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DEPARTMENT OF ECOLOGY

Diploma Thesis

Estimation of intensity of settlement activities in the Early Medieval Hillfort Královice according to accumulation of anthropogenic elements in the soil.

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Estimation of intensity of settlement activities in the Early Medieval Hillfort Královice according to accumulation of anthropogenic elements in the soil

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Objectives of thesis

Human settlement activities are connected with accumulation of anthropogenic elements in the soil. Extend of accumulation is connected with the intensity of settlement activities in the past so mapping of elemental composition of soils on archaeological sites can reveal differently settled areas. The question which has not been answered so far is how intensive were settlement activities in different parts of the early Medieval hillfort Královice in Prague. The aim of this thesis is therefore to identify level of accumulation of different anthropogenic elements in different parts of the Královice hillfort and to estimate the intensity of settlement activities in the past.

Methodology

Student will collect 60 soil samples of arable layer in the control out of the hillfort, in the forefield, and in the acropolis of the hillfort. Using portable XRF, elemental composition of dessicated soil samples will be identified in the laboratory conditions. Obtained data for different elements will visualised into maps using ArcMap and evaluated using different statistical methods.

The proposed extent of the thesis

30 -50 pages

Keywords

Geochemistry, Phosphorus, Calcium, Zinc, Cupper

Recommended information sources

Entwistle, J.A., Abrahams, P.W., Dodgshon, R.A., 1998. Multi-element analysis of soils from Scottish historical sites. Interpreting land-use history through the physical and geochemical analysis of soil. J. Archaeol. Sci. https://doi.org/10.1006/jasc.1997.0199

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Head of department	Dean

Prague on 04. 06. 2020

Declaration

I declare that I have worked on my diploma thesis titled "Estimation of intensity of settlement activities in the Early Medieval Hillfort Královice according to accumulation of anthropogenic elements in the soil." by myself and I have listed all sources used to acquire the information included in this thesis.

In Prague on 30.06.2020 Ramgopal Biswas

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Abstract

Ancient settlement activities relate to accumulation of anthropogenic elements which can persist in the soil for millennia. There are many early medieval strongholds in Czech Republic, but accumulation of anthropogenic elements has never been studied on them. The aim of this thesis was to study accumulation of anthropogenic elements in soils in Stronghold Královice near Prague which existed from 10th to 13th century AD. I asked following research questions: 1) Is 300 years of settlement activities enough long period for the development of a strong chemical signature in soils in the stronghold? 2) Were there any differences in settlement activities in different areas of the stronghold? 3) Are the chemical signatures in the stronghold different from the signatures recorded in deserted medieval villages in the Czech Republic? 4) What can the level of enrichment of soils by anthropogenic elements tell us about human population density?

I concluded that 1) 300 years of human settlement activities were enough long period to create strong chemical signature of anthropogenic soils in the former stronghold. 2) Intensity of chemical signature was different for Acropolis and Bailey indicating that Bailey was substantially less settled than Acropolis. 3) Chemical signatures recorded in the stronghold was much stronger than in the case of deserted medieval villages. This clearly indicate much intensive settlement activities in this stronghold in comparison to deserted villages. 4) Strongholds were thus areas with extraordinary settlement activities and with high density of humans. How many people lived in the stronghold I was not able to identify as it is unknown how much sediments were eroded and precisely to quantify the amount of accumulated phosphorus.

Keywords: Geochemistry, Phosphorus, Calcium, Zinc, Copper, pXRF, Human settlement, Soil Chemistry, Medieval village.

Abstrakt

Dávné sídelní activity jsou spojeny s akumulací antropogenních prvků, které vydrží v půdě tisíciletí. V Čechách je mnoho raně středověkých hradišť, ale dosud na nich nebyla studována míra akumulace antropogenních prvků. Cílem této práce bylo proto studovat akumulaci antropogenních prvků na hradišti Královice u Prahy, které existovalo od 10. do 13. století našeho letopočtu. Kladl jsem si následující výzkumné otázky: 1) Je 300 let dostatečně dlouhá doba pro vytvoření silného chemického signálu v půdách na hradišti? 2) Lišila se intenzita sídelních aktivit v závislosti na pozici na hradišti? 3) Jsou signály zaznamenané na hradišti odlišné od signálů zaznamenaných na opuštěných středověkých vesnicích v České republice? 4) Co nám míra akumulace prvků řekne o hustotě osídlení na hradišti?

Zjistil jsem, že 1) 300 let sídelních aktivit byla dostatečně dlouhá doba k vytvoření silných chemických signálů antropogenních půd na bývalém hradišti. 2) Intenzita chemických signálů byla jiná na akropoli a v předhradí, což indikuje podstatně méně intenzivní osídlení předhradí ve srovnání s akropolí. 3) Chemické signály zaznamenané na hradišti byly podstatně silnější ve srovnání se signály ze zaniklých středověkých vesnic. Tento výsledek indikuje podstatně intenzivnější osídlení na hradišti ve srovnání se zaniklými vesnicemi. 4) Hradiště byly oblasti s vyjímečně intenzivním a hustým osídlením. Kolik lidí žilo na hradišti jsem ale nemohl zjistit, protože nevíme kolik půdy bylo oderodováno, a tak jsem nebyl schopen přesně kvantifikovat množství akumulovaného fosforu podle nějž je možné počet obyvatel dopočítat.

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1 INTRODUCTION

Since prehistory, settlement activities were associated with the accumulation of anthropogenic elements in archaeological soils and sediments, particularly P, K, Ca, Mg, Zn, Cu, and Sr (Wells et al., 2000; Hejcman et al., 2011; Šmejda et al., 2017). The accumulation of these elements was associated with the deposition of organic waste, excrement, and biomass ash (Entwistle et al., 1998; Hejcman et al., 2011; Hejcman et al., 2013a; Howard, 2017). These settlements are mostly characterized by extraordinary fertile anthropogenic soils in comparison to their surroundings, even after hundreds of years.

As P cycles in geological times, it accumulates in high quantities and is easily detectable using different analytical approaches. The so-called "phosphate" analysis was frequently used on many archaeological sites to detect different activity areas (Holliday, 2004; Holliday and Gartner, 2007). As there is almost no or limited removal of accumulated P from archaeological localities, P can be used for the estimation of the human population size in the past (Nowaczinski et al., 2013). One person accumulates approximately 1 kg of P per year if only dietary P is considered (Blume, 2010; Nowaczinski et al., 2013). With other sources of P such as animal husbandry and biomass ash, the total accumulation of P per one person can be substantially higher thus, the calculation of population size according to accumulated P has a high level of uncertainty.

The estimation of population size in past settlements is very essential as it provides an idea of the intensity of human impact leading to a certain degree of accumulation of anthropogenic elements as well as information on land use and management (Nowaczinski et al., 2013).

In Central Europe, many archaeological localities are used as arable fields for crop production. There have been doubts by many archaeologists if arable layer preserves ancient chemical signatures. According to the previous research of prehistoric and medieval settlements (Hejcman et al., 2011, 2012, 2013a, b, c), it was concluded that such signatures are well preserved despite a hundred years of ploughing. Determination of the elemental composition of the arable layer is thus, a useful tool for identification of the extent and intensity of ancient settlement activities.

Burning activities contribute to the accumulation of soil organic carbon which ensures the increase of organic matter in the soil and creation of strongly magnetic minerals (e.g. magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3)). The concentration of these magnetic minerals can be easily measured by parameter magnetic susceptibility (volume- and mass-specific magnetic susceptibility κ [SI units] and χ [m^3/kg], respectively).

The main advantage of this parameter is an easy application for *in situ* measurements on large data sets and under certain conditions, it can be used as a proxy parameter replacing expensive and time consuming soil chemical analyses (e.g.; Petrovský and Ellwood, 1999; Lecoanet et al., 2003). Magnetic minerals are extremely sensitive to their environments; therefore, magnetic susceptibility can be linked to geochemical parameters to provide effective analysis tool (Le Borgne, 1955; Evans and Heller, 2003; Szuszkiewicz et al., 2016; Jordanova, 2016). In the case of archaeological investigation, magnetic susceptibility can be efficiently applied for more accurate interpretation of geochemical analyses for discrimination between anthropogenic and lithological elements (Łyskowski et al., 2018).

Early medieval stronghold in the Czech Republic (Dřevíč) was studied by the team of Professor Michal Hejcman. He recorded strong elemental signatures in anthropogenic soil there in comparison to its surroundings without settlement activities (Asare et al., 2020). However, it related to very intensive settlement activities that lasted from prehistory up to the early medieval period. Such signature is much stronger than in deserted medieval villages which existed for only several hundred years and had only a small number of inhabitants (Horák et al., 2018).

To determine, weather 300 years of settlement activities are long enough for the development of strong chemical signatures in anthropogenic soils, an early medieval stronghold Královice near Prague is selected for the study. In comparison to Dřevíč, this stronghold was used only over a relatively short period (from 10th to 12th centuries AD; Štefan and Hasil, 2014) so it can be well used for the estimation of the intensity of medieval settlement activities as it is not biased by prehistoric settlements.

The next advantage of this stronghold is the existence of a Control area out of the stronghold which has been used as an arable field in the same way as areas within the stronghold but had no ancient settlement activities. A comparison of the content of elements in the soil of the Control area with soils of studied areas in the stronghold enables calculation of enrichment factors for different anthropogenic elements.

2 AIMS AND OBJECTIVES

This chapter briefly describes the main aim and objectives as well as the research of my thesis. I asked the following research questions:

1) Is 300 years of settlement activities long period enough for the development of a strong chemical signature in soils in the stronghold?

2) Were there any differences in settlement activities in different areas of the stronghold?

3) Are the chemical signatures in the stronghold different from the signatures recorded in deserted medieval villages in the Czech Republic?

4) What can the level of enrichment of soils by anthropogenic elements tell us about human population density?

3 LITERATURE REVIEW

This section of the thesis presents a comprehensive overview of the chemical signatures in past settlement soils using different analytical approaches.

A comprehension of the properties and archaeological significance of phosphorus found in soil as a segment of phosphate mixes is fundamental to this investigation. The experiment was performed for this research to find out the intensity of human settlement activities according to the accumulation of anthropogenic elements in the early medieval hillfort Královice. The following literature review expands upon the discussion on how phosphorus and other elements behave in soil and effect on the archaeological site.

3.1 Phosphorus in Soil

It is complex to comprehend the element phosphorus does not occur in soil in pure atomic form but as ions (Bethell and Máté, 1989). Those ions make a bond with oxygen atoms to form phosphate and the phosphate make a bond with other elements such as iron, aluminium and calcium to form the chemical compound (Dietz, 1957; Eidt and Woods, 1974; Holliday and Gartner, 2007).

Here in this research, I am concerned about measuring the phosphorus including other elements such as K, Ca, Fe, Zn, Cu, Mn etc. There are different kinds of method used to measure the phosphorus in soil. The portable XRF can measure the phosphorus and other elements in the soil. The composition of phosphate is depending on the different soil condition (Sjöberg, 1976; Holliday and Gartner, 2007) however, it depends on some factors such as organic content, pH, moisture, time, soil particle size and human activity that affect soil phosphate stability in the soils. The different bond of phosphate with other elements can change the contamination of phosphorus in phosphate. That can provide a different classification of phosphorus sometimes it could be a fraction (Bethell and Máté, 1989).

This research will be concerned about the accumulation of phosphorus and other anthropogenic elements. Herz and Garrison (1998) infer that the anthropogenic phosphorus in the soil should be present in many forms or fraction though the fact that soil phosphorus exists in the soil as part of a dynamic soil (Bethell and Máté, 1989).

In addition to, the character of extremely low "loss factor" make phosphorus more well-grounded soil elements to study past human activities, when phosphorus deposited in the soil it is staying bonded to the original deposition site with horizontal and vertical migration and no gaseous escape (Leonardi et al., 1999). The form of phosphate could be changed by different physical, chemical, or biological process similarly, the role of phosphorus is also in this form (Holliday and Gartner, 2007) and this process allows phosphorus to going through a cycle.

Moreover, the organic and inorganic phosphorus is also adding in the soil by animal waste, but they play an important role to remove the phosphorus by grazing (Leonardi et al., 1999). On the other hand, plants are taking a modest quantity of accessible phosphorus from the soil and through their root they expel phosphorus in the surface of the soil. For the crop plants, the loss of phosphorus is permanent however the instance of natural growing plants has unique, when they pass on the defilement of phosphorus on their tissue is back in the surface soil (Leonardi et al., 1999).

It is considered that the impacts of animal and growing plants on the soil is a transformation of phosphorus (Cook and Heizer, 1965), after all the total amount of phosphorus in the soil is staying the same also human activities can roll out a tremendous change of phosphorus in native soil (Bethell and Máté, 1989). Additionally, the removal of crops directly affects the soil phosphorus, it is lessened the total amount of phosphorus in the soil, so farming can reduce the level of the phosphorus in the soil (Eidt, 1973).

3.2 Phosphorus in Archaeology

Phosphorus has been the most studied and widely applied in archaeological soil chemistry and considered the indicator of human activity along other character make it more suitable, that it can exist in the pH range of the most soil (Holliday and Gartner, 2007). It is well known that human activities can changed the chemical content of the soil and the change rely on the receptivity of the chemical elements and climate condition of the area (Leonardi et al., 1999). The fact about the accumulation of phosphorus is high in human activates area compare with the surrounding area and it was first introduced in 1911 by Hughes in Egypt (Bethell and Máté, 1989).

It is considered that the phosphorus could be present in the soil in three-stages included 1) absorbed in the surface of the soil particle 2) liquefiable minerals 3) organic compounds (Larsen, 1967). Although, there are several ways to the movement of phosphorus 1) the activity of soil animal 2) massive flow of water and 3) diffusion.

In archaeology, the measurement of phosphorus in soil could be helpful to determine the settlement activity, to decode the archaeological information and the capacity of different archaeological sites (Selskiene et al., 2017). It is believed that, the archaeological soil chemistry first introduces in Europe (Cook and Heizer, 1965; Bethell and Máté, 1989) by Walter Lorch who used phosphorus test in Germany in the1930’s and 1940s.

3.2.1 Application

It is important to note, that phosphorus is an element in a cell which present in plant and animal tissues (Cook and Heizer, 1965; Eidt and Woods, 1974). It could be added in soil by different human activities. Those elements are accumulated on archaeological soil through human waste, human burials, livestock dung (Cook and Heizer, 1965; Eidt and Woods, 1974; Holliday and Gartner, 2007; King, 2008). Also, there are some elements affected by human activities which can be relevant to the archaeological research studied such as calcium (Ca), potassium (K), nitrogen (N), and zinc (Zn) (Holliday and Gartner, 2007). The unique character of phosphorus is that it is unaffected by the movement of water through the soil (Cook and Heizer, 1965) and that makes phosphorus as a key element to track the human activities from the past.

Therefore, the phosphorus analysis could be useful to identify the location and activities of the area. King (2008) proposed that the low accumulation of phosphorus in archaeological sites can be connected to human pathway, workhouse, or entrance. and the distribution of phosphorus and soil chemistry could be related to the ancient activities.

Marwick (2005) interpreted the accumulation of phosphorus to explain the settlement in Australia. The analysis of soil phosphorus can be used to learn the characters of an area, for example, the phosphorus analysis has been widely used to detect the attribute of Native American sites in the USA (Shirk, 1979).

3.3 Phosphorus as an indicator of Human settlement

The influence of human settlement activity may affect the chemical composition of the soil (Oonk et al., 2009b) for example, the study of organic and total phosphorus is universally used in archaeology. In present day phosphorus is the most prominent anthropogenic indicator of archaeological soils, along with some other elements such as Ca, K, Mg etc. Despite P, the elements which are affected by human activities are C, N, Na, P, and Ca with small amount of K, S, Cu, Zn and other elements (Holliday and Gartner, 2007).

As a result, the past human activities could have changed the chemical contrast of the soil. Oonk et al., (2009b) categorised the past human land use in two different way by occupational and productional activities or agricultural activities and he stated, the main difference between occupational and productional activities or areas can be seen at pottery ceramics, bones, and other elements of daily activities. On the other hand, the agricultural use of the land is less visible. So, the anthropogenic soil analysis in the archaeological sites can tell us more about the past.

3.4 Anthropogenic elements

There are some other elements with a significant contribution on archaeological soil including alkaline elements such as Ca, K, Mg, and Na also they are the most common elements in soil and relatively mobile (Oonk et al., 2009a). The trace elements are depended on the soil pH, the clay mineral, FeO (Ferrous Oxide), phosphate etc (Kumpiene et al., 2007). However, before the Industrial Revolution, the most important elements indicated the human activities are nitrogen(N), potassium(K), calcium (Ca), magnesium (Mg) and sulphur(S) (Leonardi et al., 1999)

Several studies suggest that different elements have a strong influence on human activities (Kabata-Pendias, 2000). It is common to find an enormous amount of Ca, Cu, Mg, K, Na, P, and Zn in archaeological sites (Cook and Heizer, 1965). Despite this, some specific elements can describe the past on-site activities such as Ca, P and K. Those elements might be related to the metal-related activities.

Ca, Cu, Mg, K, Na, P and Zn were connected to the living organism and waste (Oonk et al., 2009b). The high concentration of barium (Ba), phosphorus (P) and manganese (Mn) was found in organic waste disposal at Piedras Negras in Guatemala (Parnell et al.,2002). Entwistle et al., (1998,2000) described the high concentration of strontium (Sr) and calcium (Ca) is related with the fields area on the other hand, the concentration of potassium (K), rubidium (Rb) and thorium (Th) are an indicator of the settlement of small firm with less certainty.

