 700 considerably influence the environments of the river system.

3.3. Bioavailability, speciation and mobility of Pb in the environment

Several studies on contaminated soils propose that physicochemical soil properties such as pH and clay and organic matter content are the main influences controlling metal toxicity and bioavailability (Janssen et al. 1997). A wide array of analytical instrumentation allows highly precise and sensitive determination of soil sample composition, which is essential for regulatory compliance monitoring as well as for

understanding the origins of pollution and the method that can be employed for remediation. Lately, there has been a shift towards the assessment of “environmentally accepted endpoints”, an approach based on the understanding that interactions of pollutants with the soil matrix may affect the risk of these contaminants. However, while it is commonly accepted that the overall concentration of metals does not automatically reflect its availability to living organisms, the favored methodologies for determining the bioavailability of metals in the soil have always been debatable (Hamelink et al. 1994). In general, two approaches have been recognized:

1. Extraction processes centered upon the assumption that the leached fraction is considered available. The sum of released metal is studied as a function of the mode of soil extraction: simple aqueous washes, acids, bases, or organic solvents. These and related techniques provide what may be called “bio-accessibility” data, but the final assay is always chemical rather than biological. The underlying statement of this approach is that the less accessible the metal, the tougher would be the conditions necessary to remove it from the soil. In an effort to obtain a direct approximation of the metals released within a human body, the proposed extraction techniques are commonly based on saliva and gastric fluids (Ruby et al. 1999).

2. Bioassays were designed to quantify the result of the tested sample on a test organism after a standard exposure procedure. Such tests attempt to differentiate between the bioavailable fraction of a compound and its overall concentration. Expectedly, the latter procedure often contains biologically inert, unavailable forms of the target compound (Ivask et al. 2004). This phenomenon, often of concern when remediation endpoints to be ascertained carry particular significance for metal contamination

Studies using recombinant bacteria as tools for investigating the bioavailability of Pb in soils have revealed that the presence of carbonate and quartz makes roughly half of the desorbed (potentially available) Pb unavailable to microorganisms, while kaolinite makes almost 90% of the dissolved Pb unavailable. Because of their vast adsorption capacity, Fe-oxide and organic matter are capable of taking up enormous amounts of Pb and do not release any detectable Pb to solution, lessening the bioavailability of Pb (Sauve 2002). It is also shown that the bioavailability of Pb depends on the type of the

soil and the components it comprises of. For example, arid and semi-arid soils which comprises of large amounts of carbonates and have little organic matter will affect differently the solubility of Pb and hence its bioavailability when compared with temperate soils which usually lack pedogenic carbonate but have large extents of organic matter.

Although CaCO_3 , quartz, and kaolinite desorb significant amounts of Pb, studied polluted soils (150–300 ppm Pb), which are known to contain these three minerals did not release any measurable Pb. It is rational to believe that Fe-oxide and organic matter, that are present in small amounts in these soils have important role in determining Pb bioavailability (Teutsch et al. 2001). The ratio amongst different soil components can determine the extent of Pb pollution which is still unavailable to microorganisms. According to the study results for instance, 1% of organic matter in the soil can complex up to 200 ppm Pb, thus turning it to be unavailable. Bioavailability attentions are of particular concern with respect to remediation of polluted soils because of their great adsorption capacity and their ability to serve as a sink for metals (Heinz et al. 2004). While soils might be considered as polluted based on their total toxic metal loads, cleanup procedure will necessitate bioavailability assays to provide additional evidence that will affect the goals and hence the cost of the remediation efforts by proving that part or even all of the metals in the soil are not available. The study validates the close link between soil composition (i.e., the presence or absence of certain components) and the bioavailability of Pb with a focus on microorganism which might however be different from bioavailability within the digestive system of humans (Heinz et al. 2004).

As soils are significant sinks for Pb, they can also release them into the ecosystem. It is therefore important to comprehend the content, chemistry and geology of Pb in soil as well as the chemical forms. The assessment of specific chemical species or binding forms is difficult and often virtually impossible and for this reason, sequential extraction process are typically employed because they provide information about the fractionation of metals in the various lattices of the solid sample, which is a good compromise method that gives evidence on the environmental contamination. Polluted soils have always been major environmental problems and therefore are subjected to detailed risk assessment

and management studies. This assessment gives a relative distribution Pb fraction in the soluble (bioavailable) and insoluble (non-bioavailable form) using spectroscopy to assess their potential environmental influences (Scancar et al., 2000)

Chemical speciation usually controls food chain transport and risk from toxic metals in the environment and in the case of Pb-rich urban soils and dusts, chemical speciation, particle size, and human nutritional factors appear to each be very significant in Pb exposure risk. Furthermore, the ultimate question of speciation is the chemical form of Pb in the duodenum of humans when contaminated soil is included in the diet with meals or between meals (Chaney, 1988).

Prior to phasing out of Pb gasoline in 2000, the major origin of Pb in the environment is from its use as an antiknock additive to petrol and research has repeatedly shown that these small Pb-rich particles reaching the surface of a soil profile mostly remain on or near the surface for a long period. Humans often mix these soils to support growth of plants or cover old contaminated soil with new using amendments as soda or potting soil. Additionally, soil movement by earthworms through macro pores allows mixing of surface soil and transport Pb to deeper strata in the horizon, affecting the Pb concentration at different soil depths (Nriagu and Pacyna, 1988).

Perhaps the most significant aspect of mobility of soil Pb is its ability to be transported into homes and become part of house dust. It is clear from the strong association of soil Pb concentration and house dust Pb concentration in several large surveys that soil Pb contributes to house dust Pb. This is particularly significant because research has shown that smaller dust particles are more easily transferred to the hands and tend to remain on hands longer and normally, particles remaining on hands are <50-100 microns in diameter. Hence higher concentration of Pb in smaller soil/dust particles increases the potential risk of soil Pb, the smaller particle size and greater Pb concentration in the smaller particles both increase the bioavailability of Pb in dust and soil (Duggan *et al.*, 1985). Scientist have employed four general approach to characterize the chemical species of Pb in soils, dusts, and street dusts: (1) Identify crystalline Pb compounds using X-ray diffraction; 2) Determine which compound controls the solubility of Pb in soil solution; 3) Extract soils with different reagents and compare results with known

compounds added to soils; and 4) Add compounds to soil and see if they persist or are altered to other chemical species. The form in which Pb is available depends on a variety of soil properties, such as: the organic matter content, pH, cation exchange capacity, and the activity of microorganisms. These properties of the soil are thus important in the processes of sorption, complexation and immobilization of Pb, and its bioavailability (Park et al., 2011).

