Chemical characterization of freshwater sediments in central Italy: a tool to discriminate between anthropogenic pollution and natural geogenic sources

Damianić, Bernarda

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FAKULTET KEMIJSKOG INŽENJERSTVA I TEHNOLOGIJE
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KEMIJSKA KARAKTERIZACIJA SLATKOVODNIH SEDIMENATA U SREDIŠNJOJ ITALIJI: ALAT ZA RAZLIKOVANJE ANTROPOGENIH I PRIRODNIH IZVORA ONEČIŠĆENJA

DIPLOMSKI RAD

Voditelj rada: Ana Lončarić Božić, izv. prof. dr. sc.

Članovi ispitnog povjerenstva:

1. Ana Lončarić Božić, izv. prof. dr. sc.
2. Hrvoje Kušić, doc. dr. sc.
3. Tomislav Bolanča, prof. dr. sc.

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SAŽETAK

Sedimenti u rijekama predstavljaju spremnike onečišćivala, a jedna su od klasa najštetnijih onečiščivala teški metali zbog svoje toksičnosti, bioakumulacije, postojanosti te utjecaja na ekosustav i ljudski organizam. Teški metali u okoliš dospijevaju iz prirodnih izvora i antropogenih aktivnosti poput industrijskih procesa, prometa, agrikulturalnih aktivnosti, kanalizacije i sl.

Cilj ovog rada bio je odrediti kemijske parametre (u ovom radu koncentracije teških metala), u porječju rijeke Nestore te razlikovati utjecaj prirodnih izvora od utjecaja antropogenih aktivnosti.

Kao zanimljiv primjer promjene koncentracije metala u vremenu i prostoru pokazalo se porječje rijeke Nestore u pokrajini Umbria u srednjoj Italiji. Koncentracije metala u sedimentima su praćene za vrijeme četiri godišnja doba tijekom 2010. godine na deset različitih lokacija. Izbor stanica napravljen je na temelju prehodnog biološkog istraživanja. Npr. stanice 1 (rijeka Nestore), stanica 9 (rijeka Fersinone) i stanica 10 (rijeka Calvana) su se pokazale kao ekološki nekontaminirane te su njihove vrijednosti uzete kao referentne pri proračunima.

Uzorci su tretirani kiselom mikrovalnom digestijom, a koncentracije teških metala su određene metodom induktivno spregnute plazme - atomske emisijske spektroskopije (*ICP-AES*). Vrijednosti koncentracija metala podvrgnute su statističkoj analizi koja je uključila ukupne prosječne vrijednosti, sezonske vrijednosti, faktor obogaćenja i analizu Metodom glavnih komponenata (*Principal Component Analysis*).

Kako bi se odredila razlika između prirodnih i antropogenih izvora, moguće je izračunati prirodnu koncentraciju koja se definira kao 95% predviđenih raspona koncentracije prema prosjeku u normalnom uzorku. Predstavlja prirodan sadržaj teških metala bez ljudskih utjecaja te ukazuje na informacije o prirodno prisutnim koncentracijama metala u pojedinoj regiji.

Ključne riječi: riječni sedimenti, teški metali, antropogeno onečišćenje, induktivno spregnuta plazma - atomska emisijska spektroskopija, prirodna koncentracija, rijeka Nestore

ABSTRACT

Sediments in rivers represent tanks of contaminants and one class of the most harmful pollutants are heavy metals because of their toxicity, bioaccumulation, persistence and the impact on the ecosystem and the human body. Heavy metals are released into the environment from natural sources and anthropogenic activities like industrial processes, traffic, agricultural activities and sewerage system etc.

The aim of the present Thesis work has been to determine chemical parameters (i.e. heavy metal concentrations) in the Nestore River Basin and to distinguish the impact of natural sources from that of anthropogenic activities.

The Nestore River basin in Umbria, Central Italy shows an admirable example of heavy metal pollution in space and time. Concentrations of metals in sediments are tracked during the four seasons in the year 2010 in ten different sampling locations. The choice of the sites has been made on the basis of previously made biological investigation. For example, station 1 (The Nestore River), station 9 (The Fersinone River) and station 10 (The Calvana River) are shown like ecologically uncontaminated are their values were taken as the reference values in calculations.

Samples have been treated with a microwave acid digestion and heavy metal concentrations have been obtained with Inductively Coupled Plasma - Atomic Emission Spectroscopy. The values of metal concentrations have been then discussed with a statistical analysis, which included total average values seasonal trends, enrichment factor, Principal Component Analysis.

In order to discriminate between natural and anthropogenic sources it has been possible to calculate baseline concentration which is defined as the 95% of the predicted ranges of metal concentration toward an average in a normal sample. This estimate represents a natural content of heavy metals without human impact and points the information about naturally present metals in a specific region.

Key words: river sediments, heavy metals, anthropogenic pollution, ICP-AES, baseline, the Nestore River

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Author

Bernarda Damianić

CONTENTS

1. INTRODUCTION

The purpose of this thesis is to extend the previously made study on Nestore River Basin (Umbria, Central Italy), in which biological and physical- chemical indicators were used to assess the ecological health of river ecosystem[1], to the determination of chemical indicators, as concentrations of metals in sediments, in order to detect the chemical level of anthropogenic disturbance.

Tracking of river sediments is very significant because they play a major role in regulating water quality. They may show the biological, chemical, physicochemical and physical conditions of a water body. Sediments adsorb contaminants coming out of water, decreasing the amount of contaminants in the water. Contaminants that are chosen for tracking in this thesis are heavy metals (Cadmium, Cobalt, Chromium, Copper, Iron, Molybdenum, Manganese, Lead, Antimony, Selenium, Vanadium and Zinc). They are considered as serious pollutants in river sediments and nowadays present problem because of their toxicity, bioaccumulation, persistence and the impact on the ecosystem and the human body. Despite the heavy metal concentrations, there were tracked concentrations of other metals in sediments too (Aluminium, Calcium and Strontium).

The sampling campaign was made during four seasons of year 2010 on ten stations along the Nestore River Basin. Sampling preparation and analysis were done from March to July, 2016 in the laboratory of Environmental Chemistry and Technologies in the Department of Chemistry, Biology and Biotechnology of University of Perugia, Italy.

The recent made biological study pointed out that tested stations 1 (Nestore River), 9 (Fersinone River) and 10 (Calvana River) are ecologically uncontaminated. In this study that conclusion is investigated and the previously made study is extended with chemical parameters – concentrations of a large number of metals, including heavy metals. Since they may originate from natural and anthropogenic sources like industrial processes, traffic, agricultural activities and sewerage systems, it is important to distinguish this two types of sources and follow trends of heavy metals behavior, what was made in this thesis.

2. GENERAL PART

2.1. RIVER SEDIMENTS

Run-off water generally consists of a lot chemical components such as: heavy metals, polycyclic aromatic hydrocarbons, organometallic groups, grease, fossil fuels like petrol and diesel, anti-corrosion and anti-freeze agents, lubricating and transmission oils. These chemical contaminants may change the chemistry of rivers and be destructive to biological ecosystems. The rapid industrial and agricultural development was occurred in expanded pollution of heavy metals, a powerful environmental threat for invertebrates, fish, and humans. A significant role in regulating water quality is performed by sediments in rivers[2] and their picture is presented in Fig 2.1.1.

Fig. 2.1.1. River sediments [3]

Geochemical aspects of the sediments can be utilized to presume the weather behavior and the causes of pollution. [4] They can behave as a carrier and a potential origin of contaminants in water systems. When disposed on land, they may also influence the groundwater quality or agricultural products. By definition, contaminants are not lastingly settled by the sediment, but may be recycled by biological and chemical agents in the sediment section and the water column. Bioaccumulation and food chain transmission could be damaged by sediment-correlated amount of pollutants. Specifically, benthic organisms are in touch with sediment, so the contaminant quantity in the sediment could affect more on their survival than aqueous concentration could do. Owing to the modern research, sediments show the biological, chemical, physicochemical and physical quality of a water body.[5] Suspended sediments adsorb contaminants coming out of water, in this way decreasing the amount of contaminants in the water. Contaminants could be still released if the sediments are disturbed. Bottom sediments supply residence and a food origin for benthic organisms. Contaminants can be directly or indirectly poisonous to the vegetation and animals in water. The consequence of contaminants may also be spotted on land as a result of bioaccumulation of the food chain. [2] The connection between pollutants, sediments and food chain in freshwater systems are shown in Fig 2.1.2.

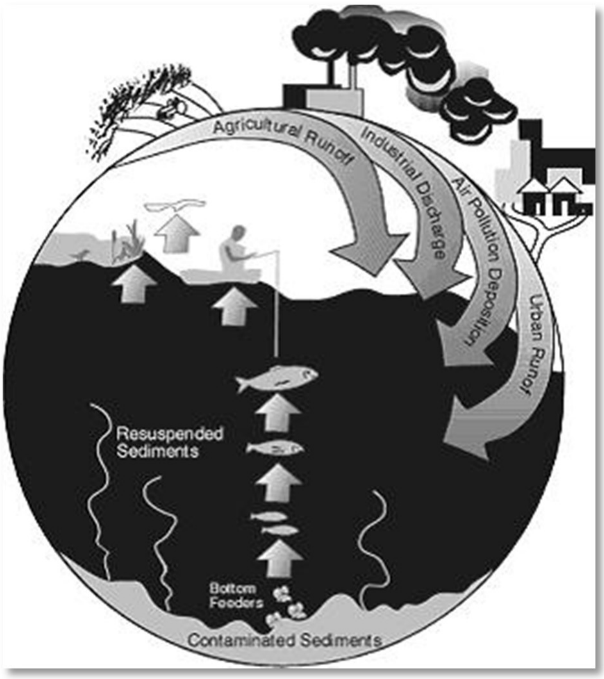


Fig. 2.1.2.The impact of contaminated sediments [6]

2.2. HEAVY METALS

Metals are essential components of stones, soils, sediments, and water.[5] Usually, by using a heavy metal term it is spoken about metal with a specific density of more than 5 g/cm^3. [7] According to this classification, position of heavy metals in Periodic Table of the Elements is presented in Fig 2.2.1.