The soil Calcium (Ca) play a significant role in the archaeological soil and it is considered as an indicator of food preparation area of the past. It is contained in the ash of the burning charcoal and high content of Ca is present in teeth and bones (Vranová et al., 2015). Therefore, it indicates the presence of human in the site.

Cu is one of the major elements in archaeological sediment because it is almost stable in soils (Fontes and Gomes, 2003). However, Cu has high stability in acidic soils compare with alkaline soils (Oonk et al., 2009a) and it has been used since from later prehistory (Bintliff et al., 1990). The contamination of Cu in archaeological sediment is related to the mining and metal-related activities (Wells et al., 2000).

Similarly, Zn is also showing the spatial pattern like Cu except that Zn is relatively mobile and could be exchanged by other trace metals (Cao et al., 2004). It is believed that Zn is available in form of free and complexed ion in the soil (Kabata-Pendias, 2000). According to Bintliff et al., (1990) Zn was unknown in Europe until the15th century.

Mn is an important element as it was used for lightening the glasses in ancient time. Though the soil chemistry suggests that it is not a good indicator for archaeological sediment because the metal was not isolated till 19th century (Bintliff et al., 1990).

K is also considered one of the essential elements in archaeological sediments because it indicates the building construction, the deposition of biomass ashes and faces (Hejcman et al., 2011; Hejcman et al., 2013a). However, Hejcman et al., (2013b) mention that in the high perception area the calcium and magnesium concentration is mobile. Nielsen and Kristiansen (2014) proved that strontium (Sr) in the soil provides information about animal manure, bone fragments and household waste.

Although, Si is one of the most stable elements in the earth craft but some special condition it could be transported and Si is more mobile at high pH level (Kabata-Pendias, 2000). Therefore, different Archaeological features are related to different anthropogenic elements, below (Table 1) show the details about the relation between Archaeological features and elements.

Table 1: Different Archeological feature with related elements exaggerate the soil (modified from Oonk et al., 2009a).

Archeological feature	Elements	References
Burials/ Grave	P, Cu, Mn, Ca	Cook and Heizer, 1965; Parsons, 1962; Keeley, 1981; Bethell and Smith, 1989
Hearths **Middens**	P, K, Mg, P, K	Barba et al., 1996; Knudson et al., 2004; Wells et al., 2000; Parnell et al., 2001
Farmhouses, Human pathway, Human workhouse, Entrance	P, Ca, Mg, Fe, K, Th Rb, Cs, Pb, Zn, Sr, Ba	Entwistle et al., 2000; Parnell et al., 2001; Wilson et al., 2005,2006; King, 2008
Mining, metal smelting and Production sites	Cu, Pb, Mn	Hong et al., 1994; Pyatt et al., 2002; Monna et al., 2004
General archaeological sites	B, Cu, Mg, Mn, Ni, P, Se, Zn, K, Ba, Ca, Na	Cook and Heizer, 1965; Ottaway and Matthews, 1988; Bethel and Smith, 1989
Building construction, Biomass Ashes and faces **Animal manure, bone fragments and household waste**	K Sr	Hejcman et al., 2011; Hejcman et al., 2013a Nielsen and Kristiansen, 2014
Wood Ashes, burning of forests, food preparation, production of pottery, burning of wooden building	Ca, K, Mg, P	Campbell, 1990; Huang et al., 1992; Hytönen, 2003; Patterson et al., 2004; Pitman, 2006; Saarsalmi et al., 2010; Hejcman et al., 2011

3.5 pXRF

The pXRF (portable X-ray fluorescence) spectrometers are nowadays popular because they enable to easily examine the chemical analysis of soil or other elements, However, it was designed to identifying the hazardous metal. But the reliability and easy transfer make it popular to the scientist and non-scientist.

The XRF technology can identify and measure the present elements in an object by exposing the target to X-ray energy and calculating the wavelength and the consumed energy that is re-emitted (Swanson and Mark, 2006). X-ray is a kind of energy which is produced from the kinetic energy of moving electrons that are converted to electromagnetic radiation when it is hit an object (Laing, 1981). The consequence of the frequency of a X-beam is determined by the measure of dynamic vitality involved by the moving electrons. (Laing, 1981). So, an XRF device can calculate the quantity of each element by measuring the wavelength they produce (Swanson and Mark, 2006). The fluoresce energy of Phosphorus is 2.1 KeV (kilo-electron volts), so an XRF device calculate the total amount of phosphorus by measuring the intensity of energy received at this wavelength. The first form of data received by XRF is energy spectra graph and then the internal device calculate the estimation of the elements and present it as the form of parts per million (ppm).

XRF technology is a powerful tool to diagnose the soil composition and has been using in archaeological soil analysis for a long time (Shackley, 2011). After examination 75 soil sample in pXRF and ICP-AES Rouillon and Taylor (2016) proclaimed that pXRF is a better alternative to ICP-AES. However, Hunt and Speakman (2015) have confirmed that pXRF cannot precisely determine the amount of some elements in the archaeological ceramic and sediment.

3.6 Ancient population size

One of my main goal of this thesis is to find out the human activities and ancient population size on the study area according to the accumulation of anthropogenic elements in the soil. It is important to estimate the size and distribution of ancient human population to renovate the human settlement. Zorn (1994) described two levels of estimation the size of ancient population, one is the size of population of specific settlement(micro level) which is related to the information of function and resources of population and the other is the size of population of the whole region(macro level) which is related to the social and economic information of the region. A different approach has been applied to find the ancient population size included archaeological, geophysical, ethnoarchaeological (Nowaczinski et al., 2013), the density of habitation coefficient and the natural resource (Zorn, 1994).

However, the intensity of settlement activity depends on the population size. In this case, phosphorus is the anthropogenic component and universally acknowledged as a pointer of human movement since it has exceptional act that it is unaffected in relocating water (Holiday and Gartner, 2007). The main sources of Phosphorus in archaeological soil is animal or human faces so therefore the total phosphorus accumulation by the area could provide the population size of this area (Nowaczinski et al., 2013) though still, it is a question of accuracy. Nevertheless, phosphorus could be measured correctly by portable XRF spectroscopy analysis (Gauss et al., 2013). Nowaczinski et al., (2013) was succeeded to calculate the ancient population size of Fidvár (a small town in Slovakia) through the contamination of phosphorus by using portable XRF.

3.7 Human Impact on the Soil

Humans change soil in numerous points of view those include accelerated, salinization, lateritization, podzolization and acidification. Jenny (1941). Proposed the factor of natural soil is (Goudie, 2013).

S=f (cl, o, r, p, t..)

The factor includes

S= any kind of soil property

cl= the regional climate

o= the biota

r= the topography

p=the parent material

t= time or period of the soil formation

the dot represents additional unspecified factors

In general, there are huge difficulties in estimating erosion rate in pre-human times but in a recent analysis, the soil is not merely a passive and dependent factor in the environment. So, the equation clarifies that the impact of human in the soil is advantageous (Bidwell and Hole, 1965). The beneficial adding minerals fertilizers, accumulating shells and bones, accumulating ash locally, land forming and structure building, raising the land level by the accumulation of materials (Goudie, 2013).

The unfavorable is exposing soil to inordinate insolation, decreasing natural substance of soil through grazing, over-brushing. The human made fire has a significant impact on soil because fire quickly changes the distribution of plant nutrient in the ecosystem (Goudie, 2013). Moreover, the burning forest can increase the amount of P, Mg, K and Ca in the soil (Raison, 1979) and increase the amount of pH in the soil and make an alkaline condition of the soil (Goudie, 2013).

3.8 The medieval settlement in the Czech Republic

Before the 19th century, there was no written source about early medieval in Bohemia (Štefan et al., 2016). In AD 872, the Annals of Fulda is considering the first-known member of Přemyslid dynasty, and Bořivoj I the first person who built the first church in Bohemia (Štefan et al., 2016). Only a small area near Prague was ruled by Přemyslid. In AD 935 there was a historical turning point in Bohemian history as Wenceslas was killed by his brother and Boleslav I (ruled AD 935-972) took the power and expand his territory (Štefan et al., 2016).

The second half of the ninth century and the first half of the tenth century is the period when most of the fortified of the central Bohemia is constructed. According to Ivo Štefan on that time there were around 10 fortified strongholds in central Bohemia. Jiří Sláma the person who first interconnected the central Bohemian hillfort system into a one single complex system which was built by the first Přemyslids. But the system was questionable because of the lack of written evidence. And there is not enough evidence about the Přemyslids Control in central Bohemia. Ivo Štefan considers the stronghold of central Bohemia in three time period, the first is the turn of the 9th and 10th century which included Mořinka, Kosoř, Butovice, Šárka, Zámka, the second period origin around AD 900 which included Budeč, Praha, Klecany, Boleslav, Mělník, Tetín and the third period about the origin from AD 930 which included Břežany, Královice, Vyšehrad, Vinoř, Libušín.

Moreover, the hillfort of Královice was excavated by Štefan and Hasil (2014). According to the documentation (Bartošková, 2010a) there was one Bailey which was added around AD 900 to the Acropolis of the Budeč stronghold and almost 15.2 ha massive ramparts was surrounded by. During the middle of the 10th century the hillfort (7.2 ha) was built as a final stage of the hillforts of Přemyslids dynasty (Štefan and Hasil, 2014).

4 METHODOLOGY

4.1 Study Area

The early medieval stronghold Královice (50°02'37.5"N 14°37'52.9"E, Figure 1) is located,17 km NW of Prague, the capital of the Czech Republic. The Czech Republic has a surface area of 78,866 km^2 and is in center of Europe within the temperate climate zone of the northern hemisphere. The maximum length in the longitudinal direction is 452 km and the maximum latitudinal width is 276 km. The countries natural environment is characterized by a moderate, humid climate and four alternating seasons. The geomorphologic point of view, the western and central parts of Czech Republic encompass the Bohemian upland of Paleozoic origin, which were partly flooded by the sea during the Mesozoic Era and made a thick layer of sediment (Tolasz, 2007).

A wide range of soil found in Czech Republic, In the lowlands of Southern Moravia and the Labe Basin, fertile chernozems are the most common soil type. At the medium elevations, brown earth dominated, and the higher elevation the illimerized soils and podzol soils are common (Tolasz, 2007).

The size of the fortified area with the occurrence of anthropogenic soils is 11 ha. with average annual air temperature and rainfall 8.6^{o}C and 500.7 mm (long term average climate data period 1981-2010) and in 2018 the annual air temperature was 10.5^{o}C and perception was 391mm respectively (Statistical Yearbook of Prague, 2019). However, the soils type was classified as haplic cambisol in the Control area (Kozák, 2010). As there is the same geological substrate in the stronghold and Control area, anthroposols in the stronghold developed from the haplic Cambisol (Kozák, 2010).

Figure 1: Aerial photographs (photo by Martin Gojda) of studied Královice stronghold and its location within Prague and the Czech Republic. Soil samples were collected in the Acropolis (A), the Bailey (B), and in the Control (C) field out of the stronghold. The promontory with the stronghold is surrounded by Markéta dam build upon the Rokytka river in the 1970s.

4.2 Historical background

The early medieval Přemyslid's stronghold Královice existed form the first half of the 10th century to the end of 12th or the start of the 13th century AD. It is not known the original name of the stronghold as it is not mentioned in any early medieval written resources (Štefan and Hasil, 2014). Perhaps, the main aim of the stronghold was to Control and protect the access road to the Prague agglomeration which was the center of the Přemyslid domain during 10th century AD.

The stronghold was divided by two fortification walls into Bailey (B) and Acropolis (A) (Figure. 1). Although the fortification wall of the Acropolis has never been studied and exactly dated, the fortification wall of the Bailey was excavated by Štefan and Hasil (2014). However, the last ring was dated to the year 912 AD and several youngest rings were missing so the inner wooden construction was not built up before year 918 AD.

The question if the fortification of the Acropolis is older or of the same age cannot be answered and requires further research. The total area of the stronghold was 7.2 ha, 2.4 and 3.7 ha of inner area in Acropolis and Bailey, respectively. In the Acropolis, there is the baroque style church of Sant Margaret last renovated in the years 1739-1740 additionally the original stone church was established in the gothic style around the year 1300 on the place of an older church that existed in the same place during the lifetime of the stronghold in fact, several buildings in the surroundings of the church were build up in the late 19th and early 20th centuries.

4.3 Soil sampling

Soil samples from the arable layer (upper 10 cm using soil probe with 3 cm in diameter) were collected from the internal area of the stronghold called Acropolis (A), Bailey (B) and Control (C) field (Figure 1). The collected samples were from out of the stronghold where no ancient settlement activities recorded earlier. Twenty-four mixed soil samples were taken in the Acropolis, each composed from five sub-samples collected in 10 m^2 to obtain the representative soil sample without extreme values. In the Bailey, 20 mixed samples were collected in two parallel lines and the Control field, 17 mixed samples were collected in one line. In total, 61 mixed soil samples were collected for further analysis.

4.4 Analytical and Statistical methods

All the soil samples were air-dried and subsequently oven-dried at 40°C for 48 hours. The small stone and waste materials were removed from the sample by hand, following, the samples were hand ground in a porcelain mortar in fraction size under 2mm.

The ED-XRF (pXRF) analyser is utilized to Delta Professional by Olympus InnovX with the Soil Geochem estimation mode to examine the soil examples (for the applications of XRF spectrometry, see Canti and Huisman, 2015; Hall et al., 2014; Hürkamp et al., 2009; Kalnicky and Singhvi, 2001; Šmejda et al., 2017). The samples were performed over a time of 1 minute with 30s of a 10-kV beams and then 30s of 40-kV beams. Each sample was examined three times and the result was considered the arithmetic mean of the three examinations. The pXRF provides almost the total content of the elements in the soil.

The standard of the device results was successfully tested by BAS Rudice Ltd. Company (www.bas.cz) on 55 reference materials (e.g. SRM 2709a, 2710a, 2711a, OREAS 161,164, 166, RTC 405, 408). Total contents of P, K, Ca, Mn, Fe, Al, Si, Ni, Cu, Zn, Sr, and Pb, were determined as they were above the detection limit in all the samples except for Ni which was not detected one time. In this case, the missing value was replaced by half of the detection limit. However, the total contents of elements such as S, Mg, Cl, Cr, Mo, Co, Se, Sb, Cd, Sn, Ti, In, Sn, Sb, Ba, W, Bi, Ag, Tl, Au, Th, and Hg in all samples were omitted from further analysis as they were either not detected or above the detection limit only in a few cases.

The magnetic susceptibility measurements of all the soil samples were performed in the Laboratory of Rock Magnetism, at the Institute of Geophysics of the Czech Academy of Sciences, Prague. Soils were filled into cylindrical plastic pots of 10 cc volume and weighed. Volume-specific magnetic susceptibility was determined by AGICO MFK1-FA Kappabridge (resolution up to 2×10^{-8} SI, AGICO Ltd., Czech Republic). All samples were measured three times under AC frequency of 976 Hz and a magnetic field amplitude of 200 A/m; obtained data were averaged. Mass-specific data were calculated after weighing the sample and are related to sample density.

The pH (H_2O) of all soil samples was determined at ratio 1:1 (soil/water) using a Voltcraft PH-100 ATC pH meter. The reliability of data obtained by the pXRF was assessed by randomly selecting six soil samples from the Acropolis, Bailey and the Control (2 samples per each site). These samples were analyzed to determine the total contents of P, K, Ca, Mn, Fe, Si, Al, Cu, Zn, Ni, Sr, and Pb in an independent accredited laboratory where extractions of elements in *Aqua regia* extract [3ml HCl(Hydrochloric acid) and 1ml HNO_3,(Nitric acid) International Organization for Standardization USEPA 3052], were analyzed by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7700x Agilent Technologies Inc., USA).