It is defined that the major form of Pb in the natural state in soil samples is PbS. During weathering PbS gradually oxidize and have the ability to form carbonates and also to be incorporated in clay minerals, in Fe and Mn oxides and in organic matter. (Pendias et al., 1986).

3.4. Techniques of Isotope Fingerprinting

Determination of Pb isotope ratios in geological samples may be carried out using a variety of analytical techniques like spectroscopy and in past decade or so, inductively-coupled plasma mass spectrometry (ICP-MS) has established itself as an exceptional method for determination of Pb isotope abundances. Measurement of Pb isotope ratios with ICP-MS has been shown to be feasible on all types of environmental samples these can vary from atmospheric aerosols, gasoline, fresh, saline waters and digested samples. If the ICP-MS is used in conjunction with a laser probe, the determination of Pb isotope ratios can also be carried out on solid samples, permitting in situ determination of Pb isotope systematics in specific mineral grains thus further reducing preparation and analysis time (Feng et al. 1993). Application of ICP-MS techniques to Pb isotope determinations is helpful in studies of mineral resources and metallogeny in the sense that rapid reliable analysis of samples is permitted at reasonably low cost, the method therefore offers important promise for the future. In this paper, the application of inductively-coupled plasma mass spectrometry (ICP-MS) to direct determination of Pb isotope ratios in aqueous or digested soil samples is investigated.

Pb has four natural isotopes: ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb , and the abundance differences of the last three isotopes is as a result of the radioactive decays of ^{238}U , ^{235}U , and ^{232}Th over geological time as shown in Table 2. The least abundant and the only

non-radiogenic Pb isotope, ^{204}Pb , have stayed essentially constant at 1.4% in abundance, whereas the abundances of ^{207}Pb , ^{206}Pb , and ^{208}Pb co-vary intensely and depend on when the ore was formed. As a result, the Pb isotopic composition in different types of Pb-containing minerals is subjected a number of processes, including radioactive decay of U and Th to Pb, the relative proportion of U–Th–Pb in the system, and mixing of Pb from different origins (Fature, 1986).

Table 2: Decay process of ^{238}U , ^{235}U , ^{232}Th and their half-lives (Fature, 1986)

Reaction	Decay constant (year^{-1})	Half-life (years)
$^{238}\text{U} = ^{206}\text{Pb} + 8^4\text{He} + 6\beta^-$	1.55125×10^{-10}	4.468×10^9
$^{235}\text{U} = ^{207}\text{Pb} + 7^4\text{He} + 4\beta^-$	9.8485×10^{-10}	7.038×10^8
$^{232}\text{Th} = ^{208}\text{Pb} + 6^4\text{He} + 4\beta^-$	4.9475×10^{-11}	1.4008×10^{10}

Several different types of ore deposits and anthropogenic sources of Pb have specific isotope signatures. The facts that U, Th and Pb have different geochemical behaviors, and that Pb isotopic composition of any material is the composite of three autonomous decay chains create the potential for great variability in Pb isotopic composition (Table 2). The typical variations of Pb isotope ratios found in natural materials are: 14–30 for $^{206}\text{Pb}/^{204}\text{Pb}$, 15–17 for $^{207}\text{Pb}/^{204}\text{Pb}$, and 35–50 for $^{208}\text{Pb}/^{204}\text{Pb}$; however values outside of these ranges are not unusual (Doe, 1970). The Pb from each ore carries an exclusive isotopic identity, and Table 3 reviews the Pb isotopic compositions of Chinese Pb ore deposits, coals, and soils.

Table 3. Relative abundance variations of Pb stable isotopes in terrestrial materials (Rosman and Taylor, 1998).

Nuclide	Lower level for isotopic abundance (%)	Upper level for isotopic abundance (%)
²⁰⁴ Pb	1.04	1.65
²⁰⁶ Pb	20.84	27.48
²⁰⁷ Pb	17.62	23.65
²⁰⁸ Pb	51.28	56.21

Isotopic fractionation in Pb does not occur in industrial and environmental processes (Amelin and Neymark, 1998). The Pb isotopic composition of an ore body or anthropogenic origin does not get altered during the conversion to a secondary weathering environment except there is mixing with secondary Pb sources. Apparent Pb isotope fractionation can occur over geological time as a result of parent isotope unbalance between Th and U, rather than daughter Pb isotope fractionation (Amelin and Neymark, 1998). Published data for Fe–Mn crusts show no indication for diagenetic restructuring of Pb isotopes (Reynolds et al., 1999). The low relative atomic weight variations among Pb isotopes, and the heavy and biologically toxic nature of this element, result in negligible mass-dependent Pb isotope fractionation in natural physical, chemical, and biological manners (Zhu et al., 2000). Industrial processes seemingly do not change the isotopic composition of Pb either, and Pb retains the isotopic composition of the ore from which it originates after being released into the environment (Ault et al., 1970). As a result, Pb isotope ratios only differ according to their geological origins and the isotopic compositions determined in the samples reflect those of the Pb origins or results of mixing if several Pb sources exist. Due to the advances in analytical methods in the last two decades, analysis of metal isotope composition are used for identifying the metal origin in the environment and for apportioning contribution of different sources (Gelinas and Schmit, 1997).

4. Research Methods

4.1. Sampling area

4.1.1. Brief description

The study area is located in the Moravia Silesian Region of Northeast Czech Republic. The city of Ostrava is dominated by chemistry, metallurgy, building and electronics industries. The soils around the area receive Pb majorly from atmospheric deposition from coal powered plant, metal smelters, mining and other scattered diffuse pollution sources like incinerators and from local heating using low quality fuel (Dolezalova et al., 2014). This locality has been deliberated to be one of the regions with the worst air quality, anthropogenic pollution in this area primarily originates from the heavy steel and coal industries, also from the dense transport structure in the region (Mikuska et al., 2015).