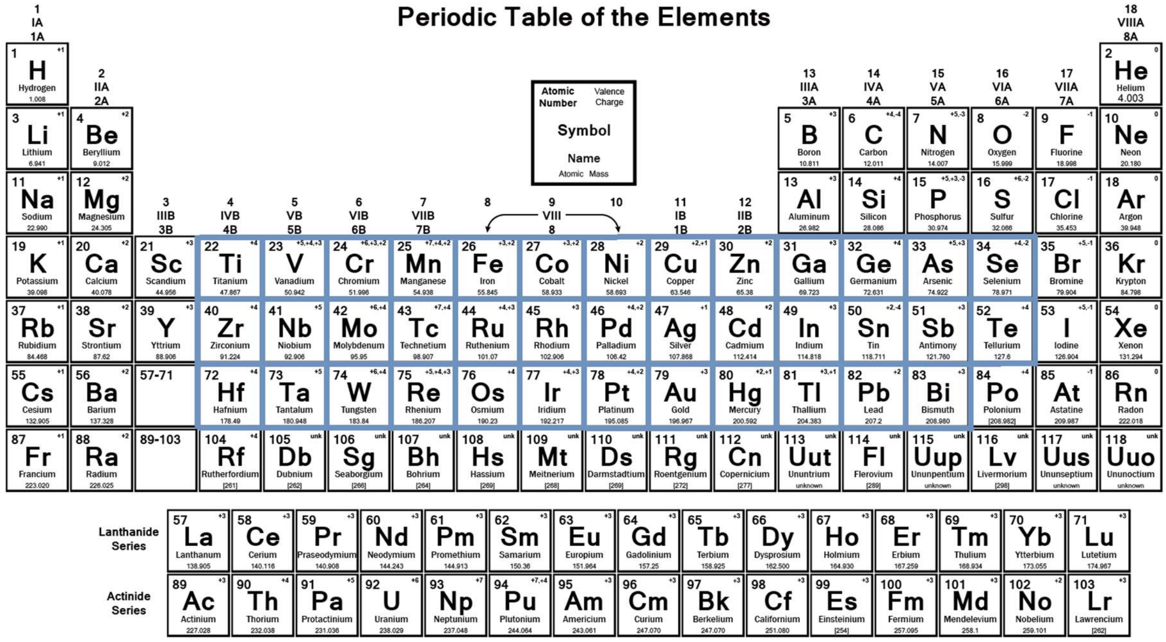


Fig. 2.2.1. Heavy metals in Periodic System of Elements [8,9]

Heavy metals are significant pollutants of environment because of their problems with toxicity, persistence and bioaccumulation. Heavy metals derived from fresh water sources are immediately taken out from the water and accumulated on sediments. The amount of heavy metals received in sediments depends of sediment characteristics: type and capacity of organic material, grain size, mineral components and cation exchange capacity.[10] Heavy metals contamination of the aquatic environment presents a global problem, as a result of their toxicity, endurance, organic degradation and accumulation in food chain. Deriving from natural geogenic sources and anthropogenic activities, like industrial wastewater, excavating, refining, agricultural works, household releases, atmospheric precipitation, heavy metals affect significant warnings to the ecosystem and human health. When heavy metals are transported inside the aquatic system, they are principally integrated into bottom sediments by adsorption, flocculation, and settling in the water column. Heavy metals can be poisonous to aquatic creatures when they arrive at threshold concentrations.[11]

Table 2.2.1. Types of components which could increase metal concentration in the sediments[12]

Detrital solids	**Endogenic fractions**	**Diagenetic fractions**
❖ from weathering, erosion and anthropogenic sources ❖ inorganic particles (clay minerals, metal oxidic carbonate, quartz) ❖ influence on the interaction processes because of the coating with hydrous manganese and iron oxides, organic substances	❖ from processes in the water column (precipitation, sorption, enrichment in organisms or organo-metallic interaction) ❖ typical mechanisms: settling of particulates, filtering organisms and flocculation	❖ substances from processes happening inside the sediments originate from the decomposition of buried organisms

2.2.1. Heavy metals toxicity

The toxicity and the movability of heavy metals in sediments is connected with the total concentration, chemical shape, binding condition, the metal properties, environmental features and soil characteristics like pH, organic substance composition and form, redox circumstances and root exudates behaving as chelates. They also accumulate in soils in different geochemical shapes (water-soluble, convertible, carbonate-connected, oxide-connected, organic-connected and residual forms). Water-soluble and convertible fragments are recognized as bioavailable; oxide-, carbonate- and organic fragments likely bioavailable and the mineral fraction is primarily not accessible to plants or microorganisms.[13]

Chemical inactivation of enzymes is the most meaningful mechanism of toxicity. All divalent heavy metals react with groups of proteins (amino, imino and sulfhydryl). Biological comprehension of trace metals can bring to changes of food webs and toxicity for man by the consummation of polluted food. The "free" or aqua-metal ion form is the most available form for organisms related to the particulate, complexed and chelated forms. Also, physical and chemical mechanisms like adsorption, filtration, sedimentation, complexation, precipitation, redox reactions can behave as sectional or full barriers to the migration of metals on their way to man.[5]

Table 2.2.2. Classification of elements according to toxicity and availability[5]

Noncritical			Toxic but very insoluble or very rare		Very toxic and relatively accessible		
Na	C	F	Ti	Ga	Be	As	Au
K	P	Li	Hf	La	Co	Se	Hg
Mg	Fe	Rb	Zr	Os	Ni	Te	Ti
Ca	S	Sr	W	Rh	Cu	Pd	Pb
H	Cl	(Al)	Nb	Tr	Zn	Ag	Sb
O	Br	Si	Ta	Ru	Sn	Cd	Bi
N			Re	Ba	Cr	Pt	

Waste components on land and in water show lasting reservoirs for the dropping of metals. Metal cycles in aquatic systems are connected with the air and soil environments, so indirect consequences from massive distress can be expected in surface and ground waters. Agricultural and residential samples are making difference in the amount of weathering and erosion. The acidification of soils increases the degree of podzolization (soil formation process) and as a consequence the distribution of many usually static metals. Low pH-values should be predicted to modify earth microbial ecology.

To success in pollution control, processes including distribution of metals should be evaded. Primary, fossil fuel burning, smelting and cement production, liming of soils should be diminished. Agricultural consummation of sewage sludge full with metals, fertilizers, dosing of wastewater has to be decreased for the benefit of food and groundwater quality. Concentrations of metals like lead, zinc and silver in some samples of waste containing metal sludge from electroplating, heat processing, inorganic pigment production, lime treatment of cans and emission control sludge from waste burning could battle with natural sources of part of elements.[5]

2.2.1. Cadmium

Cadmium is a non-essential element which may be toxic for plants and animals. It can behave as a meaningful pollutant as a consequence of its toxicity and large water solubility. In the earth's crust, natural level of Cadmium is located in the range 0.1–0.5 mg/kg. The most common sources of Cadmium in the environment are power stations, metal manufacturing, atmospheric processes, application of phosphate fertilizers, burning of solid waste, toxic outflows from industry and sewage treatment plants.[14]

2.2.2. Cobalt

Although is widely dispersed, Cobalt makes up only 0.001 percent of Earth's crust[15] with the average amount of 20–25 mg/kg.[14] It is located in small quantities in combination with other elements in natural waters, soils, plants, animals, minerals and its traces are present in many ores of iron, nickel, copper, silver, manganese, zinc, and arsenic. It is present in the structure of vitamin B12, the only vitamin known to contain such a heavy element.[15]

2.2.3. Chromium

Chromium is a crucial trace element with a role in the metabolism of lipids and proteins and for preserving a normal glucose tolerance factor. Generally, in soils and sediments Chromium occurs in two oxidation states: the trivalent Cr (III) and hexavalent Cr (VI), both may derive from weathering of chromites or industry. Since the hexavalent chromium is mobile and extremely toxic, it is more harmful than trivalent.[16]

2.2.4. Copper

Copper acts like source of food for aquatic life in freshwaters, although becomes toxic at higher concentration. Sources of copper in rivers and sediments may be natural (volcanic eruptions, decomposed vegetation, forest fires and sea spray) unto 50 mg/kg and anthropogenic (domestic and industrial wastewater,[14] especially agrochemicals like phosphorite fertilizers).[16] Copper shows a low solubility and could simply adsorb on suspended particles in water. That is why after natural processes, copper accumulates in the sediment and its amount represents degree of pollution of the water body.[14] Copper can restrain in sediment through exchange and specific adsorption mechanism, precipitate and quickly complex with organic matters. Agrochemicals (especially phosphorite fertilizers) and residential waste are the major source of the Cu.[16]

2.2.5. Iron

Iron is mainly the most abundant metal in all of the reservoirs[17] because it takes the second place among the metals, after aluminum, and fourth among the elements behind oxygen, silicon, and aluminum. The form of free metal is rare in the crust, appearing as terrestrial iron alloyed with 2–3 % nickel and in meteorites like taenite that contains 62–75 % iron and 37–24 % nickel. Iron can be also found combined with other elements in a lot of minerals. The most important ones are: hematite (ferric oxide, Fe_2O_3), magnetite (triiron tetroxide, Fe_3O_4), limonite (hydrated ferric oxide hydroxide, $FeO(OH)\cdot nH_2O$) and siderite (ferrous carbonate, $FeCO_3$).[18]

2.2.6. Molybdenum

Earth's crust consists of approximately 1.1 parts per million Molybdenum. The mineral molybdenite (MoS_2) is its general source, but it can also be found in the ores wulfenite ($PbMoO_4$) and powellite ($CaMoO_4$) or obtained as a by-product of copper mining.[19]

2.2.7. Manganese

Concentration of Manganese in the earth's crust deviates from 40 to 900 mg/kg.[14] On the one hand, manganese in the ion form is an essential trace source of nourishment in all forms of life. A large number of enzymes contain manganese cofactors (oxidoreductases, transferases, hydrolases, lyases, isomerases, ligases, lectins, and integrins). On the other hand, overbundance manganese is toxic.[20] Terrigenous sediments include manganese, but it can also arrive from sediments to the water column in low oxygen environments.[21]

2.2.8. Nickel

Nickel represents the 24th most common element in the earth crust.[17] It can be dangerous to aquatic biota at risen concentrations. Anthropogenic sources such as combustion of fuel may have some effect on increase in Ni concentrations along the roads. The greater concentration of Ni pollutant in the sediments was most probably related to natural sources and also domestic and municipal waste.[16]

2.2.9. Lead

Lead is a non-essential toxic element, delivered from natural and anthropogenic activities.[14] Among the toxic elements that are found in sediments, it is the least mobile element. Lead interferes with the synthesis of hemoglobin and concentrates within the red cells and bones, which may result as anemia, headache and dizziness.[16] In the earth's crust, concentration of Lead varies from 15 to 20 mg/kg. Main sources contain vehicular emissions, volcanoes, airborne soil fragments, wood fires, waste incineration, effluents from leather industry, paints and pesticides.[14]

2.2.10. Antimony

With its compounds, Antimony is naturally present in the earth's crust in the range of 0.2–1 μg/g. The main part is released to the atmosphere from natural sources (volcanic eruption, sea spray, forest fires) and from anthropogenic sources that are results of fossil fuel combustion, non-ferrous metals refining, coal-fired power plants or waste and sewage sludge burning. Antimony is a possibly toxic trace element that may produce different effects to humans and animals, and its toxicological behavior of this element depends on its oxidation state.[22]

2.2.11. Selenium

Selenium is a rare element, making about 90 parts per billion of the Earth's crust. Generaly it is found accompanying heavy metals such as copper, mercury, lead, or silver, but sometimes is found uncombined near sulfur and in some minerals. Its compounds have toxic characteristics to animals. Plants in seleniferous soils may accumulate the element and become poisonous. [23]

2.2.12. Vanadium

With amount of about 100 parts per million, Vanadium is ranking about 20th place among elements appearing in the Earth's crust. It can be found in a numerous minerals like vanadinite, carnotite, roscoelite, and patronite.[24] When is existent at higher concentrations, can be toxic, alhtough his complexes can decrease growth of cancer cells and progress human diabetes mellitus.[17]

2.2.13. Zinc

Zinc belongs to the potentially most dangerous group of trace metals for the biosphere.[16] His natural background levels in sediments are usually found up to 100 mg/kg (dryweight).[14] Zinc is mostly correlated with fine grained particle or is absorbed by the clay minerals. The fundamental sources are from industries, use of liquid fertilizers and composted materials.[16] Total abundance of elements in Earth’s crust in mass percentage are presented in Fig. 2.2.2.