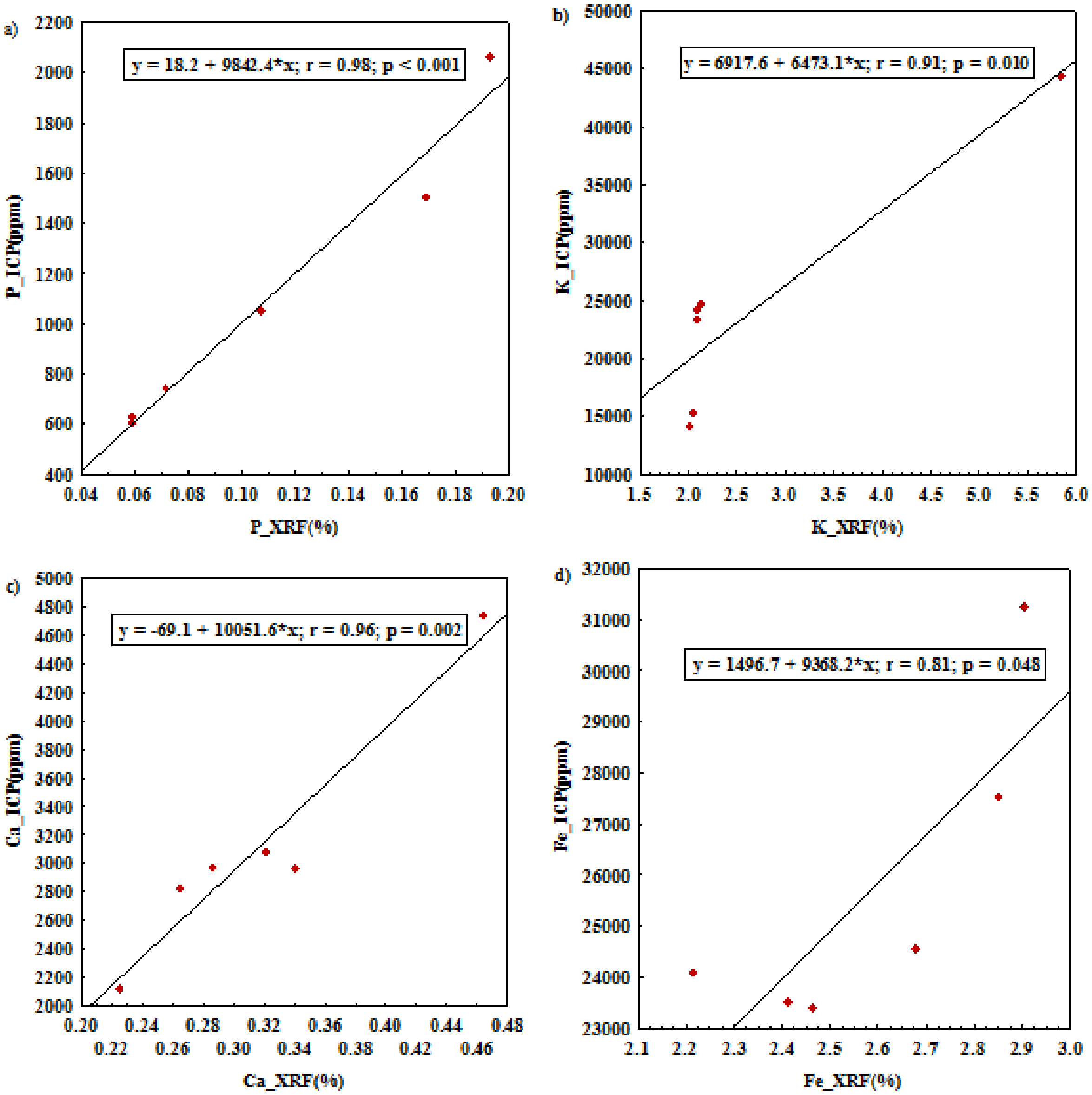

Figure 2: Relationship between XRF and ICP data for a) P, b) K, c) Ca, and d) Fe contents.

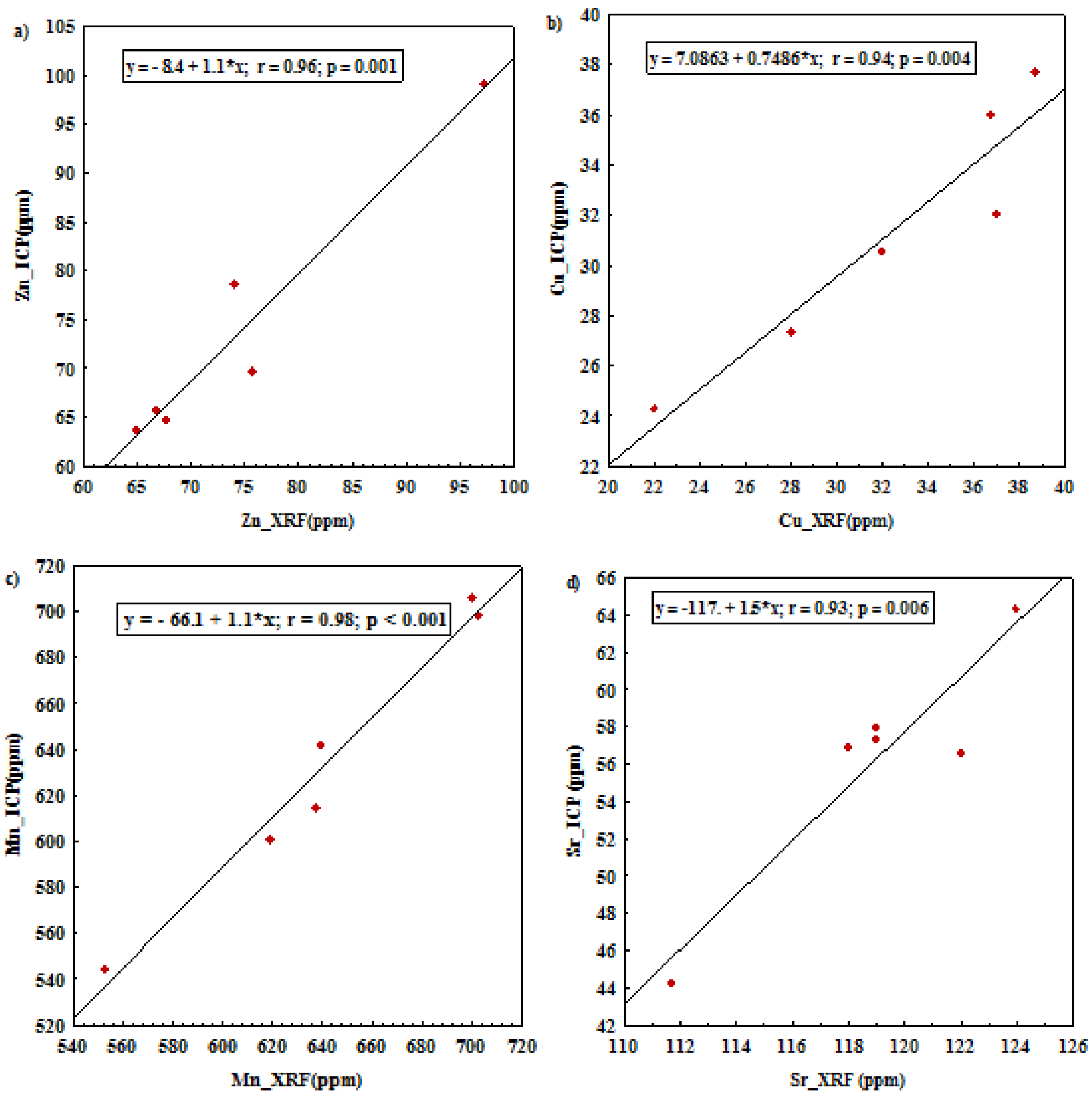

Figure 3:Relationship between XRF and ICP data for a) Zn, b) Cu, c) Mn, and d) Sr contents.

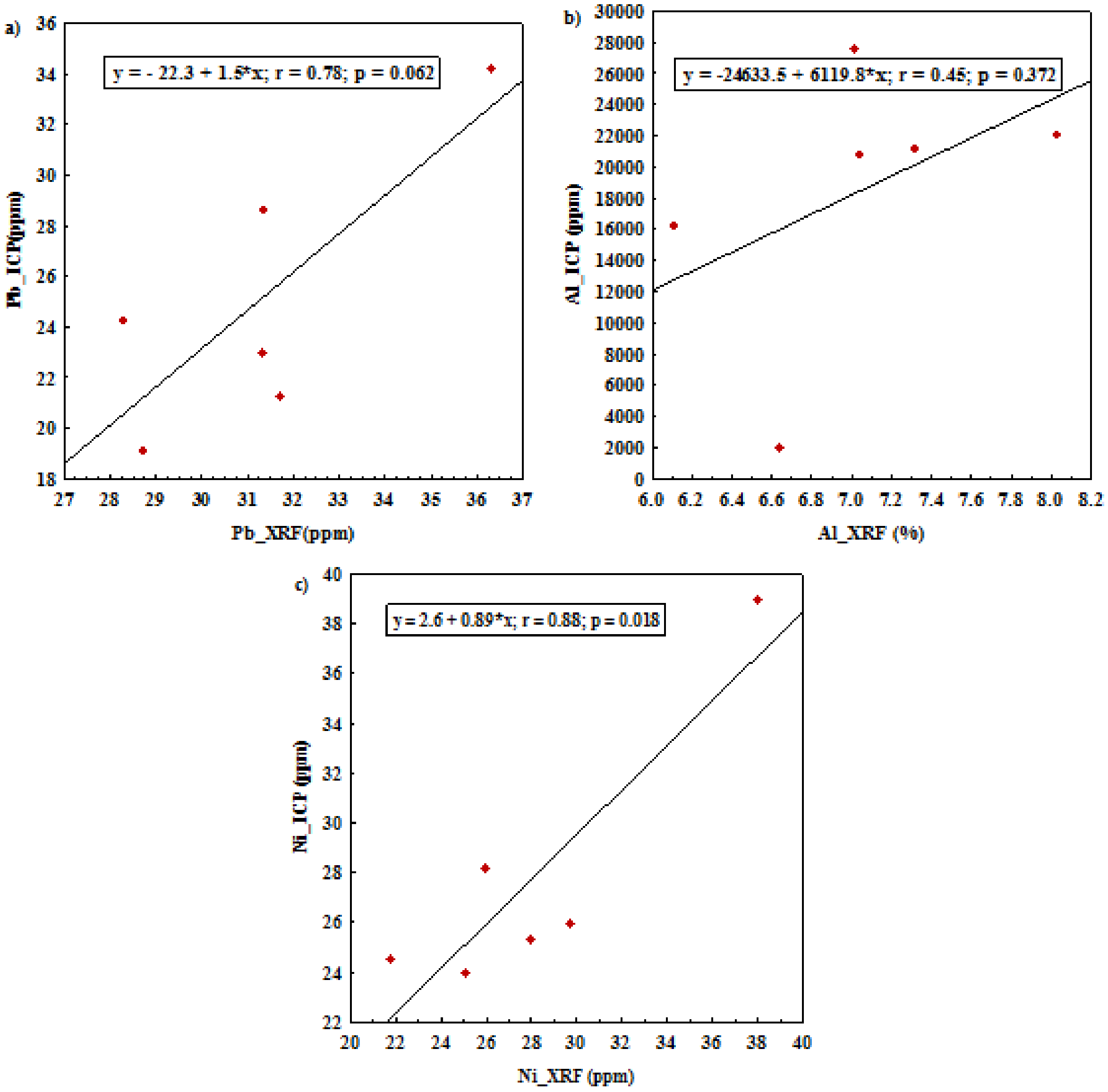

Figure 4: Relationship between XRF and ICP data for a) Pb, b) Al, and c) Ni contents.

The correlation of Si was omitted from this analysis as it is not fully soluble in *Aqua regia*. Based on the comparison of the contents obtained by both methods, it is apparent that pXRF can be used in this case for a time-saving and cost-effective mapping of soil elemental composition (Rouillon and Taylor, 2016; Šmejda et al., 2017).

4.5 Data analysis

The non-parametric Kruskal-Wallis test was used to evaluate the differences in the content of individual elements among different sites because the data was not normally distributed.

In the next step of the data examination, the contents of elements and magnetic susceptibility in the upper 10 cm soil layers in the sites were plotted onto a map using a geographical information system software (ArcGIS 10.4.1, www.esri.com) to study their spatial distribution to the known location of Early Medieval stronghold Královice.

This approach allowed for discerning areas with low and high contents of P, K, Ca, Mn, Fe, Al, Si, Cu, Ni, Zn, Sr, and Pb as well as susceptibility values that were supposed to reveal patterns important for an archaeological interpretation. The WMS view service –ZM 10 is used to get the local map, this is provided as a public view service for the Base Map of the Czech Republic 1:10000 data [https://geoportal.cuzk.cz/].

The service accomplishes technical guidance for INSPIRE (Infrastructure for Spatial Information in the European Community) view services v.3.11 and the OGC (Open Geospatial Consortium) WMS (Web Map Service) 1.1.1 and 1.3.0 standards. The projected coordinate system was S-JTSK Krovak East North which has Geographic Coordinate System GSC_S_JTSK. The Pearson correlation in STATISTICA 13. (www.statistica.io) was used to evaluate the relationship between selected elements across all the sites.

5. RESULTS

5.1 Content of the elements measured by pXRF

The spatial distribution of the contents of P, K, Ca, Mn, Zn, Cu, Fe, Al, Ni, Sr, Si, and Pb are presented in (Figures 5-7). The elements with clear accumulation in Acropolis were P, Ca, Zn, Cu (Figures 5 and 6) and for Bailey was Sr (Figure 7a). The highest mean content of P, Ca, Zn, Cu, Mn, Pb were also recorded in the Acropolis. The contents of Sr and Al were highest in the Bailey (Figures 7a and c). The content of K, Si, and Ni was similar in the Acropolis, the Bailey, and in the Control.

The statistical description of the overall content of studied elements in the three sites is presented in Table 2. There was a significant effect of area on pH and on the content of P, Ca, Zn, Cu, Mn, Sr, Pb, and Al and no effect on the content of K, Fe, Ni, Si, and Cr. The highest (6.2) pH was recorded in Acropolis followed by moderately acidic pH (5.6) in the Bailey and the lowest highly acidic pH (4.5) in the Control. The highest (0.27%) median P content was recorded in the Acropolis and the lowest (0.06%) in the Control. The highest (0.68%) Ca content was also recorded in the Acropolis and the lowest (0.31%) in the Bailey followed by a similar value (0.38%) in the Control. The highest (111 ppm) Zn content was recorded in the Acropolis and the lowest (76 ppm) in the Control. The Cu content was highest (52 ppm) in the Acropolis and the lowest (43 ppm) in both the Bailey and the Control. The highest (744 ppm) Mn content was recorded in the Acropolis and the lowest (649 ppm) in the Control and followed by a similar value (663 ppm) in the Bailey. The highest (126 ppm) Sr content was recorded in the Bailey and the lowest content (117 ppm) was recorded in the Control followed by (121 ppm) the Acropolis.

Finally, the highest (35 ppm) content of Pb was recorded in the Acropolis and the lowest (31 ppm) in the Bailey and in Control. The Control recorded overall highest (34ppm) Ni content and the lowest content of 31and 32ppm in Acropolis and Bailey.

Overall highest (3.06%) Fe content recorded in the Control and the lowest content of 2.91% and 2.92% was recorded in the Bailey and Acropolis, respectively. The Bailey recorded the highest 28.78% Si content and the lowest content of 28.19% and 28.28% was recorded in the Control and Acropolis.

Contents of P, Ca, Zn, Cu, Mn, and Pb were 1.2 – 2.3 times higher in the Acropolis in comparison to the Bailey (Table 2). Besides, the contents of P, Ca, Zn, Cu, Mn, and Pb were 1.04 to 4.5 times higher in the Acropolis compared to the Control. Contents of P, Zn and Sr were 1.08 to 2 times higher in the Bailey compared to the Control. The content of Al was higher in the Bailey and in the Control compared to the Acropolis.

5.2 Content of the elements measured by ICP

The distribution of the content of P, K, Ca, Fe, Zn, Cu, Mn, Sr, Pb, Al and Ni measured by ICP are presented in Table 3. The ICP outcome is considered the mean value of two random samples from each site. The elements with clear accumulation in Acropolis were P, K, Ca, Fe, Zn, Cu, Sr, Pb, Al, and Ni for Bailey Mn which is surprising. The content of P, K, Ca, Fe, Zn, Cu, Sr, Pb, Al, Ni is higher in Acropolis than Control and Bailey (Table 3). The content of P, K, Ca, Zn, Cu, Mn, Sr is higher in Bailey than Control. The Control has a higher content of Fe, Pb, Al, Ni than Bailey. The height content 60.6 ppm of Sr was recorded in Acropolis and the lowest 50.8 and 56.6 ppm was recorded in Control and Bailey. The high accumulation of Mn 707 ppm was recorded in Baily and lowest 593 ppm in Control. The highest P content was recorded in Acropolis and the lowest in Control as the same result with K. The content of Fe 2.27 times higher in Acropolis than Baily and 1.06 times higher in Control than Bailey. The highest Zn (88.8 ppm) content was recorded in Acropolis and the lowest 69.7 and 64.2 ppm was recorded in Bailey and Control. The content of Cu in Acropolis is 2.79 times higher than Bailey and 2.97 times higher than Control. The height content of Pb 22.8 ppm was recorded in Acropolis and the lowest content was recorded 21.1 and 19.1 ppm in Control and Bailey. The Al is surprisingly high in Acropolis 24866 ppm and 20836 ppm in Bailey and 21727 ppm in Control. The Acropolis recorded overall highest (27.1 ppm) Ni content and the lowest content 23.9 and 26.1 ppm in Bailey and Control.

5.3 Correlation between pXRF and ICP

The results obtained from the comparison of pXRF and *Aqua regia* ICP-MS revealed a strong linear correlation among the total contents of the studied elements. We obtained the following correlations for P ($r = 0.98$, $p < 0.001$), K ($r = 0.91$, $p = 0.010$), Ca ($r = 0.96$, $p = 0.002$), Fe ($r = 0.81$, $p = 0.048$), Zn ($r = 0.96$, $p = 0.001$), Cu ($r = 0.94$, $p = 0.004$), Mn ($r = 0.98$, $p < 0.001$), Sr ($r = 0.93$, $p = 0.006$), Pb ($r = 0.78$, $p = 0.062$), Al ($r = 0.45$, $p = 0.372$), and Ni ($r = 0.88$, $p = 0.018$: Figures 2-4). There is a strong correlation of P, K, Ca, Zn, Cu, Mn, Sr and Ni. However, the correlation of Al is not much significant. The Ni and Fe has relatively lower coefficient value.

5.4 Geophysical measurements

The highest ($73.8 \times 10^{-8} m^3/kg$) susceptibility was recorded in the soil from the Acropolis and the lowest ($54 \times 10^{-8} m^3/kg$) in the Control (Figure 8). An increase in magnetic susceptibility of $19.8 \times 10^{-8} m^3/kg$ in the Acropolis in comparison to the pedogenic origin of the Control strongly indicates the sum of anthropogenic stresses on the soils.