The mining of black coal in Přívoz began in the 18th century and ended as a result of a decreed government contraction program on 30 June 1994. The mining of black coal from the Ostrava Mining Basin (OMB) and Jeremenko area in the 19th and 20th centuries processed a total of 449,995,239 tons with the highest coal production occurring in the 1980s, having a production of approximately 25×10^6 tons of coal. Mining took place at a depth of approx. 50 to 1,300 m beneath the surface and the total mining area was 92.91 km², three locations presently have a total of 8 functional mines and 63 closed mines. Additionally, several stationary industrial origins of contaminants (e.g., metals, particulate matter, nitrogen oxides, sulphur dioxide, and benzo (a) pyrene) still exist directly in the city or in the close surroundings (Novak et al., 2003)

4.1.2. Climatic conditions

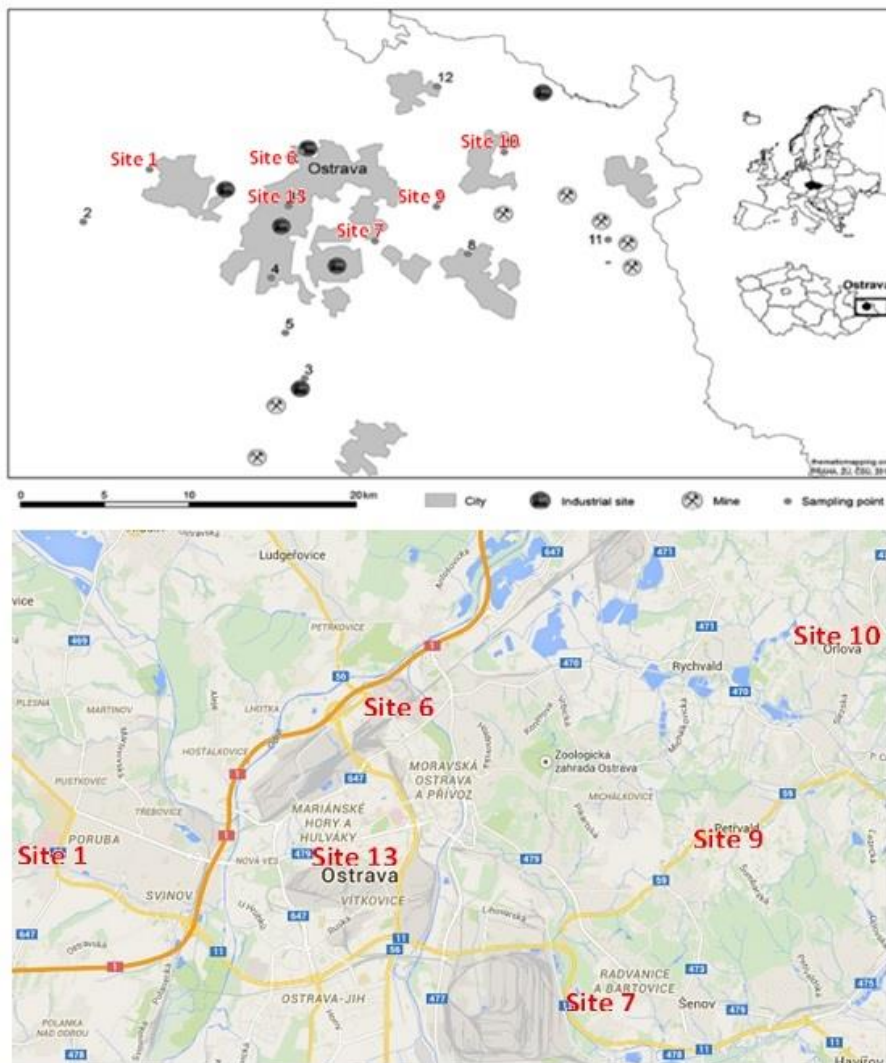
In Ostrava, the climate is warm and temperate. Ostrava is a city with a significant rainfall even in the driest month with an average annual temperature around 8.6 °C. In a year, the average rainfall is 690 mm with 28mm in January and 100mm in June which

implies that the former period of the year has more atmospheric dispersion tendencies than the latter (Climate-data.org)

4.2 Sample collection and preparation

The soil profiles from 6 sites were collected during summer 2016, sectioned into 3 or 4 parts according to the natural development and visible changes within the profile down to the mineral horizon and placed in labeled plastic bags for transport to the laboratory. The sites (see fig.2) were chosen based to the predominant wind direction and position with respect to the main industries in the region.

Fig. 2 Sample collection sites (Francova et al. 2016; Mapy.cz)



Samples were sun-dried and lightly disaggregated and dry-sieved through a 2 mm square-hole stainless steel sieve. Approximately 250 mg of soil was weighed. For coherency each sample was weighed in triplicates and transferred to a Teflon tube for the digestion.

9ml of HNO₃, 1ml of HF and 3ml of HCl was added to soil sample in each Teflon tube and transferred to the microwave digestion chamber. Decomposition was done using EPA method 3051A. After digestion, the mixture in each Teflon tube was transferred to savillex vessel and placed on a hot plate (100°C) overnight until the liquid portion completely evaporates. The residue was diluted with 20ml of H₂O, filtered using syringe filters and stored in plastic bottles for metal concentration analysis.