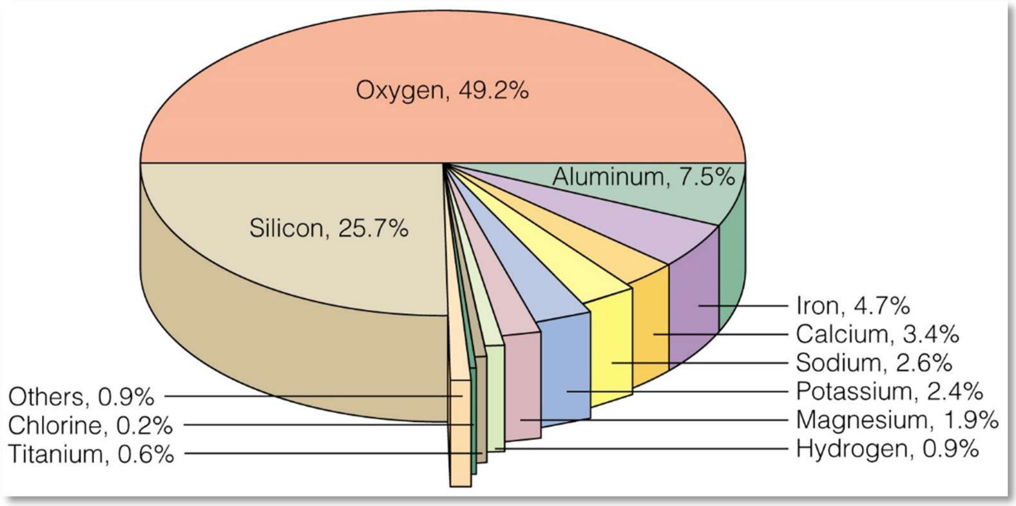


Fig. 2.2.2. Abundance of elements in Earth’s crust [25]

2.3. OTHER METALS

2.3.1. Calcium

Calcium presents the most plentiful metallic element in the human body and the fifth most abundant element in Earth's crust (3,64 %). It is essential to both plant and animal life. A lot of living organisms accumulate calcium in their shells or skeletons, and in higher animals calcium is the most plentiful inorganic element. A large number of crucial carbonate and phosphate deposits owe their origin to living organisms. The most important calcium compound is calcium carbonate ($CaCo_3$), the major constituent of limestone, marble, chalk, oyster shells and corals.[26]

2.3.2. Aluminium

The amount of aluminum in the Earth's crust is evaluated to be about 8.8 %. It is the third most abundant element in the Earth's crust, after oxygen and silicon and the most abundant metal. In nature it appears exclusively in compounds, never like a pure metal. It occurs in many different minerals. Bauxite, a combination of compounds consisting of aluminum, oxygen, and other elements, is the fundamental commercial source of aluminum.[27]

2.3.1. Strontium

Strontium forms about 0.04% of Earth's crust. Strontium doesn't exist like an essential element for higher forms of life. Its salts are usually nontoxic.[28]

2.4. BASELINE

The origin of metals into the aquatic system can be natural (weathering of soils and rocks) and from anthropogenic activities (industrial and urban wastes). Metals can be assimilated in contact with sediments or concentrated in toxic concentrations in benthic organism.[29] The exact concentration of heavy metals won't show the pollution rate of metals from natural and anthropogenic sources in sediments. Geological material can result with high heavy metal concentration rather than contamination. A geochemical approach should be used to discriminate from the natural variability of the metals in the sediments to recognize and measure anthropogenic pollution.[30]

Toxic metals in aquatic environments made by human activities generally concentrate in sediments, because of that fact it is critical to determine the concentration of heavy metals to figure out river pollution status. As reference baselines levels are used the average shale contents, crust contents, and preindustrial levels of the heavy metals. Applying individual regional geochemical background or baseline levels doesn't take into details about natural changeability of heavy metal constituents. This natural changeability generally is subordinated by the sediment particle size allocation. For that reason, particle size have frequently been needed to standardize heavy metal concentration to show the difference between geogenic and anthropogenic sources of heavy metals.[31]

Baseline concentration is characterized as 95% of the predicted ranges of metal concentration toward an average in a normal sample. It presents a natural heavy metal composition without human or urban effects and it adjusts information for naturally appearing large concentration of heavy metals in a specific region. It is crucial to have a suitable insight of the baseline concentrations to figure out the anthropogenic-caused heavy metal concentration in river sediments. Because of the long transport of pollutants in a river, truly pristine ecosystems may no longer exist and it is a challenging job to determine a baseline concentration. For example, it is impossible to collect a sediment sample completely free of Pb contamination due to long-term use of Pb-based petrol and paints. Nowadays, it is becoming really problematic to check the background levels of heavy metals due to human influence. Baseline concentration is significant to establish dependable worldwide elements concentration in environment.[32]

A few hypothesis should be made when reference components as conservative tracers of the essential metal-carrying state in the sediment parts are used:

1. The reference element changes proportionally to the naturally appearing concentrations of the metal in attention.
2. The reference element is unresponsive to contributions from anthropogenic sources.
3. The reference element is permanent and couldn't be environmentally influenced with processes like reduction/oxidation, adsorption/desorption etc.

Reference elements have a consistent flow from crustal rock sources. Anthropogenic supplements of trace metals could be determined by variations of the relation of trace metal and reference element. [33]

2.5. ANTHROPOGENIC SOURCES OF POLLUTION

Rivers obtain anthropogenic sources of metals due to human actions like industry, agriculture, mining, home waste, ship transport and construction works for urban improvement. These wastes may include poisonous heavy metals which can bio-accumulate.[34] Anthropogenic inputs can often finish in sediments, where they can endure a lot of time.[35] Sediments are reservoirs for pollutants like pesticides and are recognized as a vital sink of heavy metals which progress their discharge into water and as an indicator of pollution history. Concentration of heavy metals in sediments relies upon natural and anthropogenic sources and upon the organic matter compound, mineralogical structure and textural features of the sediment. Land use can be separated in agricultural, forestry and industrial developmental. It may be crucial in allocation of heavy metals in sediments.[34] Human activities have caused many changes in aquatic environments during the last 150 years and one of the most widespread pollutants are heavy metals. Their large amounts can be transfer into fluvial system with high velocity. Heavy metals can be released in particulate form or adsorbed on particles and be accumulated in the bottom river sediments with suitable hydraulic conditions.[36] The sediments of rivers present challenge for researchers to evaluate the intensity and degree of pollution with a large number of possible sources of heavy metals. Their contamination of sediments progressively draws people's attention. [37]

2.6. THE NESTORE RIVER

The Nestore River basin in Umbria region, represented in Fig 2.6.1., Central Italy shows an admirable example of a heavy metal pollution in space and time. It is changed by a large number of pollution sources made by urbanization, industry, agriculture and extensive livestock production. Moreover, sewage systems don’t exist or are absent in the area.[38]

Fig. 2.6.1. The Nestore river[39]

The Nestore River has a total length of about 42 km, it was born near Monteleone d'Orvieto and it flows into the right bank of the River Tiber near Collepepe. The river receives discharges of Piegaro purifier and Tavernelle. There are many towns that fall in the river basin Nestore, among them the city of Perugia, the towns of Corciano, Magione and Marciano. Industrial activities are mainly located in the band flat and low hilly, between the western portion of the regional capital and Lake Trasimeno, in the towns of Perugia, Corciano, Magione, Piegaro, Panicale (Tavernelle) and Marciano. The principal of the Nestore River tributaries are the streams Caina and Genna on the left bank and the Fersinone streams and Faina in the right.

In particular, the stream Caina, hydraulically connected to Lake Trasimeno, collects the waters of the northern portion of the basin. It runs through the towns of Perugia, Corciano, Magione and Marciano. Along its course it receives artificial effluent waters of Lake Trasimeno. In La Valle-Monte Sperello receives the waters of Fosso Formanuova receptor residential and industrial waste in the northern part of the basin Caina. The Caina river is also the receptor of treated wastewater from Corciano purifiers, Montesperello (Comune di Magione) and San Sisto (Municipality of Perugia).

The stream Genna runs in North-South sense, the western portion of the City of Perugia, to flow into the Nestore River at Vallicelle in the town of Marsciano. In the northern part, the Genna crosses through an area strongly anthropized (Pian di Massiano, Centova, Settevalli Industrial Zone, the Stone Bridge) in a typically hilly area with woodlands, also of significant size, catching the waters of the Stone Bridge purifier and Olmeto purifier. In the central and final part, the Genna flows in an agricultural context of considerable environmental value.

The Fersinone and the Calvana, characterized by particularly branched hydrography, are grown in south-western portion of the basin, flowing in sparsely populated areas and entering in Nestore just above Marsciano. [40]

2.7. INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY

Inductively coupled plasma atomic-emission spectroscopy (ICP-AES) or inductively coupled plasma optical emission spectroscopy (ICP-OES) is a widely used analytical technique[41] for determination of trace elements in different sample types.

ICP/OES is one of the most powerful and popular analytical tools for the determination of trace elements in a myriad of sample types. The technique is based upon the spontaneous emission of photons from atoms and ions that have been excited in a radiofrequency (RF) discharge and the working principle is presented in Fig 2.7.1. Liquid and gas samples may be injected directly into the instrument, while solid samples require extraction or acid digestion so that the analytes will be present in a solution. The sample solution is converted to an aerosol and directed into the central channel of the plasma. At its core the inductively coupled plasma sustains a temperature of approximately 10 000 K, so the aerosol is quickly vaporized. Analyte elements are liberated as free atoms in the gaseous state. Further collisional excitation within the plasma imparts additional energy to the atoms, promoting them to excited states. Sufficient energy is often available to convert the atoms to ions and subsequently promote the ions to excited states. Both the atomic and ionic excited state species may then relax to the ground state via the emission of a photon. These photons have characteristic energies that are determined by the quantized energy level structure for the atoms or ions. Thus the wavelength of the photons can be used to identify the elements from which they originated. The total number of photons is directly proportional to the concentration of the originating element in the sample.

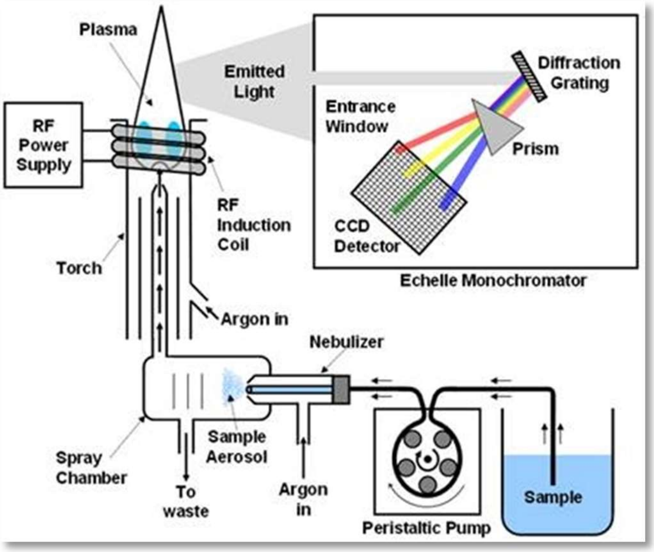


Fig. 2.7.1. Working principle of ICP- AES method [42]

The instrumentation associated with an ICP/OES system is relatively simple. A portion of the photons emitted by the ICP is collected with a lens or a concave mirror. This focusing optic forms an image of the ICP on the entrance aperture of a wavelength selection device such as a monochromator. The particular wavelength exiting the monochromator is converted to an electrical signal by a photodetector. The signal is amplified and processed by the detector electronics, then displayed and stored by a personal computer.