Table 2: Median content (± standard deviation) of elements and pH of soil samples. The p-value for each element was obtained by the Kruskal Wallis test. Median values with the same letters were significantly not different.

Site	**Macroelements**				**Microelements**				**Other elements**					
	P [%]	K [%]	Ca [%]	Ca:P Ratio	Fe [%]	Zn [ppm]	Cu [ppm]	Mn [ppm]	Sr [ppm]	Pb [ppm]	Al [%]	Ni [ppm]	Si [%]	pH [H_2O]
Acropolis	0.27 ± 0.06a	2.09 ± 0.09a	0.68 ± 0.27a	2.52	2.92 ± 0.27a	111 ± 23.5a	52 ± 5.3a	744 ± 100a	121± 3.9a	35 ± 4.2a	6.31 ± 0.5a	31 ± 5.8a	28.28 ± 1.2 a	6.2 ± 0.5 a
Bailey	0.12 ± 0.05b	2.11 ± 0.05a	0.31 ± 0.17b	2.58	2.91 ± 0.14a	83 ± 3.8b	43 ± 3.5b	663 ± 49b	126 ± 2b	31 ± 2.1b	7.09 ± 0.3b	32 ± 4.9a	28.78 ± 0.9 a	5.6 ± 0.3b
Control	0.06 ± 0.01c	2.06 ± 0.08a	0.38 ± 0.38b	6.33	3.06 ± 0.18a	76 ± 3.7c	43 ± 3.8b	649 ± 48b	117 ± 6.9a	31 ± 1.8b	7.02 ± 0.5b	34 ± 3.2a	28.19 ± 1.2 a	4.5 ± 0.27c
p-value	< 0.001	0.064	< 0.001	-	0.05	< 0.001	< 0.001	0.027	< 0.001	< 0.001	< 0.001	0.093	0.256	< 0.001

Table 3: The content of elements selected by two random values of each site and measured by ICP

Elements	Acropolis(ppm)	Bailey (ppm)	Control (ppm)
P	1787	1048	616
K	5029	4301	3930
Ca	3909	2826	2768
Fe	54771	24091	25472
Zn	88.8	69.7	64.2
Cu	61.7	22.1	20.8
Mn	656	707	593
Sr	60.6	56.6	50.8
Pb	22.8	19.1	21.1
Al	24866	20836	21727
Ni	27.1	23.9	26.1

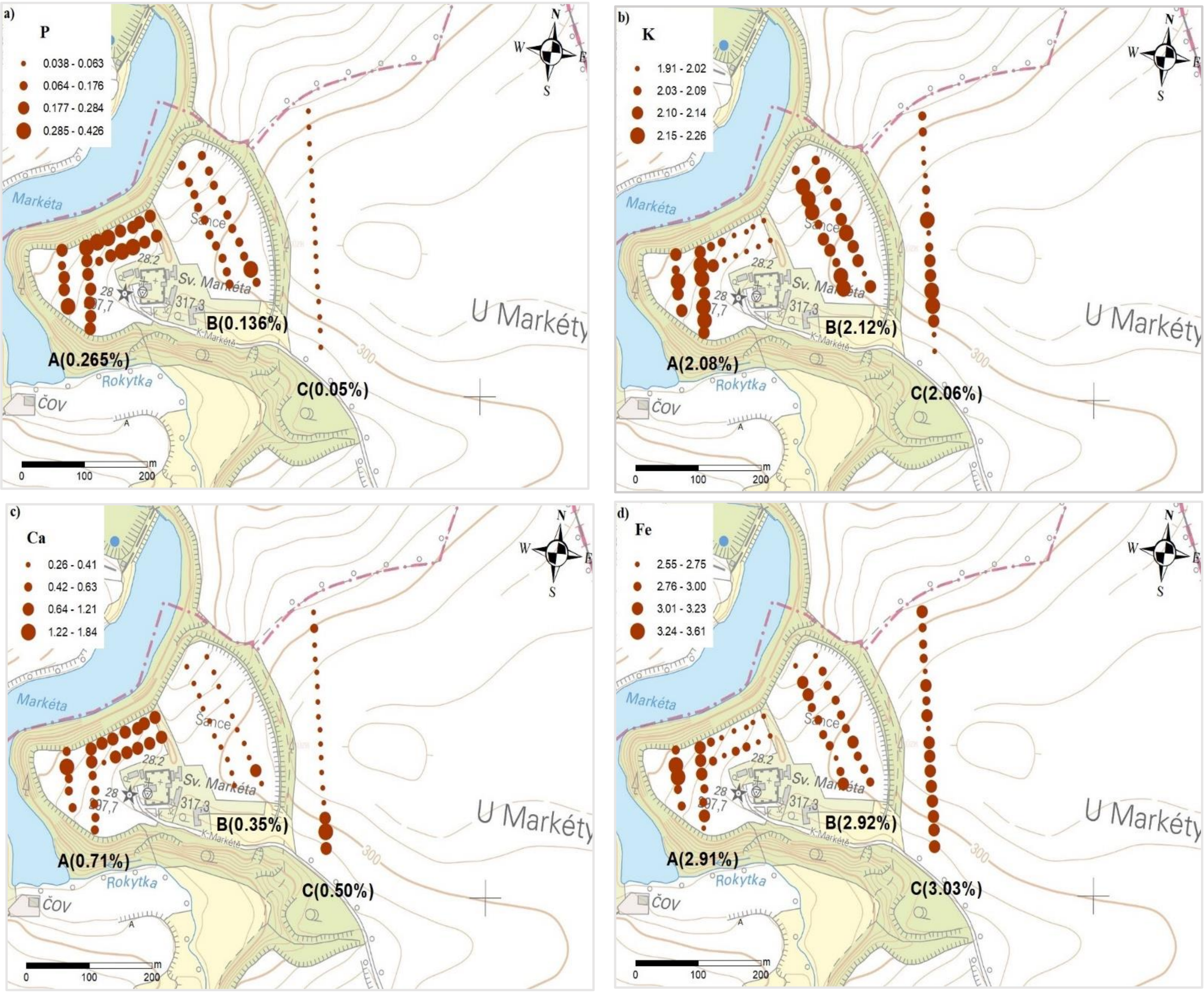

Figure 5: Content of P (a), K (b), Ca (c), and Fe (d) in studied areas A(Acropolis), B(Bailey), and C(Control). Numbers printed in bold (in %) represent the mean value over the studied areas.

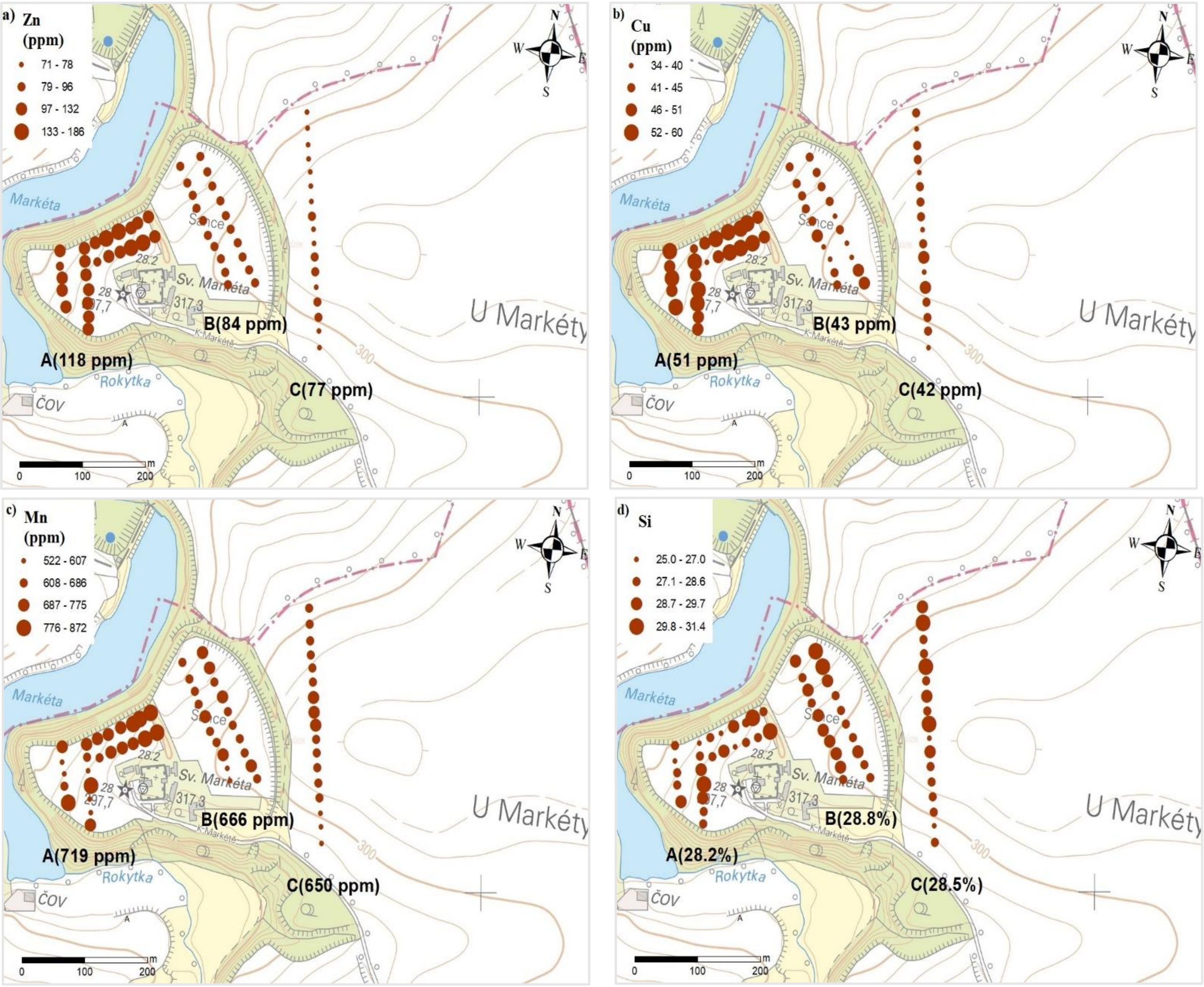

Figure 6: Content of Zn (a), Cu (b), Mn (c), and Si (d) in studied areas A(Acropolis), B(Bailey), and C(Control). Numbers printed in bold (in ppm or in %) represent the mean value over the studied areas.

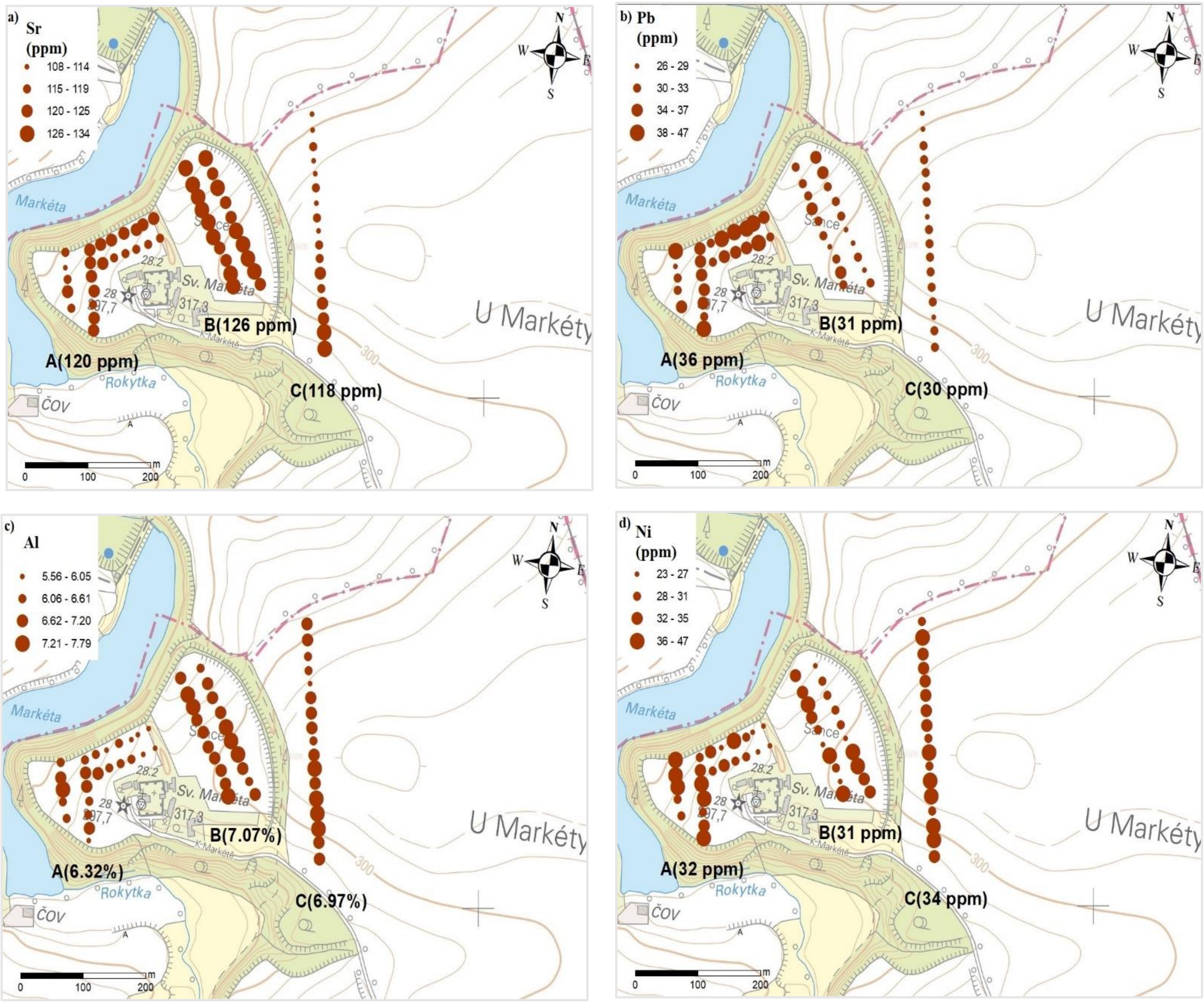

Figure 7: Content of Sr (a), Pb (b), Al (c), and Ni (d) in studied areas A(Acropolis), B(Bailey), and C(Control). Numbers printed in bold (in ppm or in %) represent the mean value over the studied areas.

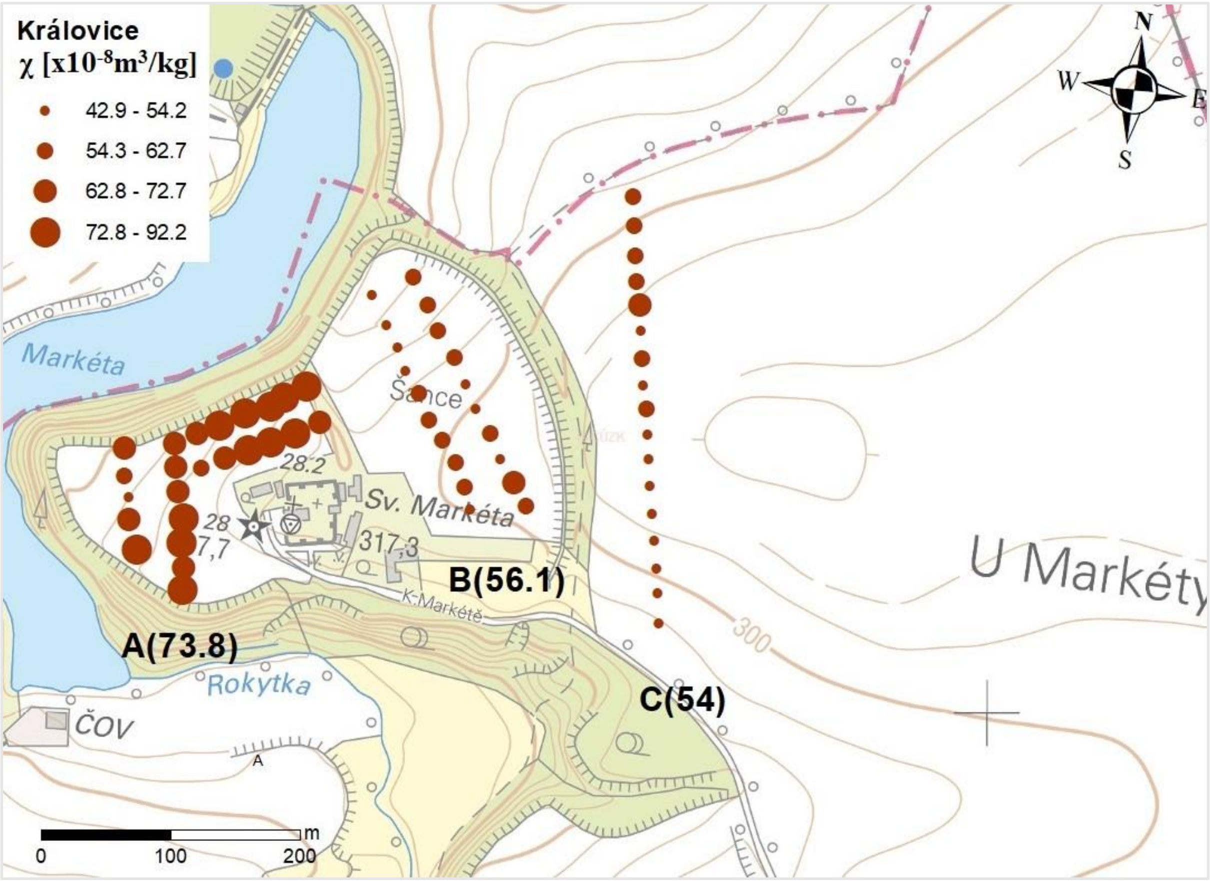

Figure 8: Distribution of the mass-specific magnetic susceptibility (χ x10-8m3/kg) for the sampled sites. .