Fig. 3 Graph showing sample digestion in microwave oven using EPA method 3051A

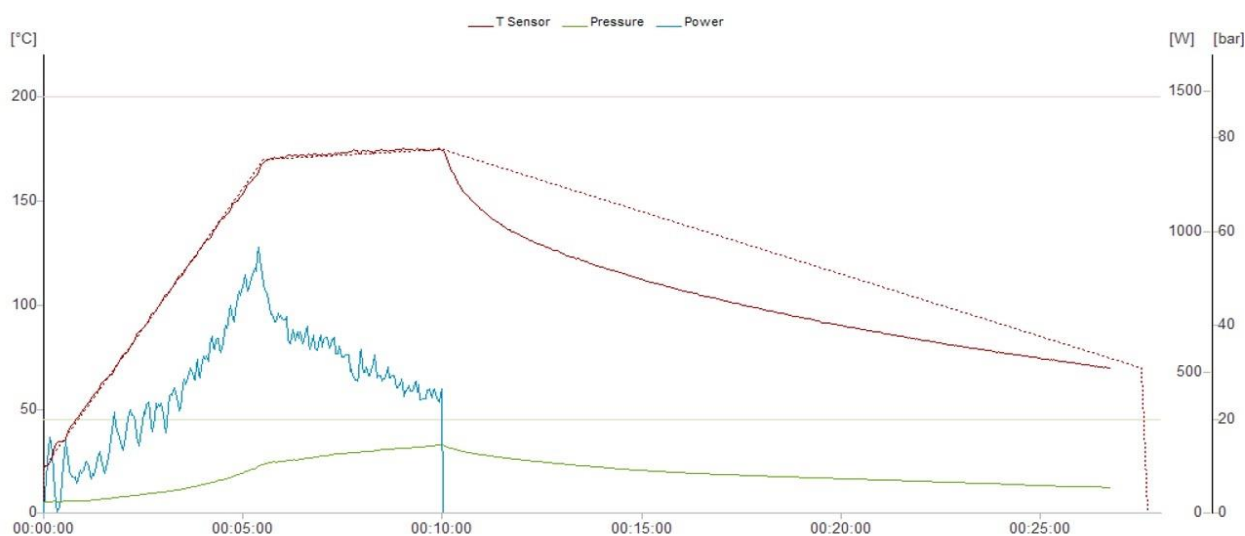


Fig. 4: Graph showing sample digestion in oven using EPA method 3051A

Max internal temperature: 176°C, max pressure: 14.5 bar, max power: 944W.

EPA method 3051A microwave extraction method is aimed at emulating extraction using conventional heating with nitric acid (HNO₃), or alternatively, nitric acid and hydrochloric acid (HCl), according to EPA Method 200.2 and Method 3050 and is not intended to accomplish complete digestion of the sample (USEPA, 2007).

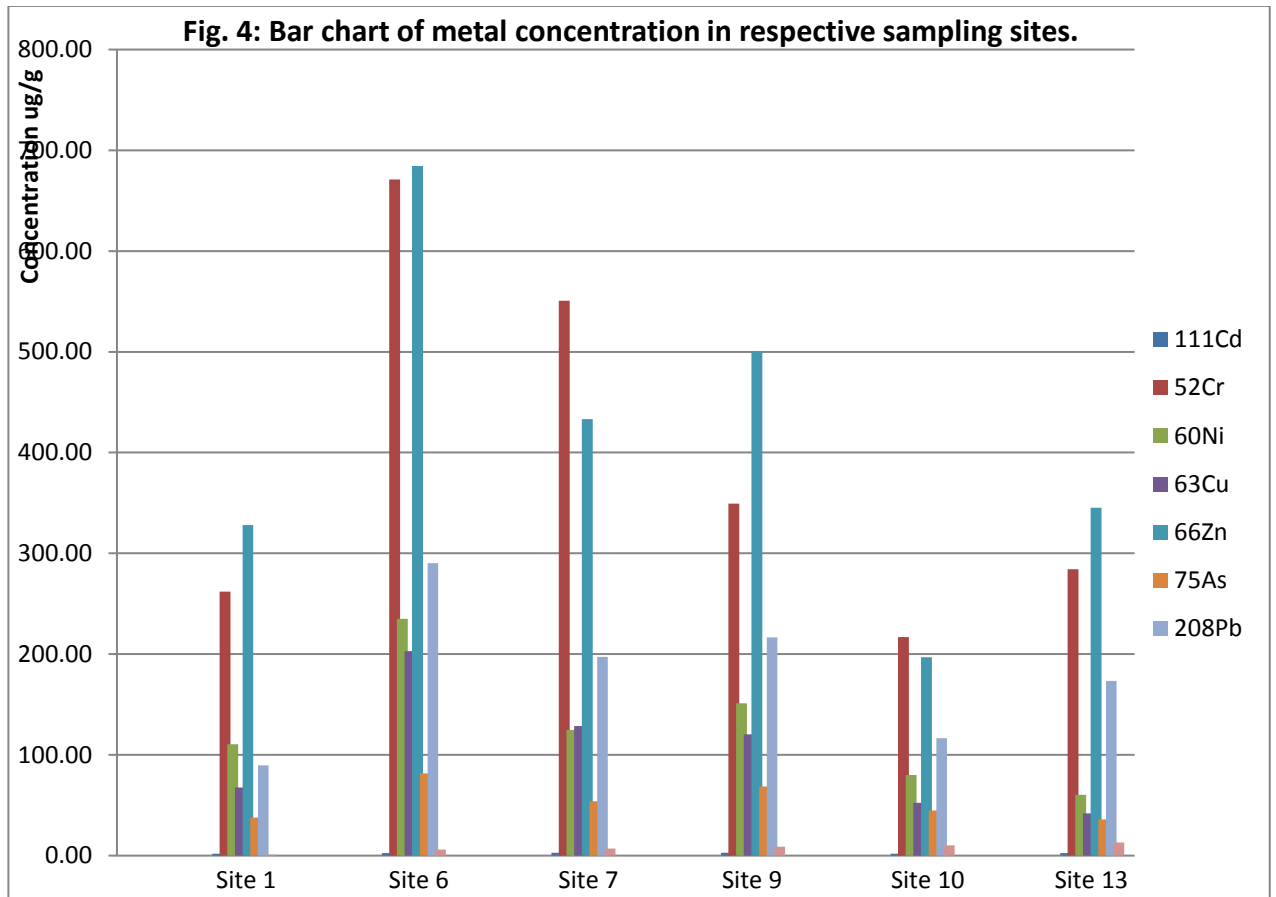
5. Results

The average concentration of 7 metal(loid)s in each soil samples are summarized in Table 4. Metal contents ranged from 1.92 $\mu\text{g/g}$ in (Cd in site 10) to 671.14 $\mu\text{g/g}$ (Cr in site 6) owing to various enrichments in the natural environment and the different emission intensities from human activities.