Liquid samples are injected into a radiofrequency (RF)-induced argon plasma using one of a variety of nebulizers or sample introduction techniques. The sample mist reaching the plasma is quickly dried, vaporized, and energized through collisional excitation at high temperature. The atomic emission emanating from the plasma is viewed in either a radial or axial configuration, collected with a lens or mirror, and imaged onto the entrance slit of a wavelength selection device. Single element measurements can be performed costeffectively with a simple monochromator/photomultiplier tube (PMT) combination, and simultaneous multielement determinations are performed for up to 70 elements with the combination of a polychromator and an array detector. The analytical performance of such systems is competitive with most other inorganic analysis techniques, especially with regards to sample throughput and sensitivity.[43]

Table 2.6.1 Advantages of ICP – AES method[43]

ADVANTAGES	
high temperature (7000–8000 K)	high stability leading to excellent accuracy and precision
high electron density (1014–1016 cm^{-3})	excellent detection limits for most elements (0.1–100 ngmL^{-1})
high electron density (1014–1016 cm^{-3})	wide linear dynamic range (LDR) (four to six orders of magnitude)
simultaneous multielement capability (over 70 elements, including P and S)	applicable to the refractory elements
low background emission and relatively low chemical interference	cost-effective analyses

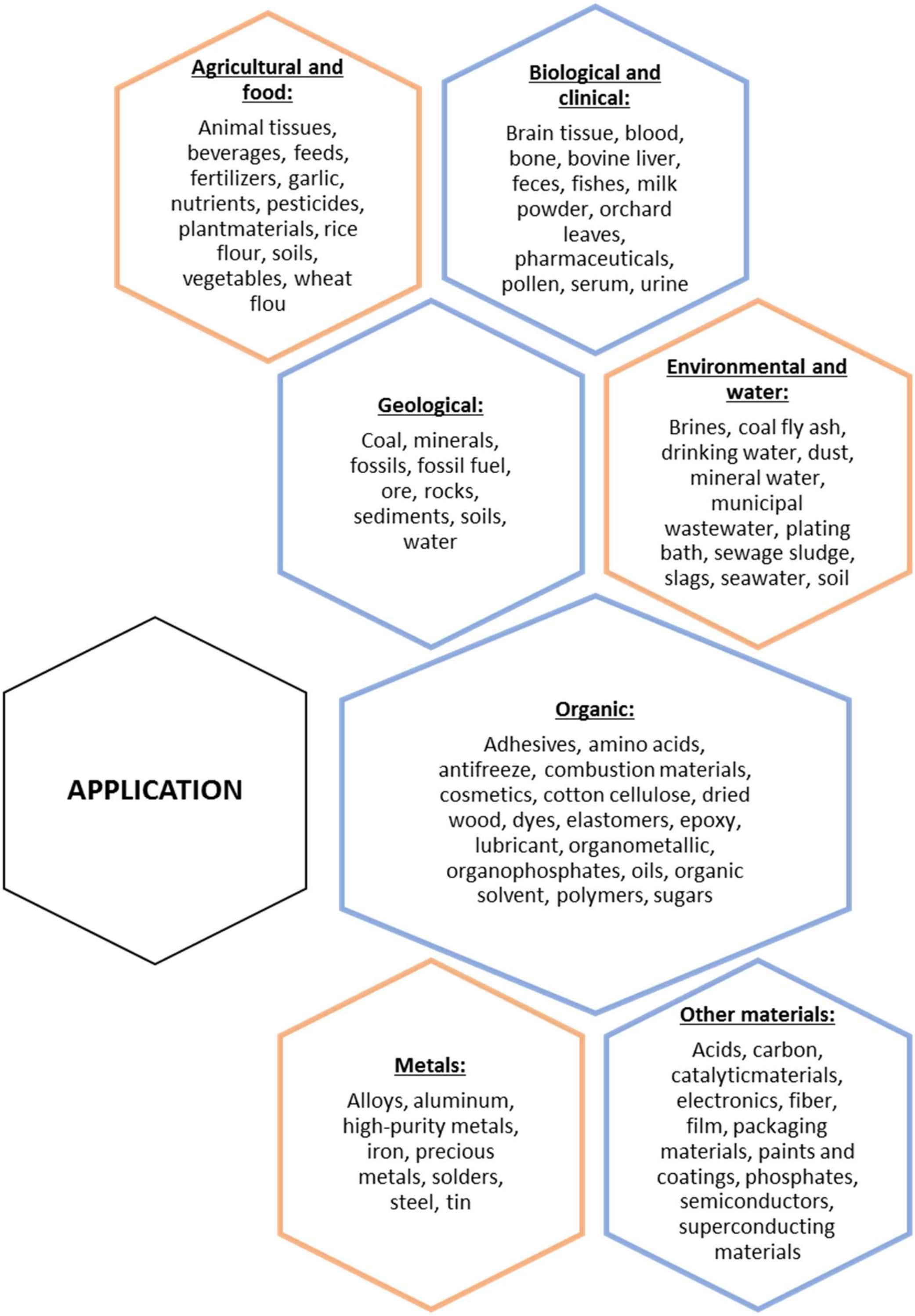


Fig. 2.6.1. Application of ICP-AES[43]

3. EXPERIMENTAL PART

3.1. STUDY AREA AND SAMPLING CAMPAIGN

The sampling included the entire Nestore River basin and was performed from March 2010 to October 2010. It consisted of four seasonal sampling sessions: 08. March, 17. May, 02. August and 12. October. Along the Nestore River, six sampling stations were picked out and four in its main tributaries, just before their confluence with the Nestore River.

Table 3.1.1.Station positions of sampling campaign

Station	Station position
ST 1	Nestore River
ST 2	Nestore River
ST 3	Nestore River
ST 4	Nestore River
ST 5	Nestore River
ST 6	Nestore River
ST 7	Caina Stream
ST 8	Genna Stream
ST 9	Fersinone Stream
ST 10	Calvana Stream

The station 1 is located above the town of Piegaro, and is surrounded by a small park area encircled by cultivated fields.

The station 2 is still located near Piegaro, after the confluence with the stream Ierna and plant of glass processing.

The station 3 is situated in the locality Oro, upstream of the Pietrafitta power plant near of an area intensively cultivated.

The station 4 is placed in the Nestore after entering the Caina in the locality Mercatello.

The station 5 is positioned in Nestore after entering the Genna near Morcella.

The station 6 takes place within the town of Marsciano after entering the Fersinone and Calvana.

The station 7 is located in The Caina Stream immediately before it is placed in Nestore.

The station 8 is situated in The Genna Stream upstream from its confluence with the Nestore.

The station 9 is located in The Fersinone Stream upstream from its confluence with the Nestore.

The station 10 is located in The Calvana Stream upstream from its confluence with the Nestore.

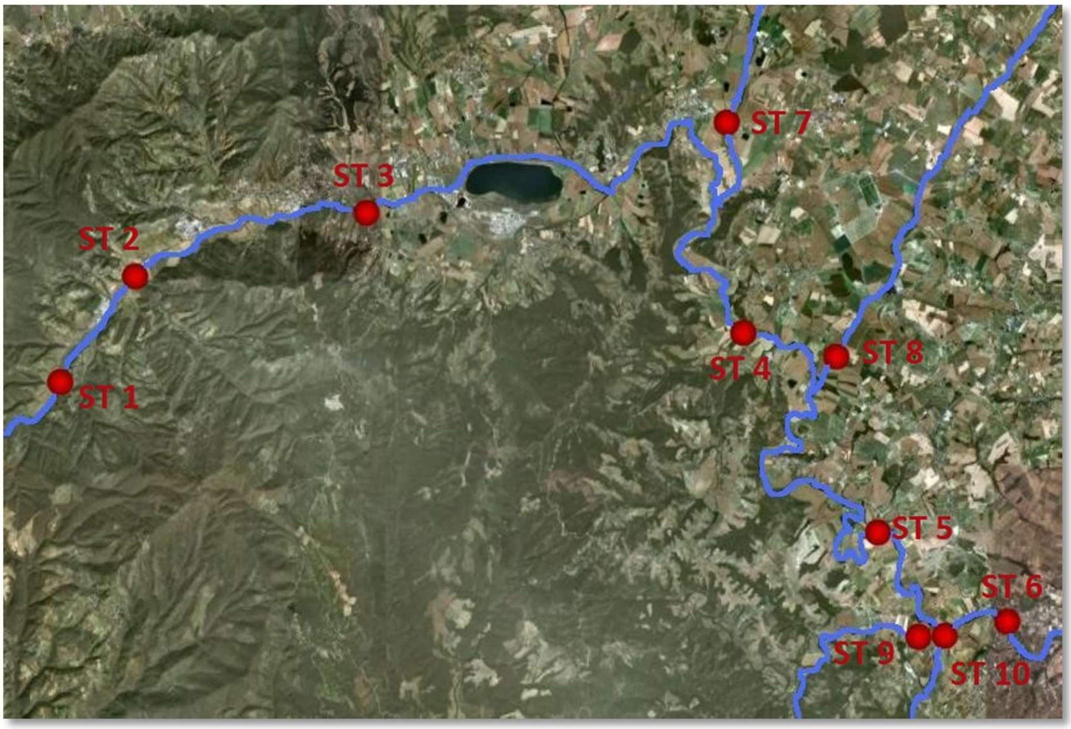


Fig. 3.1.1. Satelite view of sampling stations

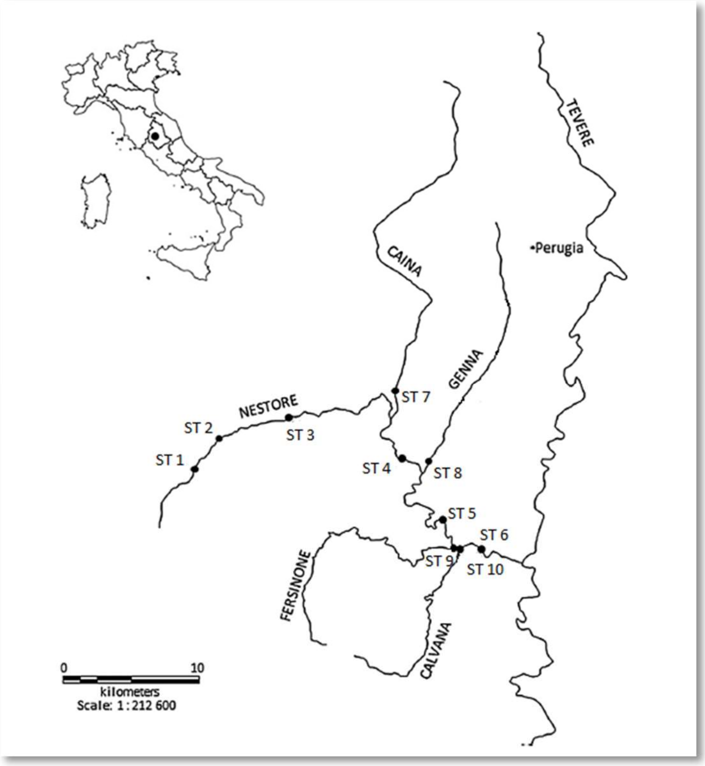


Fig. 3.1.2. Map of sampling stations

Sampling of the sediments was carried out with a hand dredge trying to dredge the superficial layer of the bottom sediments thick about 5 cm. Weight of the sampled sediments was approximately 500 g. In order to protect samples, all the amount was keeped in Pyrex glass bottles and left refrigerated at -18 °C.