5.5 Correlation between P and Other elements

There was a significant positive correlation between P and Ca, Mn, Cu, Zn, and Pb contents and no significant correlation in the case of Sr (Figures 9 and 10). The correlation ($r=0.44$, $p<0.001$) between P and Ca. The highest correlation ($r=0.86$, $p< 0.001$) was recorded between P and Zn and the lowest ($r=0.03$, $p=0.796$) recorded between P and Sr. The correlation ($r=0.75$, $p<0.001$) was recorded P and Cu. The correlation between P and Mn was ($r=0.48$, $p<0.001$) The correlation between P and Pb was recorded ($r=0.60$, $p<0.01$). There was a negative correlation recorded between Ca and Si ($r=-0.60$, $p< 0.001$; Figure 9a and 10c).

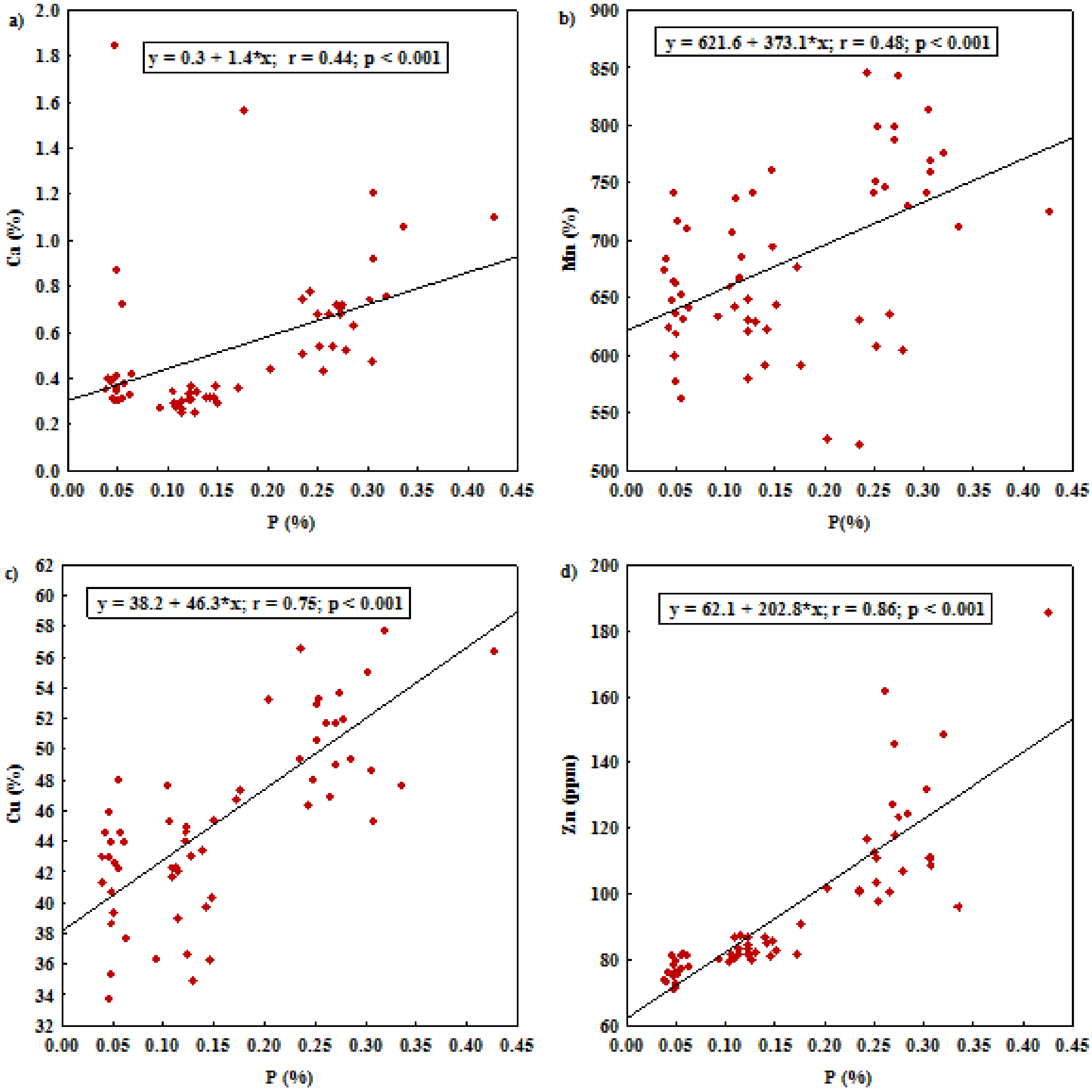

Figure 9: Relationship between P and Ca (a), Mn (b), Cu (c), and Zn (d).

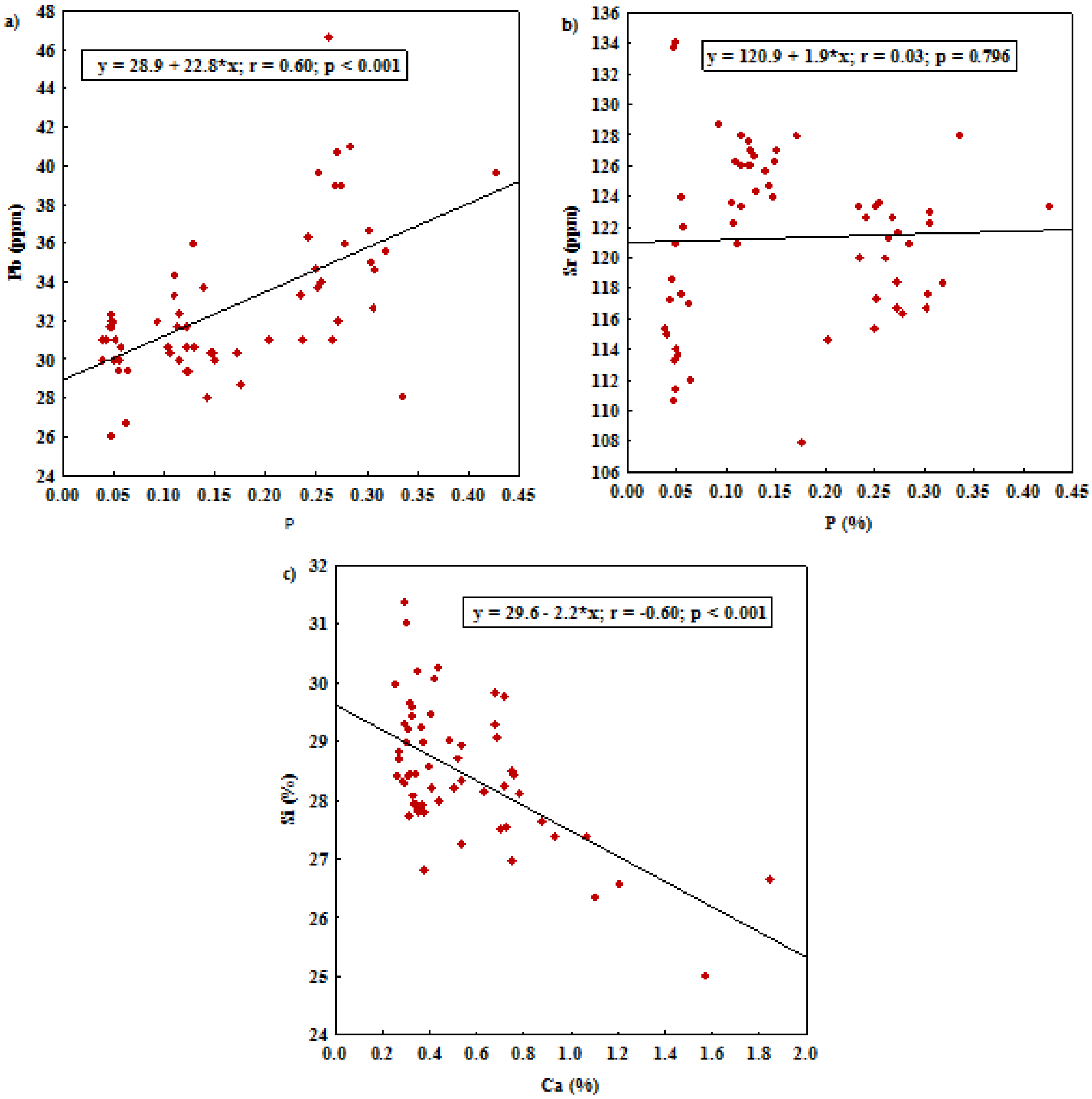

Figure 10: Relationship between P and Pb (a), P and Sr (b), and Ca and Si (c). .

6 DISCUSSION

6.1 Geochemical record of Anthropogenic elements

Although the stronghold Královice was settled for approximately 300 years, the chemical signatures in the soil are well preserved even after approximately 700 years of abandonment. The increased pH and contents of P, Ca, Mn, Zn, Cu, Pb, and Sr are visible in the Acropolis and Bailey in comparison to the Control**.** However, the signatures of these elements were very visible in the Acropolis than the Bailey. The significant enrichment may indicate that there was a high intensity of human activities in the Acropolis. This is evident in the homogenous spatial distribution of P, Ca, Mn, Zn, Cu, and Pb. The accumulation of P, Ca, Mn, Zn, and Cu in the past settlement sites relates to the deposition of organic waste (Šmejda et al., 2017), manure and ash (Holliday and Gartner, 2007; von Oheimb et al., 2010).

Although the content of Pb was significantly higher in the Acropolis, it is not supposed to demonstrate any form of intensive metallurgy as occurred in many past settlement sites. The relatively high content of Pb in all three sites resulted from recent deposition of Pb through Pb-gasoline in the period since 1929s to 2000 in the Czech Republic (Hejcman et al., 2013b).

In the Bailey, there was a clear spatial distribution of P, Zn, and Sr in comparison to the Control. The contamination of Sr as a results of biomass ashes, Entwistle (1998) was reported Sr accumulation in biomass ash in the past settlements. However, there were relatively similar patterns of distribution for Ca, Pb, Mn, and Cu.in the Bailey and Control.

The distribution of Si, Ni, Fe, and K was similar in all the three studied sites, probably reflecting the natural geology. I can therefore conclude that 300 hundred years of past human activities has substantially increased the content of P, Ca, Mn, Zn, Cu, Pb, Sr.in the soil. Nevertheless, the wooden houses, ash, burning wood, burning pottery, burning of wooden buildings were adequately intensive as observed in the case of the Acropolis.

Even though the geology of the three sites is the same, the susceptibility of these sites varies greatly. The variation in the high susceptibility of the Acropolis and Bailey in comparison to the Control was caused by an anthropogenic input of magnetic materials. At each sampled location of the settlement sites, high susceptibility values coincided with a high content of studied elements especially P, Ca, Zn, Cu, and Pb in the Acropolis and Bailey in comparison to the Control. These elements were found to be concentrated in an area with magnetism (Hopke et al., 1980), thus higher susceptibility in this study can be used as an indicator of past settlement activities.

In this, the content of Ca, Mn, Cu, Zn, and Pb correlated with P and can be used as an indicator of past settlement activities based on the order of increasing correlation coefficient. These elements again have relatively similar sources as P in the past settlement sites.

According to the previous studies of prehistoric settlement sites in the Czech Republic (Hejcman et al., 2011), the content of the studied elements particularly Ca, Zn, Cu, Mn was substantially higher even in a comparably shorter period. The higher content of these elements especially in the Acropolis indicates intensive settlement activities with a probability of a high number of the human population. Such information can help to find the size of human population on this settlement.

6.2 Intensity of settlement activities

The Královice stronghold shows a significant result that is much better than the other stronghold Dřevíč analysis by Asare et al., (2020). The signature recorded in Acropolis is marginally higher than in Control and Bailey. The common indicators of settlements activities such as P, Ca, Zn and Cu are much stronger in Acropolis than the Bailey and Control. That clearly shows a high intensity of human settlement. Mn considered as a good indicator of human activities (Nielsen and Kristiansen, 2014) for example, organic matter (Da Costa and Kern, 1999), organic waste (Wilson et al., 2008) or a product of burning (Linderholm and Lundberg, 1994). In this context, the accumulation of Mn is high in Acropolis area which positively indicates human activities in the past. The soil calcium (Ca) play a key role and consider as an indicator of food preparation area of the past, it is contained the ash of the burning charcoal and high content in teeth and bone (Vranová et al., 2015).

However, the significant amount of Ca in the Acropolis area compared with the Bailey and Control is a good indication of past settlement. Furthermore, the strong correlation between P and Ca provides evidence of settlement activities

Copper (Cu) is also stable element and more mobile than P in the soil (Fontes and Gomes, 2003). The amount of Cu in the Acropolis area is higher than in the Bailey and Control area which is a strong indication of settlement. Zinc(Zn) is usually correlated to agricultural disturbance of the soil environment (Klimek, 2002), archaeological feature (Linderholm and Lundberg, 1994; Wilson et al., 2006), burning as part of ash (Nielsen and Kristiansen, 2014) and it could increase in the vicinity of buildings (Lewis et al., 1993). The accumulation of Zn is high in the Acropolis area compare with the Bailey and Control, so it obvious that the past human activities enrich the soil Zn.

Moreover, K is related to settlement activities such as waste and ash deposition (Entwistle et al., 1998,2000; Misarti et al., 2011), burning and manuring (Wilson et al., 2009). The accumulation of K is not significant between three sites but slightly higher accumulated in Bailey. This could be caused by the deposition of the biomass ashes. In the past, the ashes were used in as the fertilizer on gardens and therefore deposited close to former houses (Janovský et al., 2020).

The Pb play a significant role in archaeological soils as it is an indicator of clays and organic matters. The difference in the accumulation of Pb between the sites is not obvious, however, I observed a little bit higher accumulation of Pb in the Acropolis area. The high amount of Sr is found in the Bailey area which specifies that this area could be used for household waste.

There is not much known about Al in archaeological sites as it was not commercially produced until 1886 (Rodgers, 2004). The increasing trend of Mn is visible, 1.12% higher in Acropolis than Bailey though it is not considered as a reliable element to know the settlement activities (Bintliff et al., 1990). However, the contamination of Ni and Si is relatively the same in the Acropolis, Bailey, and Control. It is important to note that, the bare limitation of the results is the absence of S and Mg in the soil which is surprising.

The result of the correlation between pXRF and ICP provides the accuracy of measurement and in this experiment the correlation of P, K, Ca, Fe, Zn, Mn, Cu, and Sr except Al and Pb are highly significant. The burning activities and fires could be the reasons of high magnetic susceptibility in the soil (Tite and Mullins, 1971) and the high magnetic susceptibility in Acropolis area indicate there were some burning activities happened in the past. The results distinctly show that different human settlement activities change the contamination of different elements in the soil even though the settlement was for a short period time.

7 CONCLUSIONS

The main home take message of the thesis is 1) that 300 years of human settlement activities was enough long period to create a strong chemical signature of anthropogenic soils in the former stronghold. 2) Intensity of chemical signature was different for Acropolis and Bailey indicating that Bailey was substantially less settled than Acropolis. 3) Chemical signatures recorded in the stronghold was much stronger than in the case of desert medieval villages. This clearly indicates much intensive settlement activities in the stronghold in comparison to deserted villages. 4) Strongholds were thus areas with extraordinary settlement activities and with high density of humans. How many people lived in the stronghold I was not able to identify as it is unknown how much sediments were eroded and precisely to quantify the amount of accumulated phosphorus but this study will provide additional information for further research.

The research has demonstrated that the elemental composition of anthropogenic soils is enabled to estimate the intensity of past settlement activities. In this research, I expected that the accumulation of different elements is a good indicator of past human settlement activities and it also affects the anthropogenic soil. In additionally, the pXRF could be an ideal tool to analyse the archaeological soil to disclose the past settlement activities without excavation the archaeological sites. Furthermore, the effectiveness of the data of anthropogenic elements of this experiment has been revealed by its ability to test conjecture about the human activities on the study area Královice. Moreover, the obtained data allows for a meaningful and theoretical discussion about the human settlement activities and could be the first step to count the number of people used to live there and find out their way of life.