Table 4: Average metal concentration in soil ($\mu\text{g/g}$)

Sites	Cd	Cr	Ni	Cu	Zn	As	Pb
1	2.01	262.06	110.59	67.59	327.93	37.91	89.45
6	2.44	671.14	234.89	202.82	684.82	81.45	290.19
7	2.84	550.80	124.79	128.54	433.17	53.96	197.26
9	2.96	349.49	151.26	120.29	500.12	68.51	216.67
10	1.92	216.96	80.03	52.38	196.91	44.64	116.41
13	2.40	284.25	60.38	41.96	345.06	35.99	173.54

From the result in Table 4, corresponding highest and lowest concentration is; site 9 and 10 for Cd, site 7 and 10 for Cr, site 6 and 13 for Ni, site 6 and 13 for Cu, site 6 and 10 for Zn, site 6 and 13 for As, site 6 and 1 for Pb respectively. This data is also presented on a bar chart as shown in fig. 4.



The bar chart in fig. 5 further designates that site 6 is probably most contaminated with highest overall metal concentration and site 10 as the least and since this research is primarily focused on Pb contamination, it will be necessary to present a more comprehensive data of Pb concentration in all sample sites with respect to depth (see Table 5 and fig.5.1-5.6)

Table 5: Average Concentration of ^{208}Pb /depth in $\mu\text{g/g}$

Site 1	0-2cm	67.54
	2-10cm	42.63
	10-20cm	118.83
	20-Xcm	94.42
Site 6	0-16cm	497.17
	16-Xcm	152.20
Site 7	0-15cm	257.16
	15-30cm	237.79
	30-Xcm	121.94
Site 9	0-15cm	266.87
	15-35cm	159.03
	35-Xcm	222.86
Site 10	0-2cm	123.41
	2-Xcm	112.41
Site 13	0-10cm	192.61
	10-20cm	119.46
	20-Xcm	232.94

As expected, the Pb concentrations at the sampling points revealed a marked variation in the degree of pollution within the sampling areas; more so, Pb concentration in all soil depth identifies soils in industrial, mining and transport areas as contaminated on grounds of ecological risks. At sampling site 6, the uppermost layer (0–16 cm) can also be classified as heavily polluted likely due less organic matter content with lesser

probability of getting bound to an upper mineral layer (rich in Fe-oxides and CaCO_3), hence resulting in free Pb at that depth. Pb concentration in sampling site 6, 7 and 10 has a negative correlation with respect to depth while reverse is the case at sampling point 10 despite the presence of 3 active coal mines around the location which should have a higher surface concentration of Pb as it will be expected. This is likely that the surface of the latter has more organic matter content with higher affinity to form complexes with Pb which in turn have lower dissolution. There is no observed linear correlation of Pb concentration and soil depth at sampling site 1, 9 and 13 probably due to mixing of the layers with uneven distribution of mineral and organic matter content.

This study found that both the average Pb concentration of all sample site depth would be above the maximum tolerable (permissible) limit according to World Health Organization (WHO) permissible limit of 100 $\mu\text{g/g}$ in the blood assuming the same undiluted concentration was to be maintained after ingestion or inhalation (Osio, 2009). According to Shantha et al. (2005) who recommended maximum permissible levels of Pb in soil based on the dose response relationship of lead in soil and blood Pb in children stated that an acceptable level of 600 $\mu\text{g/g}$ of lead in soil is a “safe” level and would contribute no more than 5 $\mu\text{g/dl}$ to total blood Pb of children under 12 years of age.

It is relevant to state that recent data indicates that there may be neurotoxic effects of Pb at lower levels of exposure than previously anticipated. Children are the most vulnerable segments of the population for exposure to Pb. This increased susceptibility results from combination of several factors for instance young children are more likely to play in dirt and place their hands and other objects in their mouth, thereby increasing the chance for soil ingestion, the efficiency of Pb absorption from the gastrointestinal tract and the permeable blood–brain barrier is greater in children than adults and nutritional deficiencies of iron, calcium, iron, copper and zinc which are predominant in children, may facilitate Pb absorption and exacerbate the toxic effect (Vasudevan and Streekumari, 2000).

Some characteristic clinical features of lead poisoning may be attributed to this specific anatomical pattern. Although the molecular targets for Pb are unknown, a vast amount of evidence accumulated over many years has shown that Pb disrupts processes that are

regulated by calcium. Picomolar concentrations of Pb can replace micromolar concentrations of calcium in a protein kinase C enzyme assay. Furthermore, Pb activates protein kinase C in intact cells and induces the expression of new genes by a mechanism dependent on protein kinase C which leads to neurotoxicity (Bressler et al., 1999). The cellular, intracellular and molecular mechanisms of Pb neurotoxicity are copious, as it impacts many biological activities at different levels of control: at the voltage-gated channels and on the first, second and third messenger systems. These effects could be related to Pb ability to interfere with the regulatory action of calcium in cell functions (Finkelstein et al., 1989). At a neuronal level, exposure to lead alters the release of neurotransmitter from presynaptic nerve endings. Spontaneous release is enhanced and evoked release is inhibited. The former may be due to activation of protein kinases in the nerve endings and the latter to blockade of voltage-dependent calcium channels. This disruption of neuronal activity may, in turn, alter the developmental processes of synapse formation and result in a less efficient brain with cognitive defects (Bressler et al., 1999).