3.2. CHEMICAL AND PHYCHICO-CHEMICAL PARAMETERS OF SURFACE WATER

Table 3.2.1. Physicochemical parameters of surface water that were measured in situ, regularly at the equal daytime

<table>
<tr><th>Temperature</th><th>Dissolved oxygen (DO)</th><th>pH</th><th>Conductivity</th></tr>
<tr><td colspan="2">Oximeter F-Simplair Syland Scientific
Measuring range: 0.0-20.0 O_2 mg $\cdot L^{-1}$
Accuracy: 1% of the scale value</td><td>pH-metter Hanna Instruments HI-98150
Range: 0.0-20.0 O_2 mg $\cdot L^{-1}$
Accuracy: 1% of the scale value</td><td>HI8733- Hanna Instrumets
Range: 0-1999 $\mu S \cdot cm^{-1}$
Accuracy: 1%
Resolution: 1 $\mu S \cdot cm^{-1}$</td></tr>
</table>

All the water samples were taken in polyethylene bottles of 500 mL and then stored at 5 °C in the refrigerator. Chemical oxygen demand was quantified by colorimetric method with instrument Smart 2 Colorimeter La Motte Company, COD Low Range Reagent Kit with range 0-150 mg $\cdot L^{-1}$ COD and detection limit 0,5 mg $\cdot L^{-1}$.

3.3. SAMPLE PREPARATION

After sampling campaign, the sediment samples were dried on air, sorted out with a mortar and pestle to pass through 2-mm mesh sieve, dried at 105 °C for 24 h. Prepared samples were kept in refrigerator until the moment of analysis. Before analysis, sediment samples were exposed to microwave acid digestion.

The procedure of digestion consisted of a few steps:

1. **ADDING REAGENTS:**
   8 mL of ultrapure nitric acid (Carlo Erba reagents, ultrapure for trace analysis, 67-69%; Suprapur®, 65%) and 2 ml of ultrapure solution of hydrogen peroxide (Carlo Erba Reagents, 30-32%) were added to 0,250 g of sediment samples.
2. **DIGESTION:**
   The mixture was digested in Mars microwave oven.
3. **FILTERING:**
   After cooling to the room temperature, all the digested samples were filtered with Whatman™ filter papers Grade No.42, particle retention 2,5 µm.
4. **DILUTION:**
   Samples were diluted with ultrapure water of conductivity 18 MΩ·cm at 25 °C to 50 mL.

Fig. 3.3.1. Mars microwave owen

Fig. 3.3.2. Digested samples

3.4. HEAVY METALS ANALYSIS

Concentrations of metals in sediments were detected by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Ultima 2, HORIBA Scientific) equipped with ultrasonic nebulizer (CETAC Technologies, U-5000 AT), displayed in Fig 3.4.1., after acid microwave digestion. Standard solutions for calibration were prepared using commercially produced solutions.

Fig. 3.4.1. ICP – AES instrument

To determine metals in traces (Cd, Co, Mo, Ni, Pb, Sb, Se, Sr, V) were used originally digested solutions. For quantifying other metals (Al, Ca, Fe, Mn, Zn) digested solutions were diluted 1:100 using ultrapure water.

In all diluted solutions displayed in Fig 3.4.2. was added Yttrium solution in total concentration of 10 mg/L in order to control the consistency of measurements. During the analysis , efficiency nebulizer variations and/ or anomalies in the introduction of the sample can occur. In consideration to notice these changes, the external standard of Yttrium was added to solutions. If the values of intensity factor don’t vary, measurements are reliable.

Fig. 3.4.2. Diluted solutions

3.5. STATISTICAL ANALYSIS

3.5.1. Average values and the limit of detection

For every metal, after defining concentrations in mg/L and mg/kg, average season and station values are calculated and displayed in graphs. Concentrations in mg/kg units were determined by the given formula:

$$c(metal)\,[\text{mg/kg}] = \frac{(c(metal\ sample) - c(blank\ sample))\ [\text{mg/L}] \cdot 50\ \text{mL}}{1000} \cdot \frac{1000}{m\,(sample)\,[\text{g}]} \qquad (3.5.1.)$$

To calculate metal concentrations, the limit of detection quantity was necessary to be determined.

The limit of detection (*LOD*) is generally defined as the lowest quantity or concentration of a element that can be detected with a given analytical method. The *LOD* could be explained as the lowest concentration obtained from the measurement of a sample with the researched component that we would be able to discriminate from the concentration obtained from the measurement of a blank sample, not containing the component.[44]

In this thesis, values of LOD were determined using linear calibration curve with the OriginPro 8. For this method, it is assumed that the instrument response y is linearly related to the standard concentration x for a limited range of concentration. It can be expressed in a model such as

$$y = a + bx \qquad (3.5.2.)$$

This model is used to compute the sensitivity b and the LOD. Therefore, the LOD can be expressed as

$$LOD = \frac{3S_a}{b} \qquad (3.5.3.)$$

where S_a is the standard deviation of the response and b is the slope of the calibration curve. The standard deviation of the response can be estimated by the standard deviation of either y-residuals, or y-intercepts of regression lines. This method can be applied in all cases, and it is most applicable when the analysis method does not involve background noise. It uses a range of low values close to zero for calibration curve, and with a more homogeneous distribution will result in a more relevant assessment.[45]

The atomic emission signals from the ICP are larger than those from other sources, such as a flame. This occurs because the high-temperature and inert-argon environment of the ICP leads to more efficient atomization, ionization, and excitation. In fact, the temperature of the ICP is so high that the largest signals are usually from the ionic lines. There are many other factors that may influence LOD, such as nebulizer type, view mode, and sample matrix.[43]

3.5.2. Enrichment factor

In this thesis, the Enrichment Factor technique was used to assess the level of contamination in the sediments of the Nestore River basin. According to this technique, metal concentrations were normalized to metal concentrations of average shale. Widely used elements for normalization are Aluminium and Iron. In this study, Aluminium has been used as a conservative tracer to differentiate the metal contamination to quantify the extent and degree of metal pollution. According to the previously made biological research, stations 9 and 10 were taken as reference stations because are ecologically uncontaminated.

To assess the level of metal enrichment in sediment samples of study area enrichment factor (EF) was computed using the following equation:

$$EF = \frac{\frac{c(metal)}{c(Al)}}{\frac{c(metal)_{ST9/ST10}}{c(Al)_{ST9/ST10}}} \qquad (3.5.4.)$$

Where:

$c\ (metal)$ - concentration of the examined metal in the examined station

$c\ (Al)$ - concentration of the reference metal in the examined station

$c\ (metal)_{ST9/ST10}$ - concentration of the examined metal in the reference stations 9 or 10

$c\ (Al)_{ST9/ST10}$- concentration of the reference metal in the reference station 9 or 10[17]

Table 3.5.1. Meaning of Enrichment factor values[17]

ENRICHMENT FACTOR	ENRICHMENT
<1	No
<3	Minor
3-5	Moderate
5-25	Moderately severe
25-50	Very severe
>50	Extremely severe

3.5.3. Principal component analysis

Principal component analysis (*PCA*) is a multivariate technique that analyzes a data table in which observations are described by several inter-correlated quantitative dependent variables. Its goal is to extract the important information from the table, to represent it as a set of new orthogonal variables called principal components, and to display the pattern of similarity of the observations and of the variables as points in maps.[46] Principal component analysis can organize the data standardized from all the heavy metals in all the location into one unified comparison.[37] In this thesis is displayed pattern of similarity between various concentrations of metals in space and time.

3.5.4. Baseline

Mostly, a geochemical baseline is utilized to determine if elemental enrichment exists. The criterion is determined by the distance to a linear regression line. Values that enter within the 95 % confidential intervals of the linear regression line are considered normal and outliers indicate an environment has been enriched.

In this thesis, a linear regression relationship between a heavy metal element and a reference element is shown and calculated in the program Origin Pro8. According to the previously made biological research, stations 1, 9, 10 are chosen as environmentally the purest and uncontaminated. Their values are taken and confronted with the mass percentage of reference elements by linear regression to determine the baseline range. The data outside the 95% confidential intervals was not considered. For the verification on the outliers the Q-tests (test of Dixon) was used.

$$Q = \frac{\left| suspicious\ \ value - closest\ \ value \right|}{\left(biggest\ \ value - smallest\ \ value \right)} \qquad (3.5.5.)$$

Table 3.6.4.1. Critical Q values at the significance level of 5%

Number of measurements	*Q*
3	0.970
4	0.831
5	0.717
6	0.621
7	0.570
8	0.524
9	0.492
10	0.464

For this thesis, for reference elements were chosen Aluminium, Iron and Vanadium. Alternative reference elements which can be used in calculations are Lanthanum, Lithium, Scandium and Titanium. After linear regression with reference elements was chosen the reference element with the biggest Coefficient of determination (R^2) and data of all other stations was added. On this way was possible to notice which data enters the confidence interval of 95%. It was made for every analised metal exept the ones whoose values were under the limit of detection. Also, a linear regression relationship between a heavy metal element and a reference element was calculated using the principle of normalization:

$$C_M = aC_N + b \tag{3.5.5.}$$

Where C_M represents the baseline concentration of one of the analized metals, C_N indicates the concentration of the reference element, and a and b are the regression constants of the equation.[47]

4. RESULTS

4.1. TOTAL RESULTS

Table 4.1.1. Chemical and physico-chemical parameters of The Nestore River basin surface water

	St. 1 - Nestore							St. 3 - Nestore				St. 4 - Nestore				St. 5 - Nestore			
	Mar	May	Aug	Oct	May	Aug	Oct	Mar	May	Aug	Oct	Mar	May	Aug	Oct	Mar	May	Aug	Oct
Chemical and physico-chemical parameters of the surface water																			
Water T (°C)	6,00	12,60	20,40	13,50	13,80	27,30	15,00	7,50	14,50	26,40	14,70	7,50	14,40	25,90	15,60	7,70	14,70	24,10	15,60
Conductivity (µS cm^{-1})	467	431	537	540	443	521	652	593	506	785	744	727	638	636	890	739	638	556	796
pH	8,43	8,41	8,10	8,20	8,40	8,54	8,62	8,42	8,34	7,66	7,96	8,16	8,27	8,03	8,00	8,11	8,14	7,78	8,01
D.O. (mg L^{-1})	10,30	10,90	8,10	9,00	9,80	19,40	12,80	11,90	10,80	5,60	8,30	11,20	10,40	8,50	7,40	9,80	8,80	6,90	7,40
COD (mg L^{-1} O_2)	7,00	<5.00	<5.00	13,00	<5.00	<5.00	13,00	5,00	8,00	14,00	9,00	<5.00	<5.00	20,00	16,00	9,00	<5.00	22,00	6,00

	St. 6 - Nestore							St. 8 - Genna				St. 9 - Fersinone				St. 10 - Calvana			
	Mar	May	Aug	Oct	May	Aug	Oct	Mar	May	Aug	Oct	Mar	May	Aug	Oct	Mar	May	Aug	Oct
Water T (°C)	6,90	13,80	23,30	15,50	14,60	22,20	16,00	8,30	15,00	21,40	15,20	6,70	13,00	21,60	---	7,60	13,10	---	---
Conductivity (µS cm^{-1})	672	593	528	750	689	805	924	844	771	783	881	541	497	553	---	613	605	---	---
pH	8,28	8,27	7,91	8,18	8,21	7,86	8,07	8,27	8,16	7,73	7,88	8,37	8,40	7,75	---	8,30	8,46	---	---
D.O. (mg L^{-1})	11,50	9,80	8,00	9,30	9,60	5,70	8,10	9,40	8,50	4,30	4,90	11,50	9,80	7,00	---	11,30	11,50	---	---
COD (mg L^{-1} O_2)	<5.00	22,00	14,00	37,00	<5.00	20,00	26,00	<5.00	8,00	16,00	31,00	<5.00	7,00	<5.00	---	<5.00	<5.00	---	---