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9 APPENDIX 1

Appendix 1-1: The obtained data from Acropolis with Magnetic Susceptibility.

sonda	category	Mass[g]	F1 KRe[S	F3 KRe[S	χ [x10^{-8}m^{3}/k	kFD13	F1-F3/m	Al	Si	P	K	Ca	Mn	Fe	Ni	Cu	Zn	Sr	Pb
38	acropolis	38.134	0.00252	0.00231	66.082761	8.45238	0.55856	6.14667	27.2533	0.252	2.09353	0.53813	0.07507	2.85083	0.00363	0.0053	0.01107	0.01173	0.00397
39	acropolis	28.6119	0.00157	0.00144	54.732471	8.3014	0.45436	6.68667	25.0233	0.17613	2.08627	1.56377	0.0591	3.44543	0.00367	0.00473	0.0091	0.0108	0.00287
40	acropolis	47.0257	0.00245	0.00225	52.120436	8.24153	0.42955	7.33667	27.99	0.2029	2.25813	0.4391	0.05277	3.60633	0.00473	0.00533	0.0102	0.01147	0.0031
41	acropolis	32.1716	0.00224	0.00205	69.595544	8.61992	0.59991	6.25667	28.3367	0.26457	2.11667	0.5379	0.06353	2.99623	0.0029	0.0047	0.01007	0.01213	0.0031
42	acropolis	43.83	0.00362	0.00331	82.523386	8.46005	0.69815	6.38	29.04	0.3036	2.12823	0.47637	0.0814	2.88543	0.003	0.00587	0.0111	0.01177	0.0035
43	acropolis	44.5166	0.00346	0.00316	77.633961	8.44907	0.65594	5.79333	28.1567	0.28437	2.11237	0.62847	0.0731	2.56687	0.0039	0.00493	0.01247	0.0121	0.0041
44	acropolis	46.4129	0.00298	0.00277	69.008783	8.1941	0.56547	6.99333	28.22	0.2353	2.1967	0.5032	0.05223	3.1561	0.0032	0.00493	0.01003	0.012	0.0031
45	acropolis	48.0979	0.0035	0.00326	78.569191	7.97586	0.62666	6.54333	28.72	0.27833	2.23677	0.5193	0.0605	2.92203	0.0029	0.0052	0.0107	0.01163	0.0036
46	acropolis	33.3236	0.00268	0.00246	80.51351	8.1625	0.65719	6.56333	30.2767	0.25433	2.13297	0.43083	0.07983	2.98463	0.00387	0.00533	0.0098	0.01237	0.0034
47	acropolis	46.5517	0.0031	0.00286	69.608923	8.66716	0.60331	6.78	28.9267	0.25117	2.18013	0.53817	0.06073	3.14243	0.0039	0.00507	0.01033	0.01233	0.00337
48	acropolis	13.167	0.00096	0.00087	72.696894	8.62934	0.62733	7.02333	28.49	0.23507	2.19537	0.74547	0.06303	3.18053	0.00333	0.00567	0.01013	0.01233	0.00333
49	acropolis	44.0713	0.00311	0.00285	70.658229	8.34939	0.58995	6.5	26.57	0.30657	2.09697	1.20547	0.07687	3.124	0.00307	0.00453	0.01087	0.01223	0.00347
50	acropolis	47.5116	0.00344	0.00315	72.466513	8.59715	0.62301	6.36	27.3767	0.30637	2.07077	0.92673	0.07603	2.9982	0.00317	0.00487	0.01107	0.0123	0.00327
51	acropolis	40.9743	0.00316	0.00291	77.170324	7.87476	0.6077	5.56333	26.3267	0.42617	2.0397	1.1012	0.07257	2.75287	0.00237	0.00563	0.0186	0.01233	0.00397
52	acropolis	10.8951	0.001	0.00094	92.151518	6.74303	0.62138	6.15333	29.2967	0.26107	1.99833	0.67507	0.07467	2.75417	0.0038	0.00517	0.01617	0.012	0.00467
53	acropolis	43.2653	0.00344	0.00315	79.393879	8.18049	0.64948	5.60667	28.2233	0.27433	2.0018	0.72037	0.0843	2.60993	0.0028	0.00537	0.01233	0.01217	0.0039
54	acropolis	44.998	0.00379	0.00348	84.225966	8.15303	0.6867	5.79	29.77	0.26877	1.9755	0.7185	0.0872	2.59173	0.00267	0.00597	0.01277	0.01227	0.0039
55	acropolis	43.5929	0.00335	0.00307	76.893256	8.35322	0.64231	5.65	28.1167	0.24207	2.0207	0.77973	0.08467	2.66903	0.0024	0.00463	0.01167	0.01227	0.00363
56	acropolis	38.1581	0.00278	0.00254	70.628537	9.07821	0.64118	5.89333	29.83	0.27133	2.00593	0.67933	0.07987	2.57013	0.00267	0.0049	0.0118	0.01183	0.0032
57	acropolis	42.5293	0.00344	0.00316	80.979466	8.3043	0.67248	5.93667	27.5033	0.27113	1.993	0.70423	0.07867	2.74923	0.00235	0.00517	0.0146	0.01167	0.00407
58	acropolis	23.4917	0.00205	0.00186	87.094591	9.18866	0.80028	6.39667	28.4333	0.31873	2.0218	0.75957	0.07753	2.95737	0.00307	0.00577	0.01483	0.01183	0.00357
59	acropolis	40.6	0.00332	0.00303	81.650246	8.50679	0.69458	6.26667	26.99	0.30197	1.98227	0.74657	0.0741	2.9101	0.00303	0.0055	0.0132	0.01167	0.00367
60	acropolis	38.7888	0.00269	0.00246	69.324135	8.66493	0.60069	6.13667	29.0467	0.2487	1.9091	0.68147	0.0741	2.5536	0.00333	0.0048	0.01127	0.01153	0.00347
61	acropolis	42.9536	0.00238	0.00218	55.47847	8.35082	0.46329	6.89333	28.45	0.12973	2.1164	0.34113	0.06283	2.96983	0.0031	0.0035	0.00823	0.01243	0.00307

Appendix 1-2: The obtained data from Control with Magnetic Susceptibility.

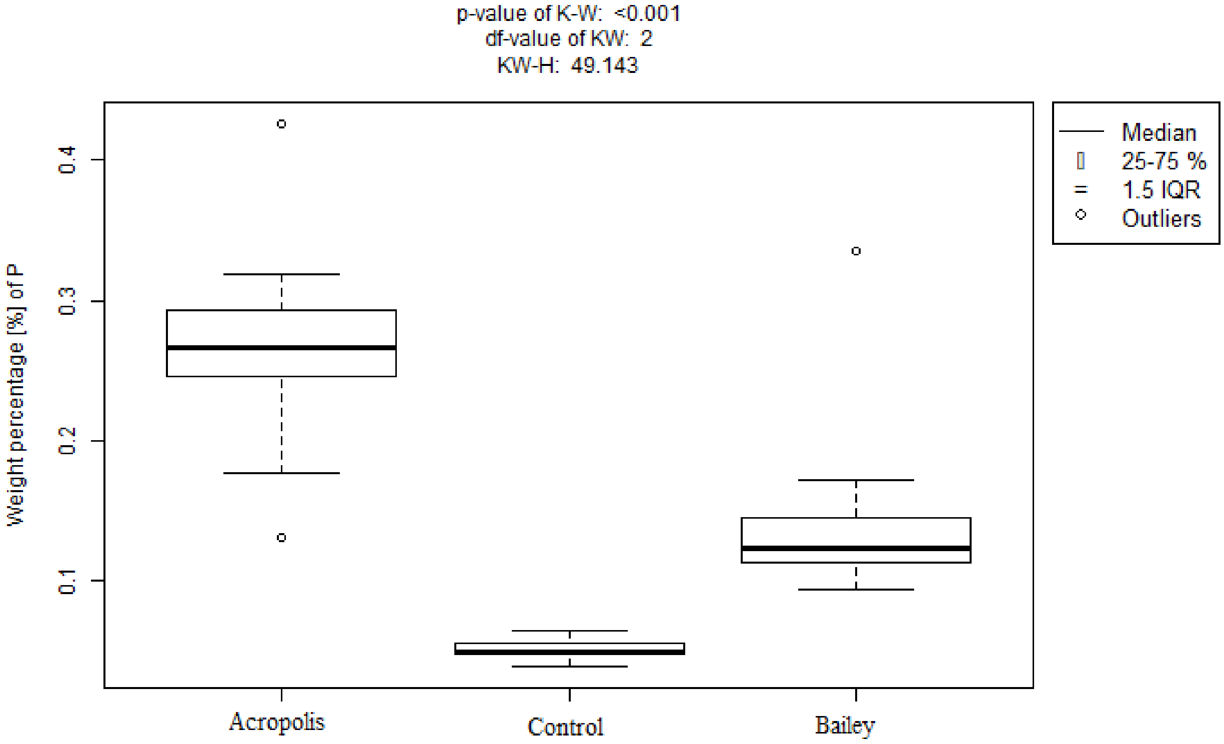
sonda	category	Mass[g]	F1 KRe[SI]	F3 KRe[SI]	χ [x10^{-8}m^3/kg]	kFD13	F1-F3/m	Al	Si	P	K	Ca	Mn	Fe	Ni	Cu	Zn	Sr	Pb
1	control	42.9461	0.002393	0.002181	55.72100843	8.85917	0.49364	7	29.4667	0.04683	2.0669	0.3999	0.06647	3.03373	0.00313	0.0043	0.00747	0.01133	0.0026
2	control	47.3184	0.002732	0.002498	57.73652533	8.56515	0.49452	6.72	30.0833	0.06327	2.04977	0.41503	0.06423	2.91707	0.0038	0.00377	0.0078	0.0112	0.00293
3	control	38.1616	0.002156	0.001964	56.49658295	8.90538	0.50312	6.61	28.58	0.03917	1.98187	0.3963	0.06853	2.9802	0.00343	0.0043	0.0073	0.0115	0.0031
4	control	40.07	0.002285	0.00209	57.02520589	8.53392	0.48665	6.18667	28.1967	0.04853	1.98383	0.40657	0.06627	2.8676	0.00317	0.0044	0.00713	0.0114	0.00323
5	control	12.8225	0.000825	0.000746	64.34782609	9.58672	0.61688	6.05333	30.1967	0.0484	1.9118	0.3445	0.0637	2.61133	0.00323	0.00353	0.0076	0.01113	0.00317
6	control	42.7935	0.002188	0.002011	51.12926028	8.08958	0.41361	6.84	27.8233	0.03805	2.06347	0.35447	0.06743	3.08917	0.0033	0.00413	0.00737	0.01153	0.003
7	control	37.3616	0.002274	0.00208	60.86463107	8.53122	0.51925	6.89	29.01	0.05147	1.99967	0.30227	0.0717	2.9899	0.00323	0.00427	0.00753	0.01137	0.0031
8	control	36.5186	0.001891	0.00174	51.78183172	7.98519	0.41349	6.95	28.0767	0.06143	2.1564	0.33023	0.07113	3.1138	0.00353	0.0044	0.0081	0.0117	0.00267
9	control	39.6599	0.002451	0.00224	61.8004584	8.60873	0.53202	6.28667	31.0067	0.04673	1.96843	0.3012	0.07423	2.66987	0.0031	0.00337	0.00707	0.01107	0.0032
10	control	44.3578	0.002311	0.002123	52.09906713	8.13501	0.42383	7.14667	26.8033	0.04237	2.0693	0.3801	0.06237	3.21517	0.00367	0.00447	0.0076	0.01173	0.0031
11	control	44.0876	0.002325	0.00215	52.73591667	7.52688	0.39694	7.66333	29.2333	0.0458	2.10463	0.30937	0.06487	3.09987	0.0031	0.0046	0.00813	0.01187	0.00317
12	control	39.1999	0.001959	0.001794	49.97461728	8.42266	0.42092	7.08667	27.7867	0.0496	2.14133	0.35697	0.06197	3.0626	0.0037	0.00393	0.00797	0.0121	0.003
13	control	41.622	0.002208	0.002014	53.04886839	8.78623	0.4661	7.79333	28.4567	0.05497	2.1721	0.3125	0.0653	3.2034	0.0039	0.0048	0.0077	0.01177	0.003
14	control	38.2361	0.00189	0.001735	49.4297274	8.20106	0.40538	7.40667	27.7967	0.05687	2.15733	0.3789	0.0633	3.23267	0.0029	0.00447	0.0082	0.0122	0.00307
15	control	40.2376	0.002027	0.001885	50.37576794	7.00543	0.3529	7.55667	27.5533	0.05517	2.1187	0.72367	0.05617	3.21843	0.00397	0.00423	0.00813	0.0124	0.00293
16	control	44.3858	0.001906	0.001788	42.94166152	6.19098	0.26585	7.04	26.6533	0.0473	1.9805	1.84247	0.06003	3.14097	0.0037	0.00407	0.00783	0.01337	0.00317
17	control	45.0359	0.002276	0.002123	50.53746012	6.72232	0.33973	7.17333	27.6333	0.049	2.02407	0.87517	0.05763	3.0314	0.00337	0.00387	0.00723	0.0134	0.0032

Appendix 1-3: The obtained data from Bailey with Magnetic Susceptibility.

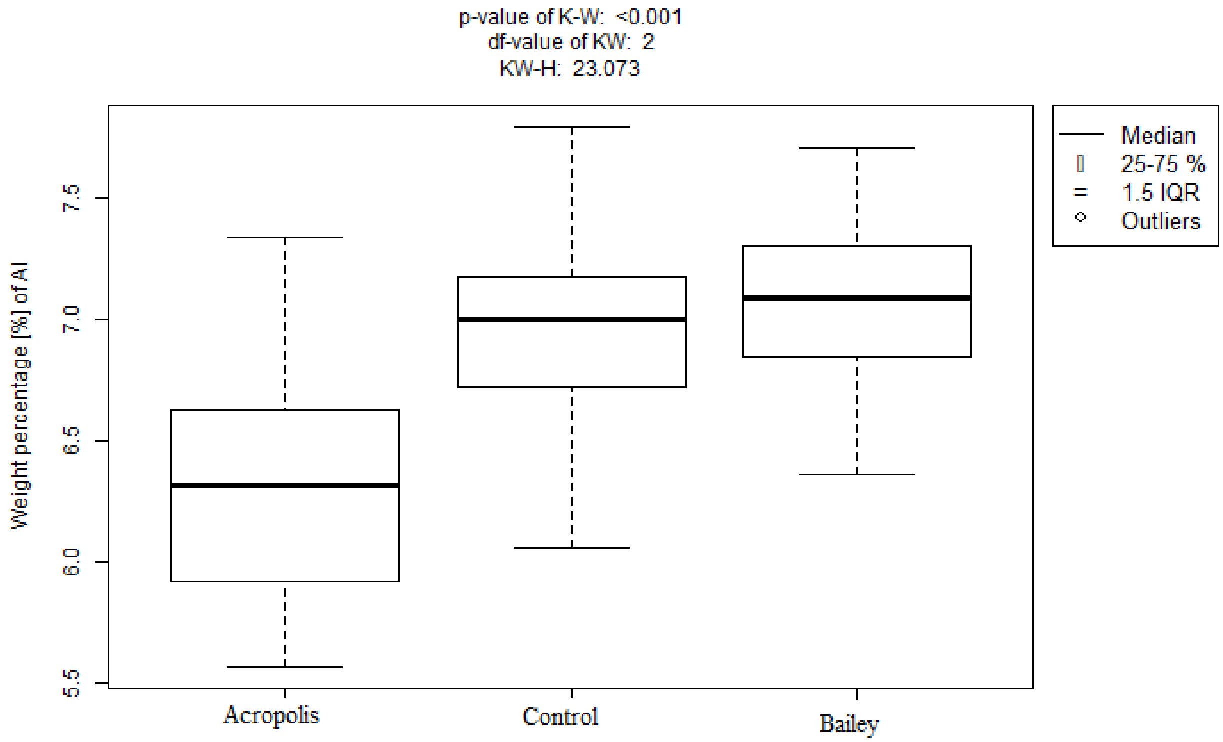
sonda	category	Mass[g]	F1 KRe[S	F3 KRe[S	χ [x10^{-8}m^{3}/l	kFD13	F1-F3/m	Al	Si	P	K	Ca	Mn	Fe	Ni	Cu	Zn	Sr	Pb
18	bailey	42.6044	0.00259	0.00239	60.83879	7.87037	0.47882	7.12	27.9133	0.1043	2.09853	0.33987	0.06593	2.97107	0.0035	0.00477	0.00793	0.01237	0.00307
19	bailey	12.17	0.00081	0.00074	66.68858	9.14243	0.6097	6.54333	27.3833	0.33543	2.01707	1.05963	0.0713	2.96343	0.00327	0.00477	0.0096	0.0128	0.0028
20	bailey	44.6657	0.00241	0.00222	53.86684	7.85536	0.42314	7.14667	28.72	0.09253	2.11513	0.268	0.0634	2.98583	0.00363	0.00363	0.008	0.01287	0.0032
21	bailey	43.9393	0.00245	0.00226	55.80426	7.95269	0.44379	7.40333	27.7267	0.1238	2.1269	0.31227	0.0649	3.0466	0.00367	0.00367	0.00843	0.0126	0.00293
22	bailey	46.3027	0.00248	0.00229	53.4958	7.67057	0.41034	7.33667	28.4133	0.12283	2.1679	0.3109	0.06217	3.00323	0.0025	0.0044	0.0082	0.0126	0.00293
23	bailey	44.3451	0.00234	0.00216	52.67775	7.49144	0.39463	7.29	28.42	0.11443	2.09253	0.25623	0.0666	2.92237	0.0028	0.0039	0.00837	0.01233	0.003
24	bailey	39.0477	0.00223	0.00205	57.08403	7.85105	0.44817	7.05	28.2967	0.10653	2.1217	0.29257	0.07073	2.89933	0.00303	0.00453	0.00817	0.01223	0.00303
25	bailey	43.8892	0.00259	0.00238	58.89832	7.89168	0.46481	6.87333	29.22	0.11363	2.0619	0.3053	0.06683	2.79937	0.00303	0.00423	0.0082	0.0126	0.00317
26	bailey	46.355	0.00254	0.00234	54.68666	7.57396	0.41419	7.04667	31.38	0.1102	2.16407	0.28767	0.07367	2.87477	0.0028	0.00423	0.00803	0.0121	0.00343
27	bailey	40.8367	0.00226	0.0021	55.34238	7.25664	0.4016	6.36	29.97	0.12723	2.07567	0.2555	0.0741	2.5836	0.0026	0.0043	0.008	0.01267	0.0036
28	bailey	51.1575	0.00242	0.00227	47.38308	6.55941	0.3108	6.94333	29.3133	0.15093	2.08287	0.2932	0.06437	2.75157	0.0032	0.00453	0.00827	0.0127	0.003
29	bailey	39.2634	0.00175	0.00163	44.67265	6.95553	0.31072	7.67333	27.9533	0.12253	2.17307	0.33493	0.06303	3.18743	0.00327	0.00447	0.00837	0.01277	0.00307
30	bailey	46.722	0.00237	0.00221	50.78978	6.8268	0.34673	7.70333	28.83	0.11487	2.15663	0.27057	0.06857	3.11647	0.00363	0.0042	0.00877	0.0128	0.00323
31	bailey	45.6583	0.00248	0.00228	54.20701	8.08081	0.43804	6.91	28.34	0.10933	2.16757	0.28003	0.06413	2.9713	0.00337	0.00417	0.00867	0.01263	0.00333
32	bailey	46.8051	0.00293	0.00271	62.68548	7.80504	0.48926	7.15333	29.0133	0.14847	2.0688	0.3704	0.06943	2.88413	0.0031	0.00403	0.0086	0.01263	0.00303
33	bailey	13.0353	0.00077	0.0007	59.24681	9.10268	0.5393	6.81667	29.2567	0.17143	2.1042	0.36123	0.06757	2.82387	0.0025	0.00467	0.0082	0.0128	0.00303
34	bailey	54.1306	0.00318	0.00292	58.74681	8.1761	0.48032	7.19667	29.6733	0.14223	2.11307	0.31787	0.0622	2.8175	0.00407	0.00397	0.00853	0.01247	0.0028
35	bailey	39.5824	0.00245	0.00224	61.99725	8.88346	0.55075	6.73	29.6033	0.14657	2.06397	0.32167	0.07607	2.73677	0.00275	0.00363	0.00813	0.0124	0.00303
36	bailey	13.1707	0.00078	0.00071	59.10848	9.44123	0.55806	6.74667	29.4433	0.13927	2.1687	0.32053	0.0591	2.90237	0.00225	0.00433	0.0087	0.01257	0.00337
37	bailey	55.4662	0.00295	0.00271	53.13146	8.04208	0.42729	7.30667	27.9067	0.1231	2.17687	0.3675	0.05793	3.1096	0.0038	0.0045	0.00867	0.0127	0.00317