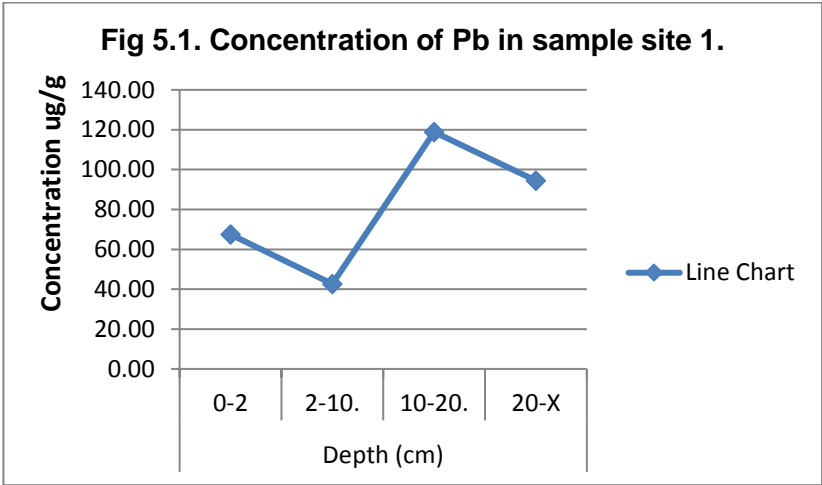


Fig 5.2. Concentration of Pb in sample site 6.

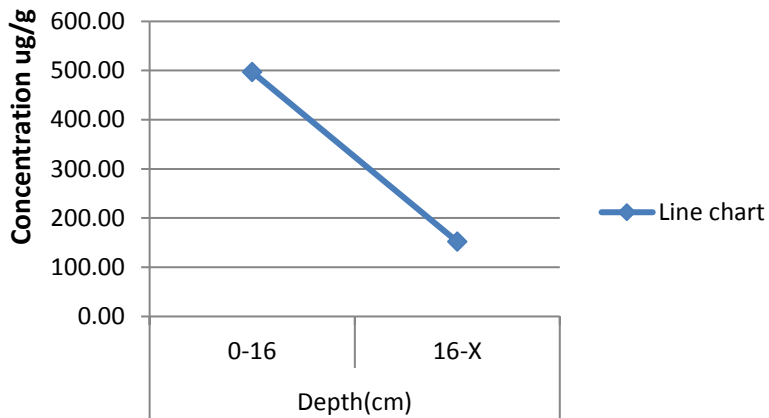


Fig 5.3. Concentration of Pb in sample site 7

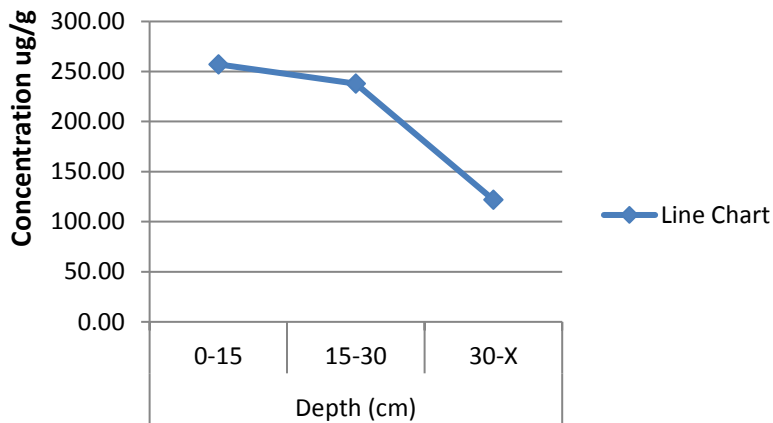
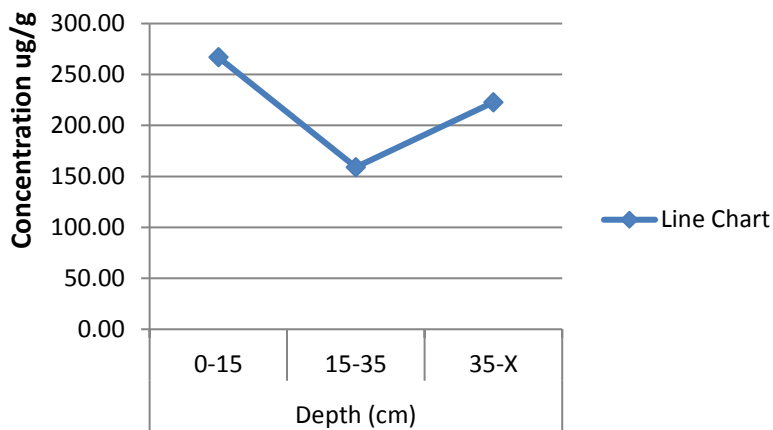


Fig 5.4. Concentration of Pb in sample site 9



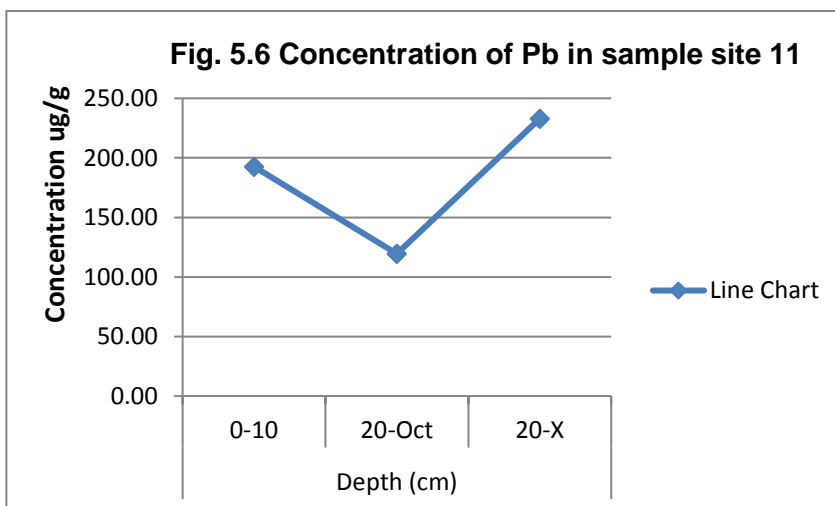
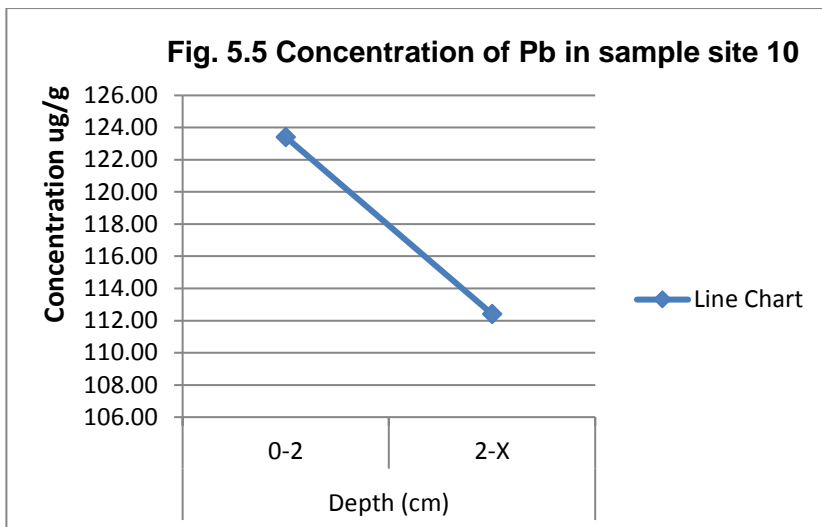