“---“, dry stream

"T", temperature

"D.O.", Dissolved Oxygen

"COD", Chemical Oxygen Demand

Table 4.1.2. Total concentrations of metals in sediments of The Nesore River basin

	St. 1 - Nestore				**St. 2 - Nestore**			
	Mar	**May**	**Aug**	**Oct**	**Mar**	**May**	**Aug**	**Oct**
Al (mg kg^{-1})	$1,79\cdot10^{4}$	$2,11\cdot10^{4}$	$2,00\cdot10^{4}$	$2,11\cdot10^{4}$	$2,11\cdot10^{4}$	$3,16\cdot10^{4}$	$2,51\cdot10^{4}$	$3,15\cdot10^{4}$
Ca (mg kg^{-1})	$1,11\cdot10^{4}$	$4,26\cdot10^{4}$	$1,24\cdot10^{4}$	$4,26\cdot10^{4}$	$2,33\cdot10^{4}$	$3,41\cdot10^{4}$	$3,41\cdot10^{4}$	$3,40\cdot10^{4}$
Cd (mg kg^{-1})	<2,00	<2,00	2,87	<2,00	<2,00	<2,00	11,06	4,19
Co (mg kg^{-1})	6,16	6,24	11,52	5,65	5,90	9,77	6,63	8,79
Cr (mg kg^{-1})	25,89	20,95	37,81	30,66	27,30	49,66	41,29	34,97
Cu (mg kg^{-1})	6,50	12,03	12,62	8,34	10,11	31,74	22,21	28,44
Fe (mg kg^{-1})	$1,54\cdot10^{4}$	$2,03\cdot10^{4}$	$2,03\cdot10^{4}$	$2,07\cdot10^{4}$	$1,81\cdot10^{4}$	$3,06\cdot10^{4}$	$2,43\cdot10^{4}$	$3,09\cdot10^{4}$
Mn (mg kg^{-1})	$1,63\cdot10^{3}$	306,0	227,6	305,7	144,8	444,0	<26,24	442,6
Mo (mg kg^{-1})	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95
Ni (mg kg^{-1})	62,21	37,44	61,02	28,74	43,16	60,87	36,49	48,49
Pb (mg Kg^{-1})	6,96	6,06	10,13	5,73	6,56	13,88	8,62	14,30
Sb (mg kg^{-1})	1,69	<1,35	<1,35	2,56	<1,35	0,98	<1,35	2,82
Se (mg kg^{-1})	2,57	2,30	5,21	2,35	3,86	3,42	4,09	4,25
Sr (mg kg^{-1})	24,23	35,11	31,28	22,23	39,34	62,13	45,38	91,59
V (mg kg^{-1})	30,16	32,63	43,40	28,20	33,32	53,37	40,23	54,94
Zn (mg kg^{-1})	229,02	<3,28	<3,28	<3,28	35,52	<3,28	120,28	<3,28

	St. 3 - Nestore				**St. 4 - Nestore**			
	Mar	**May**	**Aug**	**Oct**	**Mar**	**May**	**Aug**	**Oct**
Al (mg kg^{-1})	$1,80\cdot10^{4}$	$2,23\cdot10^{4}$	$1,98\cdot10^{4}$	$2,25\cdot10^{4}$	$2,01\cdot10^{4}$	$2,35\cdot10^{4}$	$2,29\cdot10^{4}$	$2,41\cdot10^{4}$
Ca (mg kg^{-1})	$3,96\cdot10^{4}$	$2,51\cdot10^{4}$	$2,90\cdot10^{4}$	$2,53\cdot10^{4}$	$6,82\cdot10^{4}$	$4,36\cdot10^{4}$	$5,91\cdot10^{4}$	$4,46\cdot10^{4}$
Cd (mg kg^{-1})	<2,00	<2,00	9,21	<2,00	<2,00	<2,00	9,71	<2,00
Co (mg kg^{-1})	7,83	7,97	5,45	7,26	8,17	8,76	6,82	9,98
Cr (mg kg^{-1})	53,99	32,07	45,61	16,90	16,15	14,45	16,66	16,09
Cu (mg kg^{-1})	24,08	14,27	22,36	8,79	10,51	24,25	21,45	10,98
Fe (mg kg^{-1})	$1,61\cdot10^{4}$	$2,10\cdot10^{4}$	$2,11\cdot10^{4}$	$2,15\cdot10^{4}$	$1,74\cdot10^{4}$	$2,20\cdot10^{4}$	$2,32\cdot10^{4}$	$2,29\cdot10^{4}$
Mn (mg kg^{-1})	73,3	148,3	203,7	149,4	212,1	650,9	331,0	666,1
Mo (mg kg^{-1})	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95
Ni (mg kg^{-1})	47,56	42,51	31,66	35,54	57,89	43,55	30,83	40,37
Pb (mg Kg^{-1})	7,14	8,48	25,84	5,88	10,19	8,92	9,17	11,38
Sb (mg kg^{-1})	<1,35	0,68	<1,35	2,06	<1,35	<1,35	<1,35	1,71
Se (mg kg^{-1})	3,49	2,27	1,91	2,31	3,62	1,52	1,96	1,37
Sr (mg kg^{-1})	112,89	45,00	45,79	34,60	122,81	107,55	104,72	135,85
V (mg kg^{-1})	29,27	34,86	33,43	29,97	32,56	40,09	30,92	22,98
Zn (mg kg^{-1})	44,70	<3,28	8,64	<3,28	101,29	<3,28	319,12	<3,28

"---", dry stream

Highlighted parts represent values above average for every single metal.

Table 4.1.2. is continued on the next page.

	St. 5 - Nestore				St. 6 - Nestore			
	May	May	Aug	Oct	Mar	May	Aug	Oct
Al (mg kg^{-1})	3,13·10^{4}	1,95·10^{4}	1,45·10^{4}	1,95·10^{4}	2,06·10^{4}	1,85·10^{4}	2,10·10^{4}	1,88·10^{4}
Ca (mg kg^{-1})	2,10·10^{4}	2,90·10^{4}	7,64·10^{4}	2,89·10^{4}	5,92·10^{4}	6,16·10^{4}	1,83·10^{5}	6,26·10^{4}
Cd (mg kg^{-1})	<2,00	<2,00	6,59	<2,00	<2,00	<2,00	7,98	2,05
Co (mg kg^{-1})	10,55	8,17	7,80	7,40	8,18	7,61	4,62	10,92
Cr (mg kg^{-1})	16,13	8,10	13,54	12,04	17,42	20,15	25,89	32,97
Cu (mg kg^{-1})	13,92	22,64	17,98	10,75	21,46	30,20	35,71	44,84
Fe (mg kg^{-1})	2,85·10^{4}	1,67·10^{4}	1,47·10^{4}	1,70·10^{4}	1,82·10^{4}	1,94·10^{4}	2,14·10^{4}	2,01·10^{4}
Mn (mg kg^{-1})	35,1	353,8	308,1	353,2	241,4	137,9	685,5	140,1
Mo (mg kg^{-1})	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95
Ni (mg kg^{-1})	71,15	36,22	31,43	29,78	39,05	51,93	32,49	48,43
Pb (mg Kg^{-1})	16,21	11,85	8,02	8,37	16,15	11,76	12,55	20,85
Sb (mg kg^{-1})	<1,35	<1,35	<1,35	1,39	<1,35	<1,35	1,50	1,59
Se (mg kg^{-1})	3,58	3,15	<0,80	2,23	3,98	3,47	3,07	2,47
Sr (mg kg^{-1})	52,28	119,37	160,68	147,36	145,28	138,78	237,77	184,01
V (mg kg^{-1})	64,02	34,54	24,96	23,10	36,06	41,21	36,17	15,58
Zn (mg kg^{-1})	54,44	<3,28	1,00·10^{3}	<3,28	75,17	<3,28	96,38	<3,28

	St. 7 - Caina				St. 8 - Genna			
	Mar	May	Aug	Oct	Mar	May	Aug	Oct
Al (mg kg^{-1})	2,30·10^{4}	2,42·10^{4}	1,35·10^{4}	2,46·10^{4}	1,71·10^{4}	1,69·10^{4}	1,49·10^{4}	1,71·10^{4}
Ca (mg kg^{-1})	9,80·10^{4}	8,94·10^{4}	1,17·10^{5}	9,09·10^{4}	1,61·10^{5}	1,23·10^{5}	1,28·10^{5}	1,24·10^{5}
Cd (mg kg^{-1})	<2,00	<2,00	5,18	<2,00	<2,00	<2,00	5,63	<2,00
Co (mg kg^{-1})	8,33	10,06	5,19	8,34	9,01	10,60	10,92	10,60
Cr (mg kg^{-1})	18,12	22,76	15,40	18,18	18,49	19,47	16,47	18,53
Cu (mg kg^{-1})	28,31	57,37	30,92	28,07	17,51	14,70	27,18	27,14
Fe (mg kg^{-1})	2,18·10^{4}	2,38·10^{4}	1,36·10^{4}	2,46·10^{4}	1,48·10^{4}	1,62·10^{4}	1,49·10^{4}	1,68·10^{4}
Mn (mg kg^{-1})	566,2	516,5	321,0	525,4	577,4	380,8	974,2	384,6
Mo (mg kg^{-1})	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95
Ni (mg kg^{-1})	41,87	48,75	23,47	33,03	29,82	25,31	28,67	24,63
Pb (mg Kg^{-1})	11,99	20,63	7,48	12,52	12,32	13,51	17,70	17,71
Sb (mg kg^{-1})	<1,35	<1,35	<1,35	1,80	<1,35	<1,35	<1,35	1,70
Se (mg kg^{-1})	3,43	3,07	1,92	3,49	2,63	1,14	1,44	1,95
Sr (mg kg^{-1})	252,61	256,82	260,50	315,33	266,07	262,65	242,61	324,80
V (mg kg^{-1})	36,92	46,81	21,27	31,42	22,35	26,60	21,82	18,17
Zn (mg kg^{-1})	<3,28	<3,28	898,06	<3,28	<3,28	<3,28	40,50	<3,28

“---“, dry stream
Highlighted parts represent values above average for every single metal.
Table 4.1.2. is continued on the next page.

	St. 9 - Fersinone				**St. 10 - Calvana**			
	Mar	**May**	**Aug**	**Oct**	**Mar**	**May**	**Aug**	**Oct**
Al (mg kg^{-1})	$2{,}35\cdot10^4$	$2{,}57\cdot10^4$	$2{,}34\cdot10^4$	$2{,}57\cdot10^4$	$2{,}58\cdot10^4$	$2{,}27\cdot10^4$	$1{,}82\cdot10^4$	$2{,}30\cdot10^4$
Ca (mg kg^{-1})	$1{,}33\cdot10^5$	$1{,}53\cdot10^5$	$1{,}43\cdot10^5$	$1{,}54\cdot10^5$	$1{,}50\cdot10^5$	$9{,}82\cdot10^4$	$1{,}78\cdot10^4$	$9{,}94\cdot10^4$
Cd (mg kg^{-1})	<2,00	<2,00	9,45	3,29	<2,00	<2,00	8,29	2,10
Co (mg kg^{-1})	5,40	5,85	4,90	8,90	8,00	11,21	4,00	6,10
Cr (mg kg^{-1})	19,68	20,75	18,94	---	21,30	24,98	---	---
Cu (mg kg^{-1})	17,20	17,95	26,13	---	22,66	34,54	---	---
Fe (mg kg^{-1})	$2{,}14\cdot10^4$	$2{,}44\cdot10^4$	$2{,}41\cdot10^4$	$2{,}49\cdot10^4$	$2{,}29\cdot10^4$	$2{,}43\cdot10^4$	$1{,}83\cdot10^4$	$2{,}50\cdot10^4$
Mn (mg kg^{-1})	157,5	310,2	196,2	311,4	364,6	255,3	223,2	258,3
Mo (mg kg^{-1})	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95
Ni (mg kg^{-1})	40,65	34,16	36,37	47,71	45,95	48,96	29,71	39,88
Pb (mg kg^{-1})	5,33	4,97	6,47	9,60	7,02	9,50	4,61	7,50
Sb (mg kg^{-1})	<1,35	<1,35	<1,35	<1,35	<1,35	1,36	<1,35	<1,35
Se (mg kg^{-1})	4,54	3,18	2,10	5,31	5,41	5,75	2,94	4,52
Sr (mg kg^{-1})	401,25	479,12	364,66	380,28	296,40	285,33	349,62	423,62
V (mg kg^{-1})	37,54	37,52	39,83	47,95	46,84	60,10	34,48	29,48
Zn (mg kg^{-1})	<3,28	<3,28	240,08	<3,28	<3,28	<3,28	66,83	<3,28

“---“, dry stream
Highlighted parts represent values above average for every single metal.