Appendix 1-4: The boxplot showing content of a) P, b) Al, c) K, d) Mn, e) Fe, f) Ni, g) Zn, h) Pb, i) Sr, j) Ca, k) Cu, l) Si obtained by Kruskal-Wallis test.

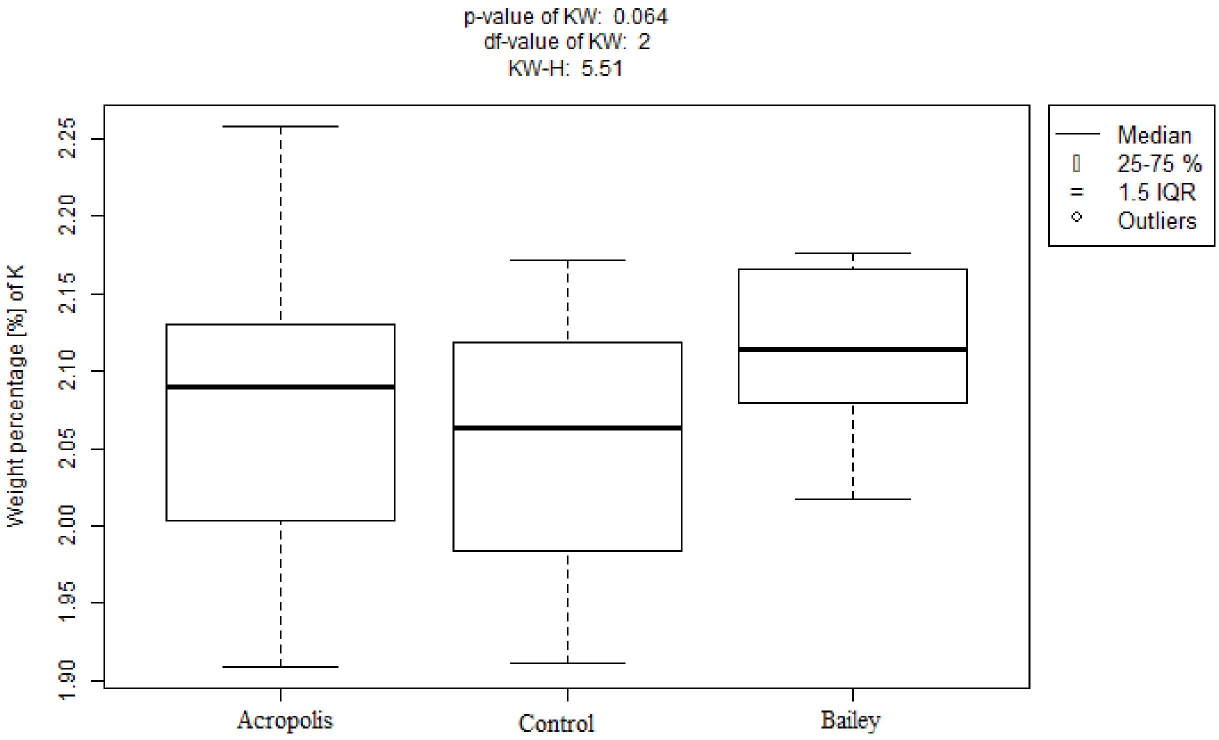
a)



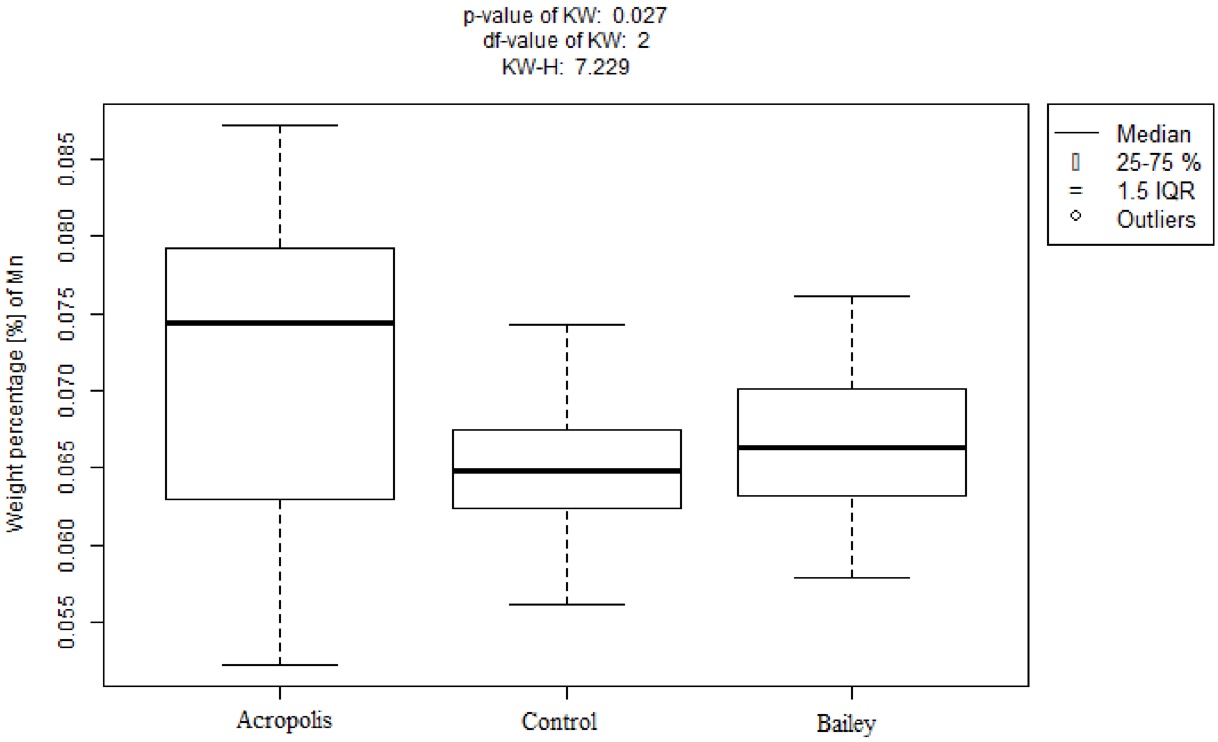
b)


p-value of K-W: <0.001
df-value of KW: 2
KW-H: 23.073
Weight percentage [%] of Al
5.5
6.0
6.5
7.0
7.5
Acropolis
Control
Bailey
Median
25-75 %
1.5 IQR
Outliers

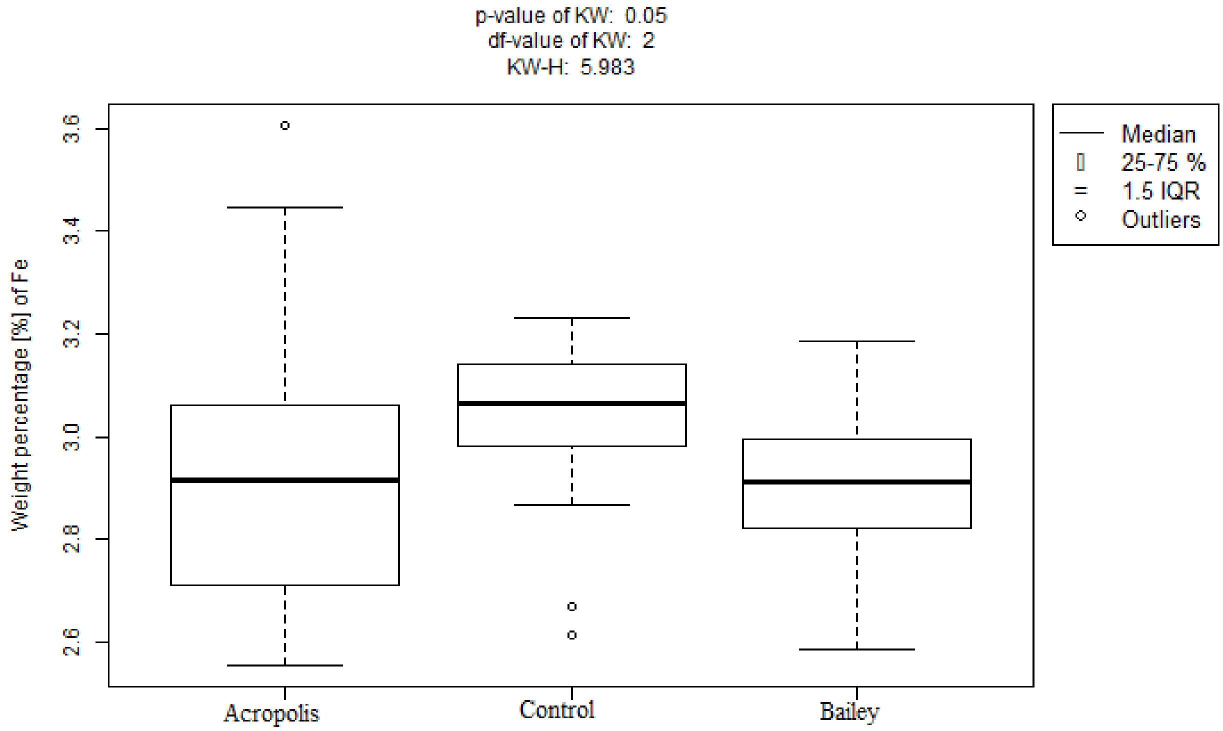
c)


p-value of KW: 0.064
df-value of KW: 2
KW-H: 5.51
Weight percentage [%] of K
1.90
1.95
2.00
2.05
2.10
2.15
2.20
2.25
Acropolis
Control
Bailey
Median
▯ 25-75 %
= 1.5 IQR
◦ Outliers

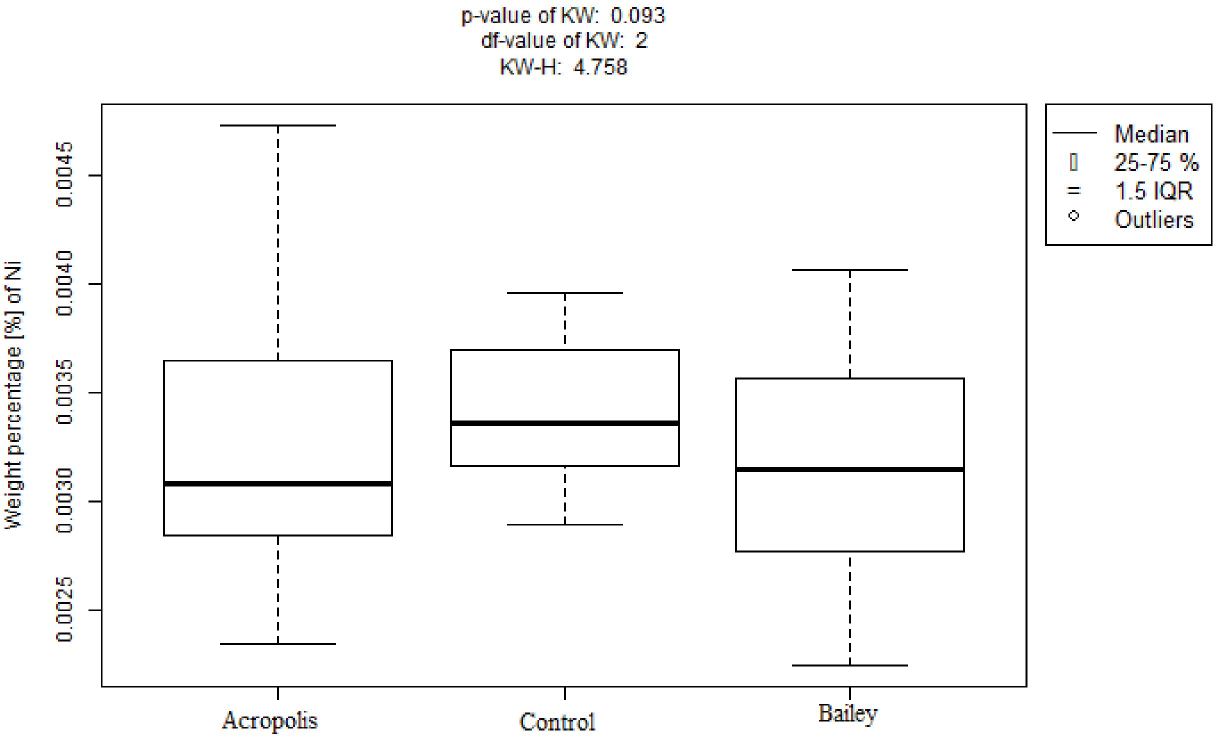
d)


p-value of KW: 0.027
df-value of KW: 2
KW-H: 7.229
Weight percentage [%] of Mn
0.055
0.060
0.065
0.070
0.075
0.080
0.085
Acropolis
Control
Bailey
Median
25-75 %
1.5 IQR
Outliers

e)

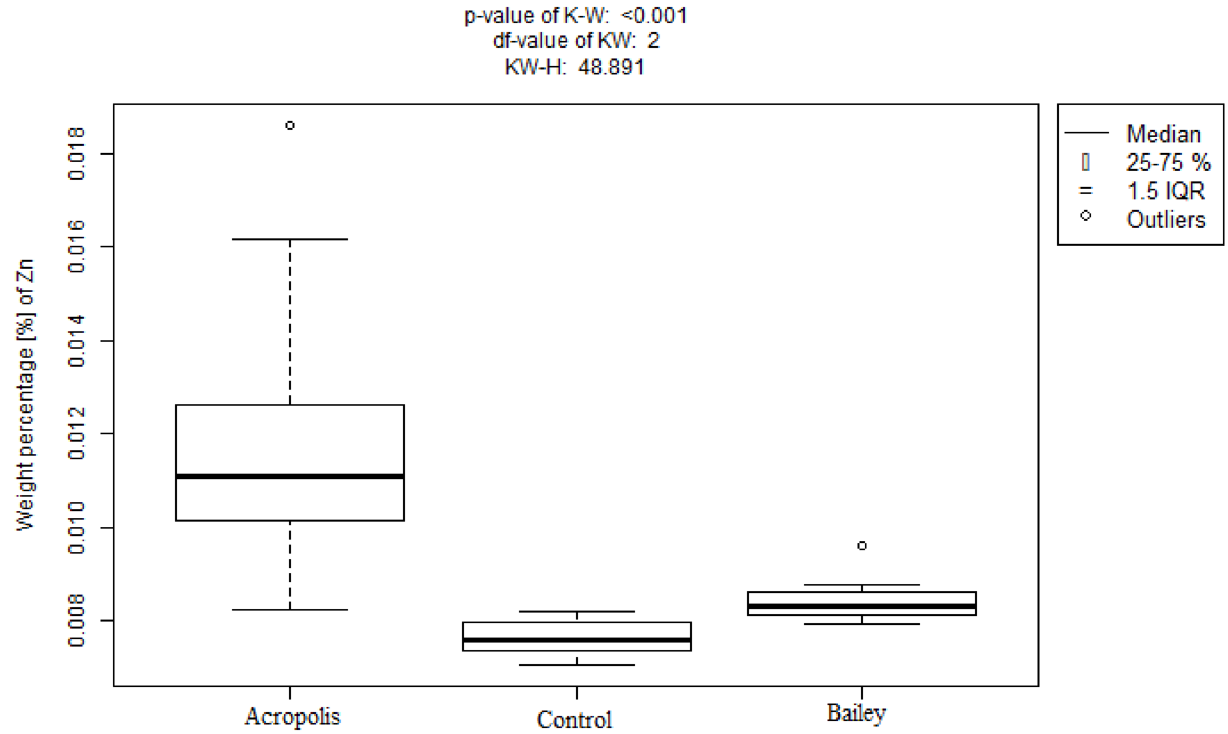

p-value of KW: 0.05
df-value of KW: 2
KW-H: 5.983
Weight percentage [%] of Fe
3.6
3.4
3.2
3.0
2.8
2.6
Acropolis
Control
Bailey
Median
25-75 %
1.5 IQR
Outliers

f)