Fig. 5.1-5.6 showed a significant difference in Pb concentrations depth pattern at the respective sample point. The distinct high concentration of Pb at site 6 mainly occurs due to several sources of contaminants around the sampling location. Black coal heating power plants are the likely sources of contaminants in sample Site 1 of **Poroba** locality of Ostrava and from Poland which have common coal basin, hence resulting in increased production of fly ash in large quantities from partial combustion of low quality coal with high ash content. Many elements (major and trace) are preferentially incorporated or remain linked with fly ash particles during coal burning (Roy et al., 1981). Chemically, coal fly ash is composed of ferro–alumino–silicate minerals containing substantial

quantities of Ca, K and Na, along with other trace elements such as Cu, Zn, Mn, Mo, Ni and Se (Jastrow et al., 1981). Co, Cr, Cu and Ni remain linked with the iron oxide fraction and the elements with relatively low mobility (Cr, Cu, Pb and V) (Nugteren et al., 2002).

In Ostrava sampling site, the concentration of metals in fly ash deposited soils was found to be in the order Zn>Cr>Pb>Ni>Cu>As>Cd. In general, the background concentration of the metal is lower compared to field samples whereas the amount of metals that can become bioavailable is more in background samples compared to the field samples. The organic fraction is also a significant host to these elements and can be released to environment on oxidation of organic matter. It is important that the metal concentration in the residual fraction represents a very crucial part of total metal concentration in fly ash. This shows that after dumping of fly ash, the concentration of mobile metals increases and is dependent on changing environmental factors. This mobile fraction will be easily available to the terrestrial and aquatic systems. Since a number of potentially hazardous chemical elements are released from fly ash, resulting from burning of coal for electric power generation, the movement of these chemicals into water and food chain is of serious concern.

Overall concentration of metals in sample site 6 and 7 is evident from the mixture of contaminants sources around **Privoz** and **Radvanice** locality through the regular use of coke in steel production and other non-ferrous metal smelting. In these localities, it will also be worthy to note the area is home to **Arcelormittal**, one of the largest metal producing companies in Ostrava region of Czech Republic. The principal sources of pollution caused by smelting are contaminant-laden air emissions and processed wastes such as wastewater and slag. One type of pollution attributed to air emissions is acid rain, the smelting of sulfide ores results in the emission of sulfur dioxide gas, which reacts chemically in the atmosphere to form a sulfuric acid mist. As this acid rain falls to the earth, it increases the acidity of soils which initiates high mobility and possible leaching of metal contaminants around the surrounding of the smelter. New technologies are playing an important role in reducing or even preventing smelter pollution. Older

smelters may have emitted most of the airborne contaminants around these localities and at present, almost all of it is captured prior to emission using new technologies.

The variations in concentration of metal in these localities might likely result from predominant wind direction, distance from the smelting plants and laboratory extraction process. Cr, Cd, Pb, Ni and Zn had concentration above 100mg/g which by far exceeds background concentration. Various previous studies have provided a measure of the distances which can be reached by smelter emissions. Zoltai (1988) found above-background concentrations of Pb, Zn, Cu and As in peat up to 100 km from the Flin Flon base metal smelter in Canada. Elevated concentrations of Pb, Zn, Cd, Cu and Ni was found in peat 42 km away from a smelter in Noranda, Quebec

Three active mines located around **Petrivald** and **Orlova** localities are closer to sample site 9 and 10. Plumes from black coal and tailing dumps occurring there are composed of rock material, which were the remains of deep mining of hard coal. Bodies of tailing dumps formed not only the rock material but also contain residual materials from treatment of coal. Mining activities produced large amounts of wastes that were a major anthropogenic source of metal pollution, the exploitation of lignite coal mines can cause severe destruction both in lignite coal mine area and elsewhere (Hu et al., 2002).

The location of sampling site 13 around the main city of Ostrava designates that the major sources of contaminants are from combustions of vehicular exhaust and three industrial objects in the area.

6. Discussion

Disturbing information is that most of the studied metals are accumulated in particles of grain size PM_{1-2.5} during emission and it is known that these particles can penetrate deeply into pulmonary alveolar. A study of Particulate matter at the localities Ostravice, Ostrava Mariánské Hory, and Ostrava Radvanice, recorded higher magnitudes of most metals in PM < 0.949 µm were found. Cr and Zn are frequently accumulated in the dust particles with a diameter greater than 1.6 µm, Zn occurred at 8 of 10 localities in PM > 1.6 µm, only the localities Ostrava Mariánské Hory and Ostrava Radvanice were different. Pb and Cd occurred mainly in the class below 0.949 µm. At 8 of 10 localities, Cd occurred in the particle size class PM < 0.949 µm, with the exclusion of Hradec nad Moravicí and Ostrava Poruba (Sykorova et al., 2017). The impact of metallurgical industry on the basis of metals in the individual particle size classes in the air within the Moravian-Silesian Region has not been explicitly proven. In the samples taken, the microanalysis was used to detect particles that are formed during metallurgical processes: Fe-oxides containing Co, Cr, Cu, Mn, Ni, and Zn, and iron-based particles based on silicates containing: Ca-Mg-K in various magnitudes originating from combustion processes. Further, in particles below 1 µm, sulphates of Zn-Fe and Pb-Ca, which affect the correlation between the content of Fe and Pb, were proven (Sykorova et al., 2017).