Concentrations of C and Cu were taken from Matteo Pallottini’s Doctoral Thesis: “Qualità biologica dei corsi d’aqua e impatto dei metalli pesanti sulle popolazione e comunità di macroinvertebrati“ and were detected by flame atomic absorption spectroscopy.

4.2. CONCENTRATIONS OF METALS IN BLANK SAMPLES

Table 4.2.1. Average values of blank samples

Element	Al	Ca	Cd	Co	Fe	Mn	Mo
Concentration (mg/L)	7,4599	15,3876	0,0028	0,0008	1,4304	0,1312	0,0044
SD	4,3712	1,0438	0,0019	0,0014	1,0438	0,0000	0,0013
RSD	58,5956	6,7832	66,9751	165,0198	72,9705	0,0000	29,8988
Element	Ni	Pb	Sb	Se	Sr	V	Zn
Concentration (mg/L)	0,0086	0,0072	0,0123	0,0068	0,0073	0,0068	6,1236
SD	0,0045	0,0012	0,0005	0,0037	0,0036	0,0032	2,1783
RSD	52,6689	16,8640	3,9330	55,0346	49,4716	46,3423	35,5717

“SD“, Standard Deviation
“RSD“, Relative Standard Deviation

4.3. CONCENTRATIONS OF YTTRIUM

Table 4.3.1. Concentrations of Yttrium in diluted solutions

	Sample	Blank	ST 1	ST 2	ST 3	ST 4	ST 5	ST 6	ST 7	ST 8	ST 9	ST 10
Concentration of Y (mg/L)	Winter	10,04	10,14	9,99	10,35	9,97	10	10,9	9,79	10,22	9,86	10,2
	Spring	10,14	9,4	10,04	10,57	10,38	9,66	10,04	10,08	10,03	9,91	9,53
	Summer	9,49	9,47	8,87	10,06	9,06	8,96	9,81	9,75	9,76	9,15	9,68
	Autumn	8,69	9,77	9,69	9,87	9,76	9,79	9,96	10,28	9,83	9,25	10
Intensity	Winter	$1,53\cdot10^{7}$	$1,54\cdot10^{7}$	$1,52\cdot10^{7}$	$1,57\cdot10^{7}$	$1,52\cdot10^{7}$	$1,52\cdot10^{7}$	$1,66\cdot10^{7}$	$1,49\cdot10^{7}$	$1,55\cdot10^{7}$	$1,50\cdot10^{7}$	$1,55\cdot10^{7}$
	Spring	$1,54\cdot10^{7}$	$1,42\cdot10^{7}$	$1,53\cdot10^{7}$	$1,61\cdot10^{7}$	$1,58\cdot10^{7}$	$1,47\cdot10^{7}$	$1,53\cdot10^{7}$	$1,53\cdot10^{7}$	$1,52\cdot10^{7}$	$1,51\cdot10^{7}$	$1,45\cdot10^{7}$
	Summer	$1,44\cdot10^{7}$	$1,44\cdot10^{7}$	$1,35\cdot10^{7}$	$1,53\cdot10^{7}$	$1,38\cdot10^{7}$	$1,36\cdot10^{7}$	$1,49\cdot10^{7}$	$1,48\cdot10^{7}$	$1,48\cdot10^{7}$	$1,39\cdot10^{7}$	$1,47\cdot10^{7}$
	Autumn	$1,32\cdot10^{7}$	$1,48\cdot10^{7}$	$1,47\cdot10^{7}$	$1,50\cdot10^{7}$	$1,48\cdot10^{7}$	$1,49\cdot10^{7}$	$1,51\cdot10^{7}$	$1,56\cdot10^{7}$	$1,49\cdot10^{7}$	$1,41\cdot10^{7}$	$1,52\cdot10^{7}$
Intensity factor	Winter	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$
	Spring	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$
	Summer	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$
	Autumn	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$	$1,52\cdot10^{6}$
	Average	$1,52\cdot10^{6}$	SD	441,146	RSD	0,029						

The intensity of the energy emitted at the chosen wavelength is proportional to the amount of that element in the analyzed sample. The intensity factor is the intensity divided with concentration in mg/L.

4.4. AVERAGE VALUES OF METALS IN SEDIMENTS

4.4.1. Average concentrations of metals

Table 4.4.1. Average concentrations of metals in sediments of Nestore River Basin in mg/kg

	Al	Ca	Cd	Co	Cr	Cu	Fe	Mn
Average	$2,17\cdot10^{4}$	$7,82\cdot10^{4}$	2,74	7,89	23,78	22,05	$2,08\cdot10^{4}$	363,05
SD	$4,23\cdot10^{3}$	$5,12\cdot10^{4}$	3,22	2,03	10,72	10,70	$4,21\cdot10^{3}$	285,16
RSD	19,51	65,53	117,38	25,78	45,10	48,53	20,23	78,55
	Mo	Ni	Pb	Sb	Se	Sr	V	Zn
Average	<1,95	40,85	10,85	<1,35	3,04	185,57	35,13	85,37
SD	--	11,23	4,88	--	1,25	129,76	10,98	213,94
RSD	--	27,50	44,96	--	40,93	69,93	31,27	250,59

“SD“, Standard Deviation
“RSD“, Relative Standard Deviation

To compare concentrations of metals from The Nestore River basin with sediments from another river, data from Drava River, Croatia was taken and presented in Table 4.4.

Table 4.4.2. Average concentrations of metals in sediments in Drava River, Croatia[48]

Metal	Cd	Cr	Cu	Fe	Mn	Ni	Pb
mg/kg	0,249	18,58	83,31	21631,7	461,2	15,22	36,87

4.4.2. Average seasonal amounts of metals in sediments

Table 4.4.3. Average seasonal amounts of metals in sediments of The Nestore River basin

	Al				Ca			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
Average	$2,19\cdot10^{4}$	$2,26\cdot10^{4}$	$1,93\cdot10^{4}$	$2,28\cdot10^{4}$	$7,64\cdot10^{4}$	$6,99\cdot10^{4}$	$9,59\cdot10^{4}$	$7,06\cdot10^{4}$
SD	$4,31\cdot10^{3}$	$4,15\cdot10^{3}$	$4,01\cdot10^{3}$	$4,11\cdot10^{3}$	$5,58\cdot10^{4}$	$4,39\cdot10^{4}$	$6,23\cdot10^{4}$	$4,43\cdot10^{4}$
RSD	19,73	18,34	20,75	18,04	73,07	62,76	65,01	62,69

“SD“, Standard Deviation
“RSD“, Relative Standard Deviation
Highlighted parts represent the biggest values for every single metal.
Table 4.4.2. is continued on the next page.

	Cd				Co			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
Average	<2,00	<2,00	7,60	2,36	7,75	8,62	6,78	8,39
SD	--	--	2,50	0,76	1,55	1,80	2,60	1,80
RSD	--	--	32,88	31,94	20,03	20,84	38,36	21,47

	Cr				Cu			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
Average	23,45	23,33	25,73	22,54	17,23	25,97	24,06	20,92
SD	11,39	11,16	12,51	8,85	6,98	13,53	6,87	13,23
RSD	48,60	47,83	48,63	39,25	40,55	52,09	28,56	63,27

	Fe				Mn			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
Average	$1,95\cdot10^4$	$2,19\cdot10^4$	$1,96\cdot10^4$	$2,24\cdot10^3$	400,07	350,36	348,08	353,68
SD	$4,22\cdot10^3$	$4,21\cdot10^3$	$4,00\cdot10^3$	$4,20\cdot10^3$	470,64	158,54	278,23	162,09
RSD	21,66	19,26	20,42	18,70	117,64	45,25	79,93	45,83

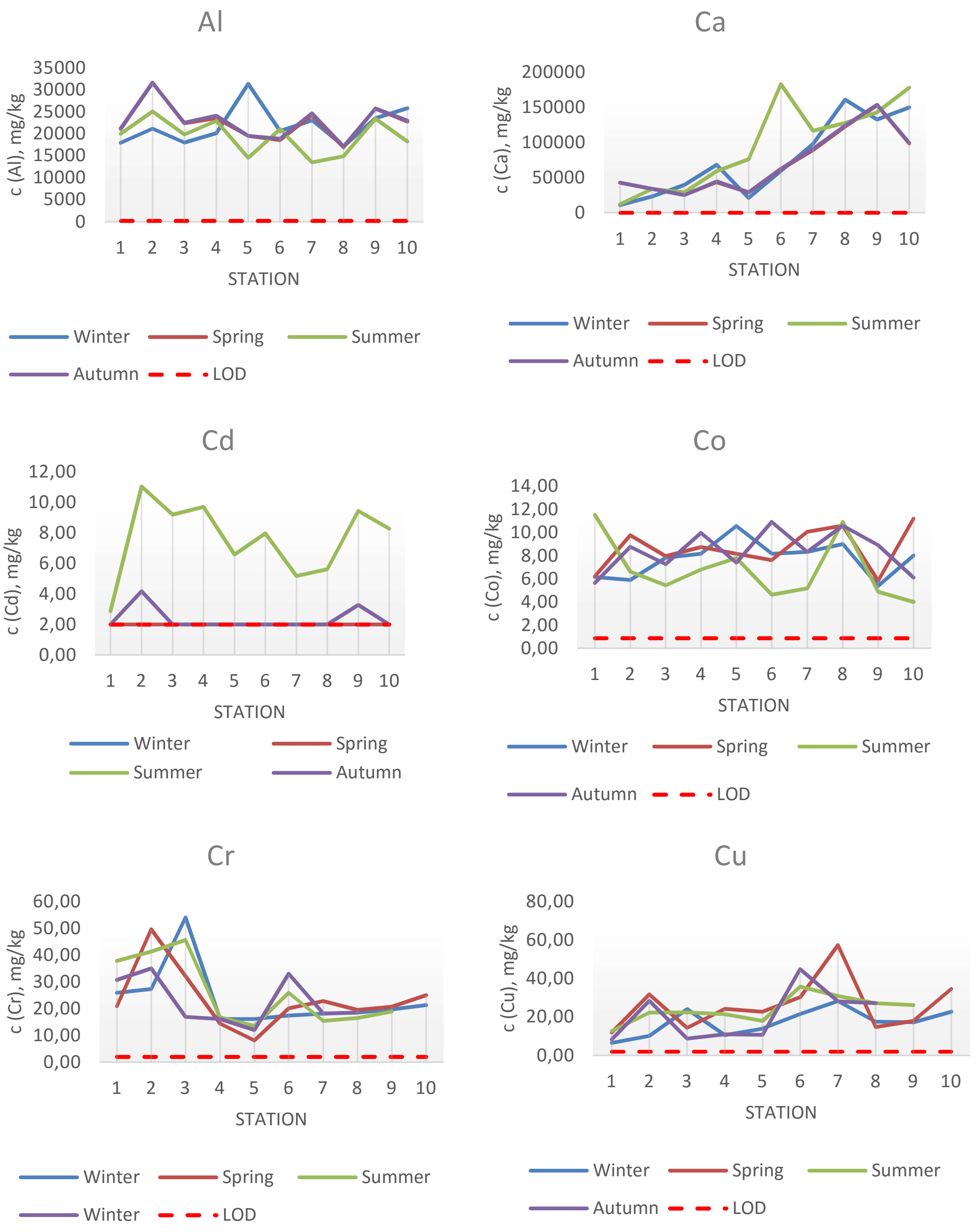
	Mo				Ni			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
Average	<1,95	<1,95	<1,95	<1,95	47,93	42,97	34,21	37,66
SD	--	--	--	--	12,32	10,20	10,13	8,72
RSD	--	--	--	--	25,70	23,74	29,61	23,15