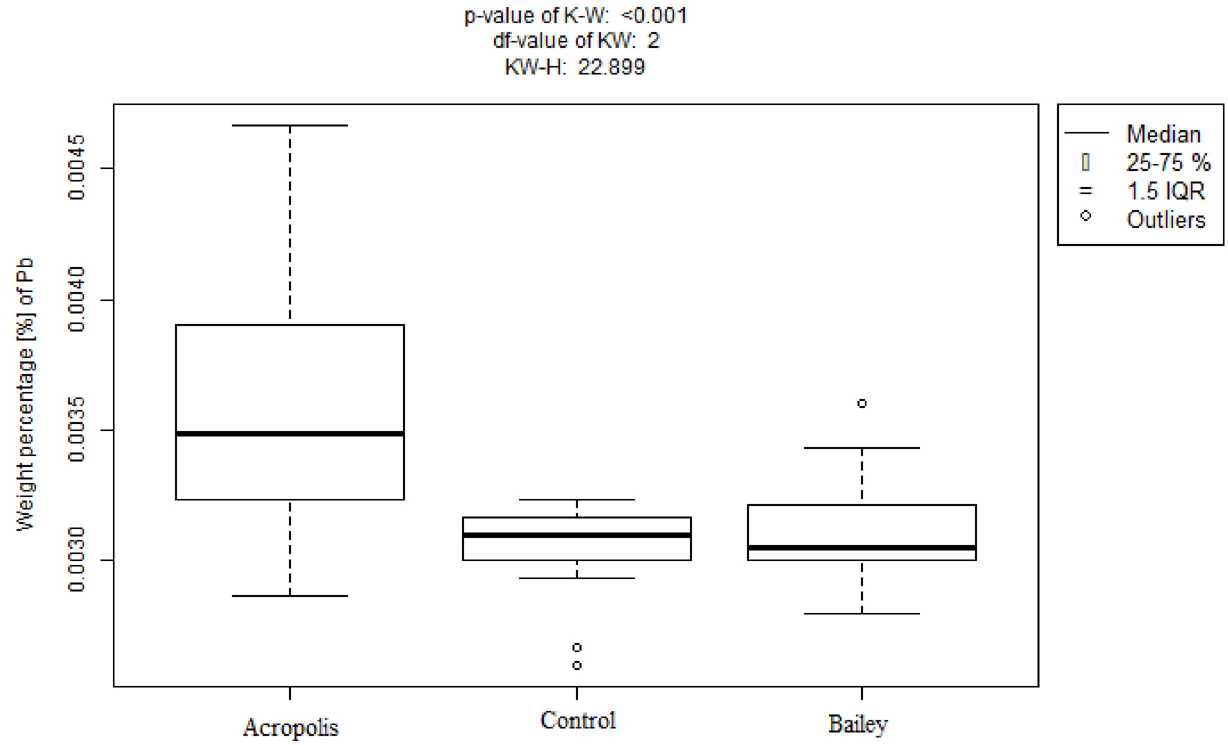


p-value of KW: 0.093
df-value of KW: 2
KW-H: 4.758
Weight percentage [%] of Ni
0.0025
0.0030
0.0035
0.0040
0.0045
Acropolis
Control
Bailey
Median
25-75 %
1.5 IQR
Outliers

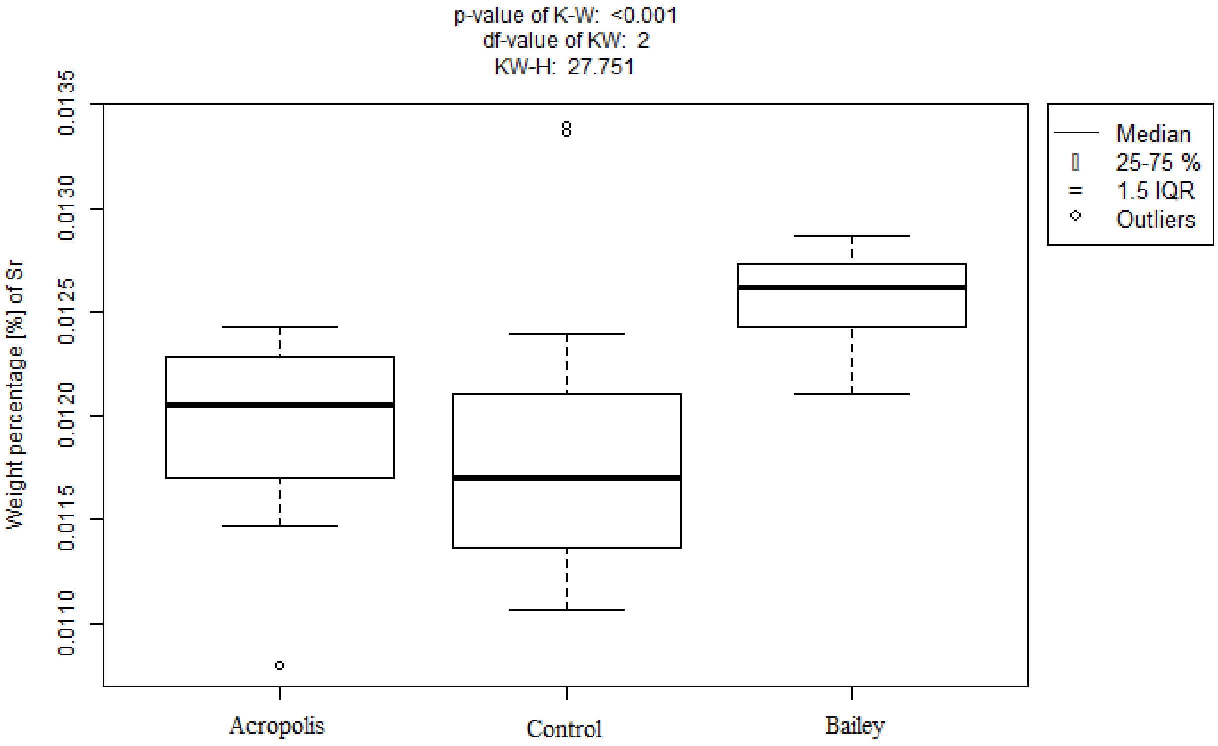
g)


p-value of K-W: <0.001
df-value of KW: 2
KW-H: 48.891
Weight percentage [%] of Zn
0.008
0.010
0.012
0.014
0.016
0.018
Acropolis
Control
Bailey
Median
25-75 %
1.5 IQR
Outliers

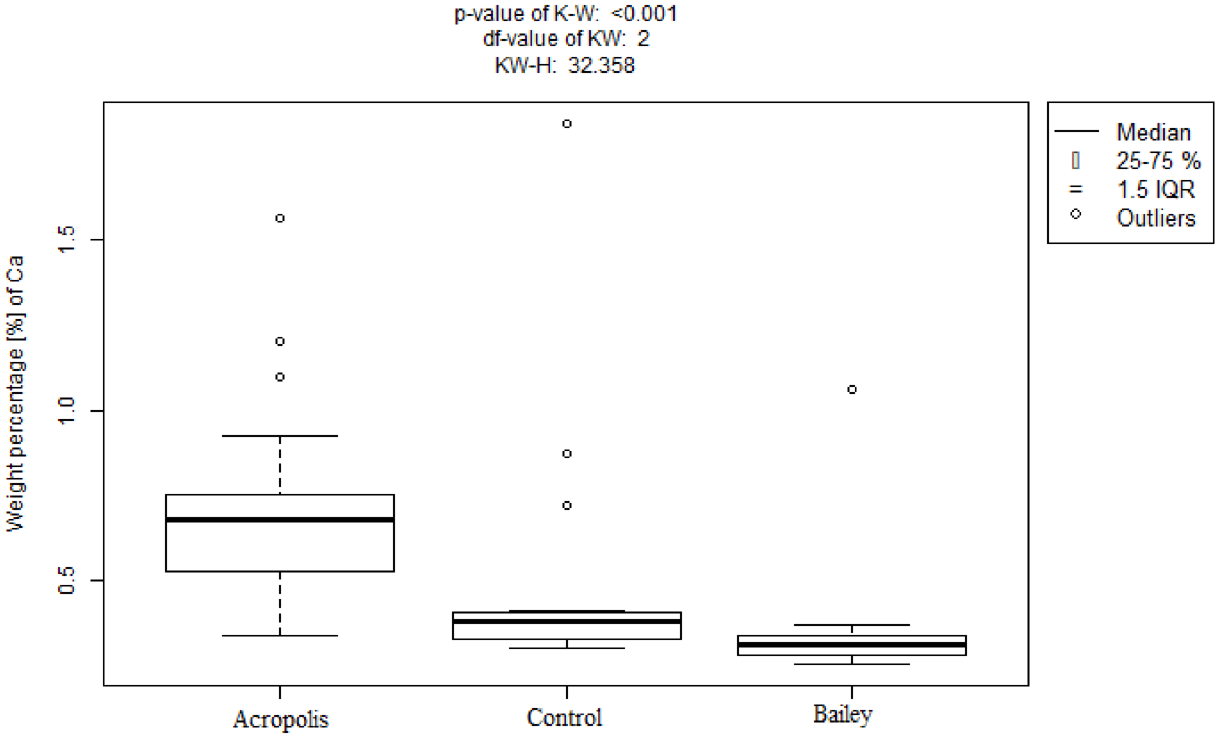
h)


p-value of K-W: <0.001
df-value of KW: 2
KW-H: 22.899
Weight percentage [%] of Pb
0.0030
0.0035
0.0040
0.0045
Acropolis
Control
Bailey
Median
25-75 %
1.5 IQR
Outliers

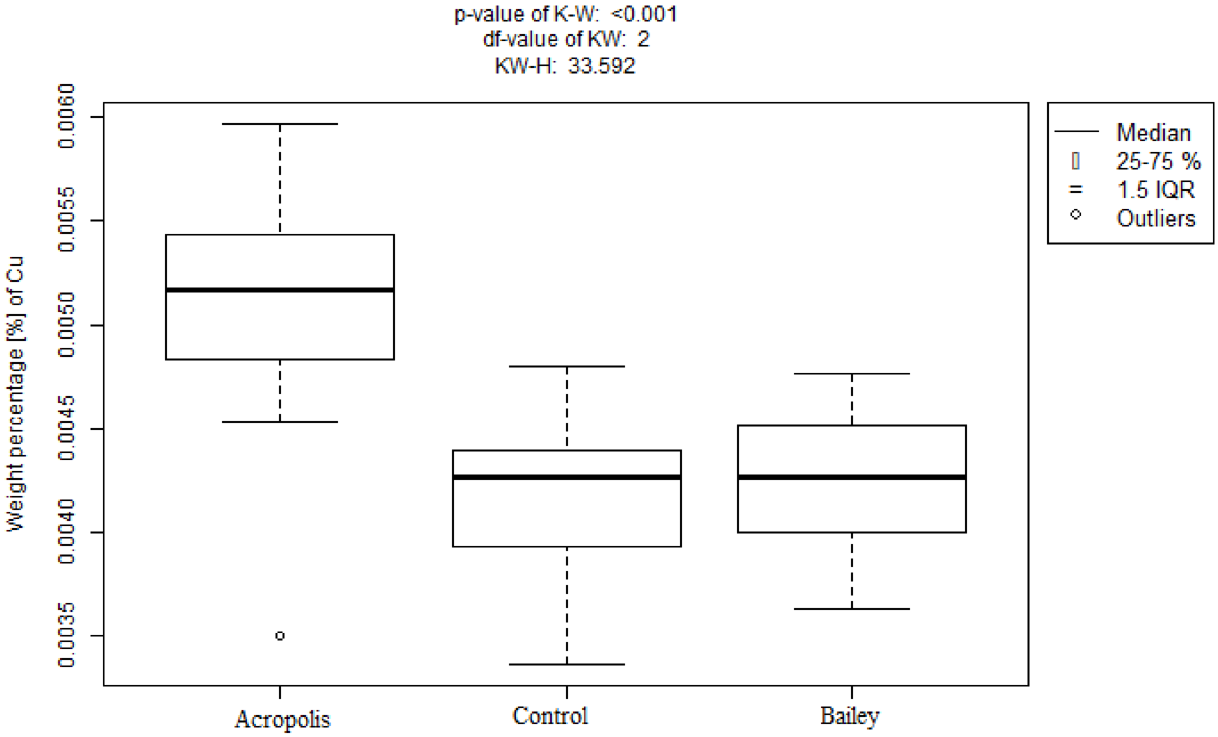
i)


p-value of K-W: <0.001
df-value of KW: 2
KW-H: 27.751
Weight percentage [%] of Sr
0.0110
0.0115
0.0120
0.0125
0.0130
0.0135
8
Acropolis
Control
Bailey
Median
25-75 %
1.5 IQR
Outliers

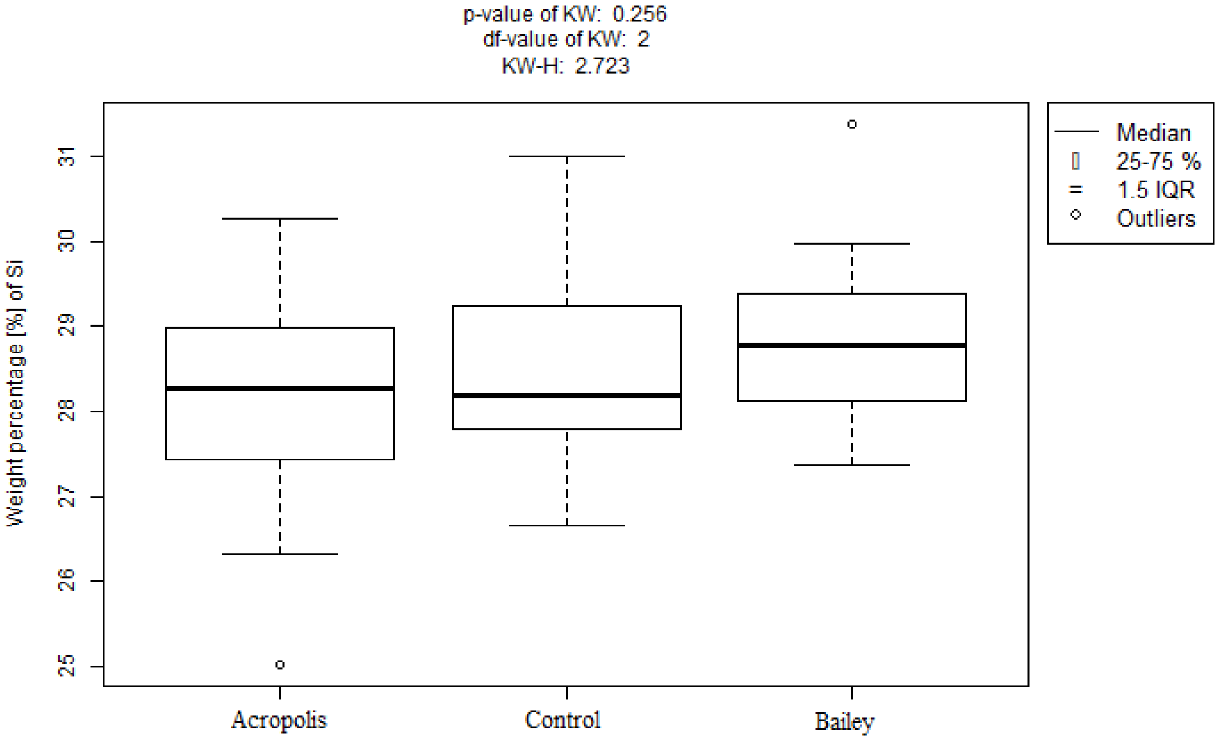
j)


p-value of K-W: <0.001
df-value of KW: 2
KW-H: 32.358
Weight percentage [%] of Ca
0.5
1.0
1.5
Acropolis
Control
Bailey
Median
25-75 %
1.5 IQR
Outliers

k)


p-value of K-W: <0.001
df-value of KW: 2
KW-H: 33.592
Weight percentage [%] of Cu
0.0035
0.0040
0.0045
0.0050
0.0055
0.0060
Acropolis
Control
Bailey
Median
25-75 %
1.5 IQR
Outliers

l)


p-value of KW: 0.256
df-value of KW: 2
KW-H: 2.723
Weight percentage [%] of Si
25
26
27
28
29
30
31
Acropolis
Control
Bailey
— Median
▯ 25-75 %
= 1.5 IQR
○ Outliers