This result has affirmed the assertion by Sucharová et al., 2008 that average Pb concentrations in Ostrava soils have constantly decreased since 1991. The causes of this Pb concentration reduction were a decreasing industrial production, mainly in the metallurgical industry, a strong reduction of industrial burning of brown coal, the desulphurization of the coal power plants (1994–1998) and the fact that leaded petrol was fully phased out in the year 2000. Car traffic has however considerably increased since 1995 and related factories have operated at the Polish site of this black coal basin area. The Pb emissions in the Ostrava region are characterized by a relatively high ²⁰⁶Pb/²⁰⁷Pb and a very low ²⁰⁴Pb/²⁰⁶Pb. Though local variation is high of Pb concentrations there is clearly a pattern of unusually high Pb values all along from

Ostrava in the east to the Ore Mountains along the border between Germany and the Czech Republic in the west.

Isotopic fingerprinting relies on the subtle differences in isotopic abundance to identify the specific sources of Pb found in the samples. When Pb isotopic ratios are measured using mass spectrometer, a standard reference material (e.g., NIST SRM-981) is necessary to calibrate the mass spectrometers and to standardize the measured ratios of the four Pb isotopes. Isotopic fingerprint of Pb can only be found in ^{206}Pb , ^{207}Pb , and ^{208}Pb as the abundance of ^{204}Pb is almost constant (at w1.4%). The isotopic compositions of different potential Pb sources gotten from direct measurements and literature can be plotted on a diagram using two of the isotope ratios of ^{206}Pb , ^{207}Pb , and ^{208}Pb , e.g., $^{206}\text{Pb}/^{207}\text{Pb}$ (commonly used in environmental studies, while $^{207}\text{Pb}/^{206}\text{Pb}$ is used in geochronology studies) and $^{208}\text{Pb}/^{206}\text{Pb}$. By plotting the Pb isotopic compositions of the samples from the contaminated site, the main sources of the Pb can be designated based on the similarity of isotopic fingerprints. From the abundances of ^{206}Pb , ^{207}Pb , and ^{208}Pb measured in the samples, contributions of up to three major Pb sources can be apportioned (Sangster et al., 2000). Given the potential intersection of isotopic signatures of Pb from different sources, and the coincidental overlap with many natural leads, the Pb isotope data should be interpreted in their specific context and substantiated with other information in lead pollution investigation. When several potential Pb origins co-exist, source apportionment should be supported with other evidence such as (1) meteorology, (2) documentation of origin emission levels or the geological origins of the constituent leads, (3) isotopic or other elemental compositions of those sources, and (4) sequential fashions of environmental Pb isotopes (Sangster et al., 2000). One of the hopeful new developments in the application of isotopic fingerprinting is the combination of this technique with geospatial analysis tools. Lately, researchers have coupled isotopic data with geographic information system (GIS) mapping in source distinction of lead pollution in the surface environment, particularly in urban settings (Caravanos et al., 2006).

The connecting of pollution and geospatial databases via GIS mapping allows the direct assessment of the relative information based on geographical patterns. According the

composite geochemical map produced, GIS spatial analysis techniques can be used to designate hot-spot areas and to assess the potential origins of pollutants in the region (Li et al., 2004). It is expected that the assimilation of GIS-based frame can lead to better assessment of lead pollution and development of cost effective alleviation actions. The development of techniques capable of direct isotope ratio measurements on solid samples requiring minimum sample preparation would substantially expand the application range of Pb isotopic fingerprinting. Combined with multiple ion collection, ICP-MS has become an established method for high precision isotope analysis with a performance comparable to MCTIMS (Pickhardt et al., 2005). Pb isotope ratios of standard reference materials SRM-610, SRM-981, and BCR-2G have been measured using this technique with results comparable to those obtained with TIMS, Pb isotope ratios in buttons obtained from fire assay of platiniferous ores, layered paint chips, and lake sediments have also been determined by this technique (Aries et al., 2001). ICP-MS can be employed as a swift analytical method for precise and accurate isotope ratio measurements (down to 0.005% with multiple ion collection) on solid samples (Aries et al., 2001). Its outstanding sensitivity and very low detection limits allow for measurement of isotope ratios with very small sample amounts, and require in general no or only simple preparation steps for solid samples. As a method with high sensitivity, comparable precision and accuracy, and requiring no complicated sample preparation procedure, ICP-MS is expected to partly replace the use of TIMS in future (Aries et al., 2001). This method will greatly simplify measurements of Pb isotope ratios in solid matrices, such as soils and sediments, in environmental studies, though the comparatively lower analytical precision (compared to TIMS) limits its application to cases where the isotopic signatures vary considerably among different Pb sources. Future research directions of Pb isotopic fingerprinting are primarily set by the state of the art in analytical instrumentation and method development.

Conclusions

Combination of Pb concentration in the soil samples from Ostrava and Pb isotope data from comparative studies shows that the major plausible source of anthropogenic Pb in Ostrava are the industrial emissions. However other sources responsible for lead pollution may be difficult to identify due to presence of Pb in multiple sources. Conventional approaches rely heavily on the statistical analysis of large databases of environmental samples and human subjects to identify the pollution sources whereas isotopic fingerprinting technique serves as better alternative in establishing the sources of lead pollution and apportioning their contributions. With a high discriminatory power, this tool requires the analysis of a small number of samples. To obtain the best results, Pb isotopic ratios should be used in conjunction with other data, such as concentrations and mineralogical compositions, and assisted with tools such as geospatial analysis, when applied to identify the sources and transport pathways of Pb in the environment. Increased availability of instrument and development of new analytical instrument requiring minimum sample preparation are expected to make this method more prevalent in future source apportionment of contaminants using Pb isotope fingerprinting.

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