	Pb				Sb			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
Average	9,99	10,96	11,06	11,38	0,83	0,59	0,66	1,72
SD	4,02	4,50	6,32	5,04	0,60	0,55	0,51	0,67
RSD	40,30	41,07	57,17	44,31	72,31	93,63	77,95	38,83

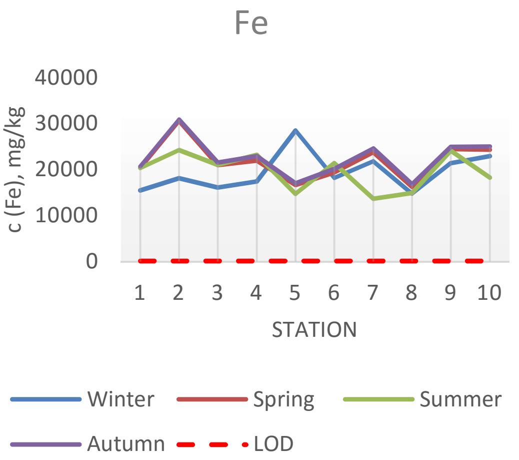
	Se				Sr			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
Average	3,71	2,93	2,50	3,03	171,32	179,19	184,30	205,97
SD	0,84	1,28	1,38	1,29	126,39	140,25	125,04	144,87
RSD	22,53	43,58	54,95	42,62	73,77	78,27	67,85	70,33

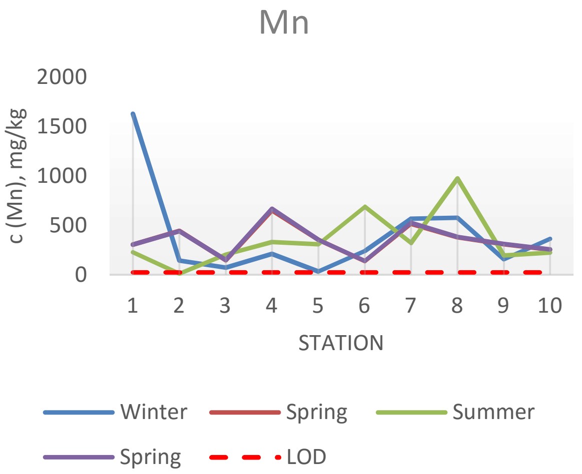
	V				Zn			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
Average	36,90	40,77	32,65	30,18	55,33	<3,28	278,15	<3,28
SD	11,46	10,12	7,82	12,44	69,93	--	369,42	--
RSD	31,07	24,81	23,94	41,24	126,40	--	132,81	--

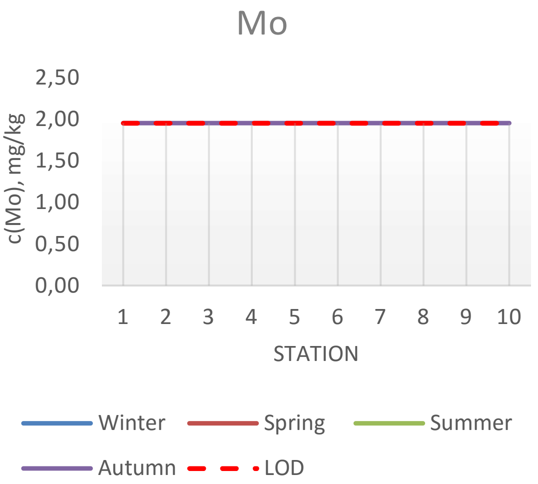
"SD", Standard Deviation
"RSD", Relative Standard Deviation
Highlighted parts represent the biggest values for every single metal.

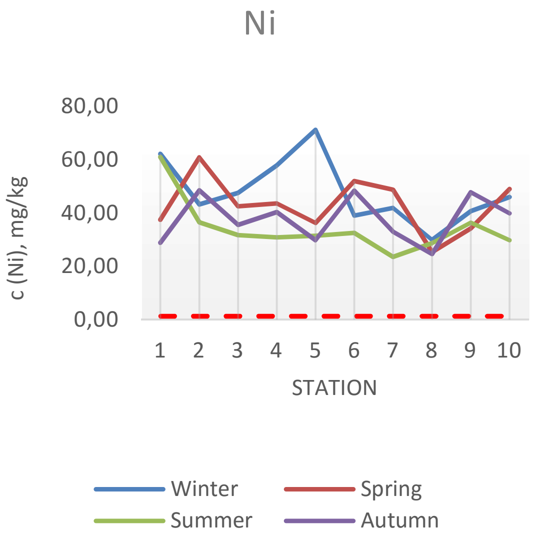


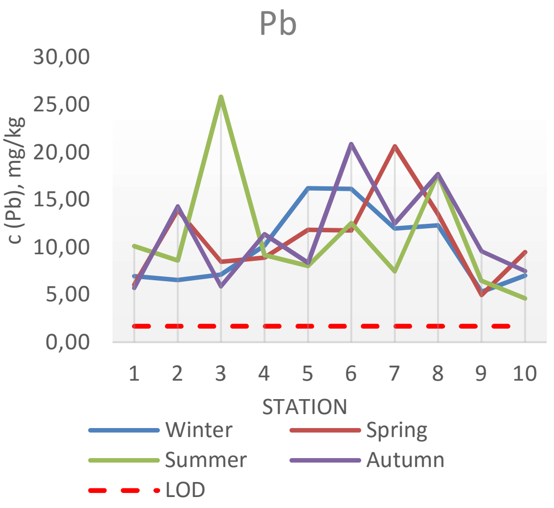
“LOD“, Limit of Detection
Fig. 4.4.1. is continued on the next page.

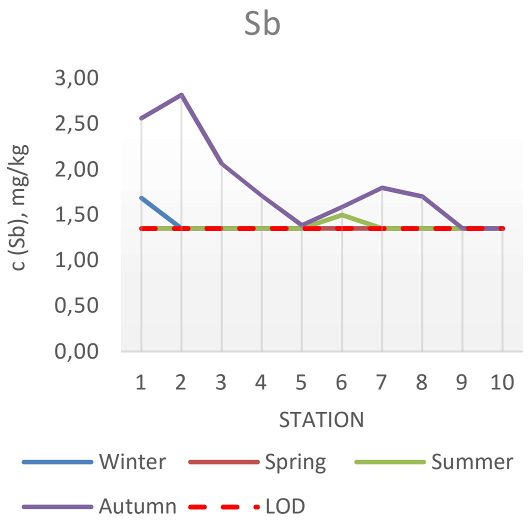




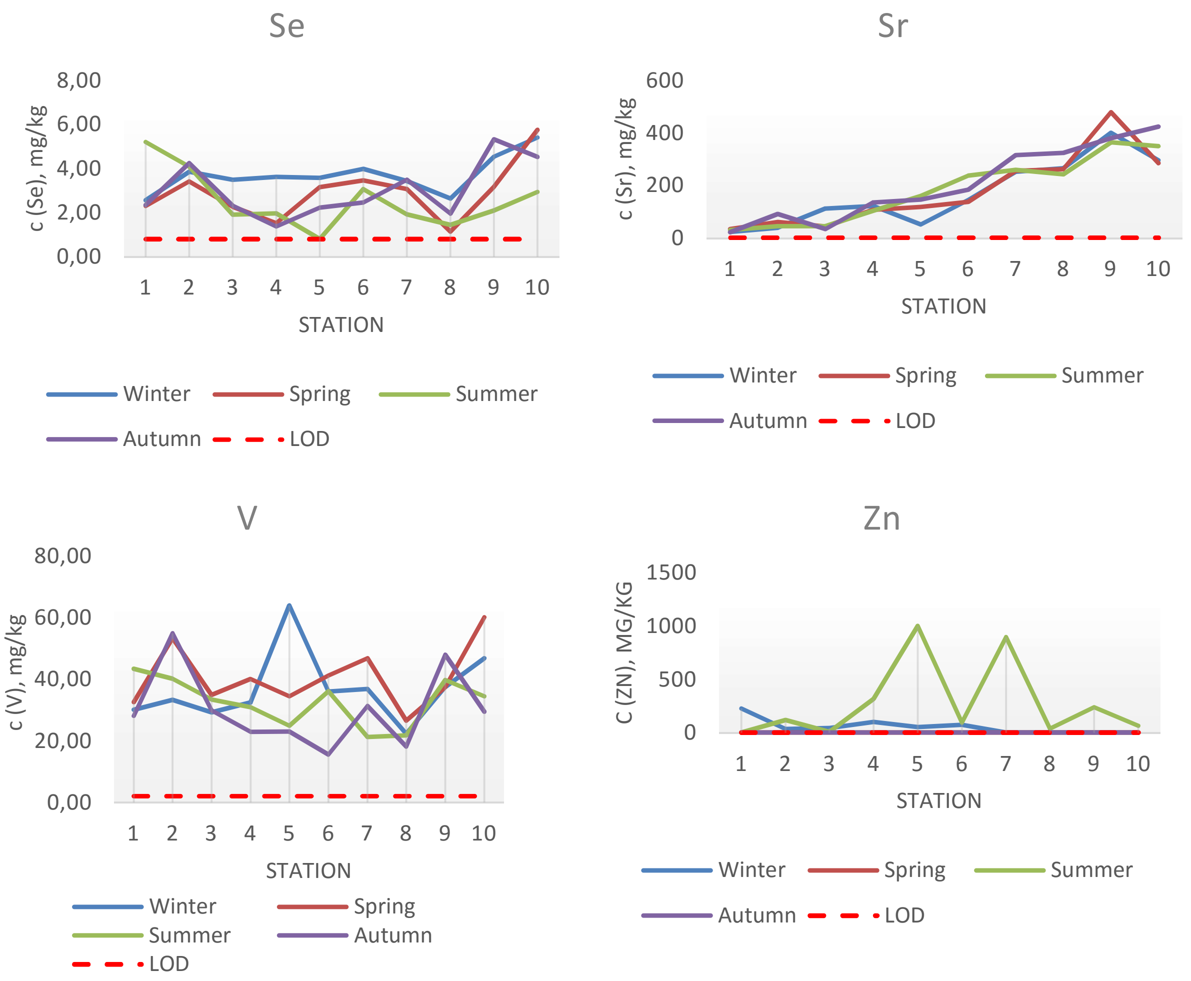








“LOD“, Limit of Detection
Fig. 4.4.1. is continued on the next page.



“LOD“, Limit of Detection

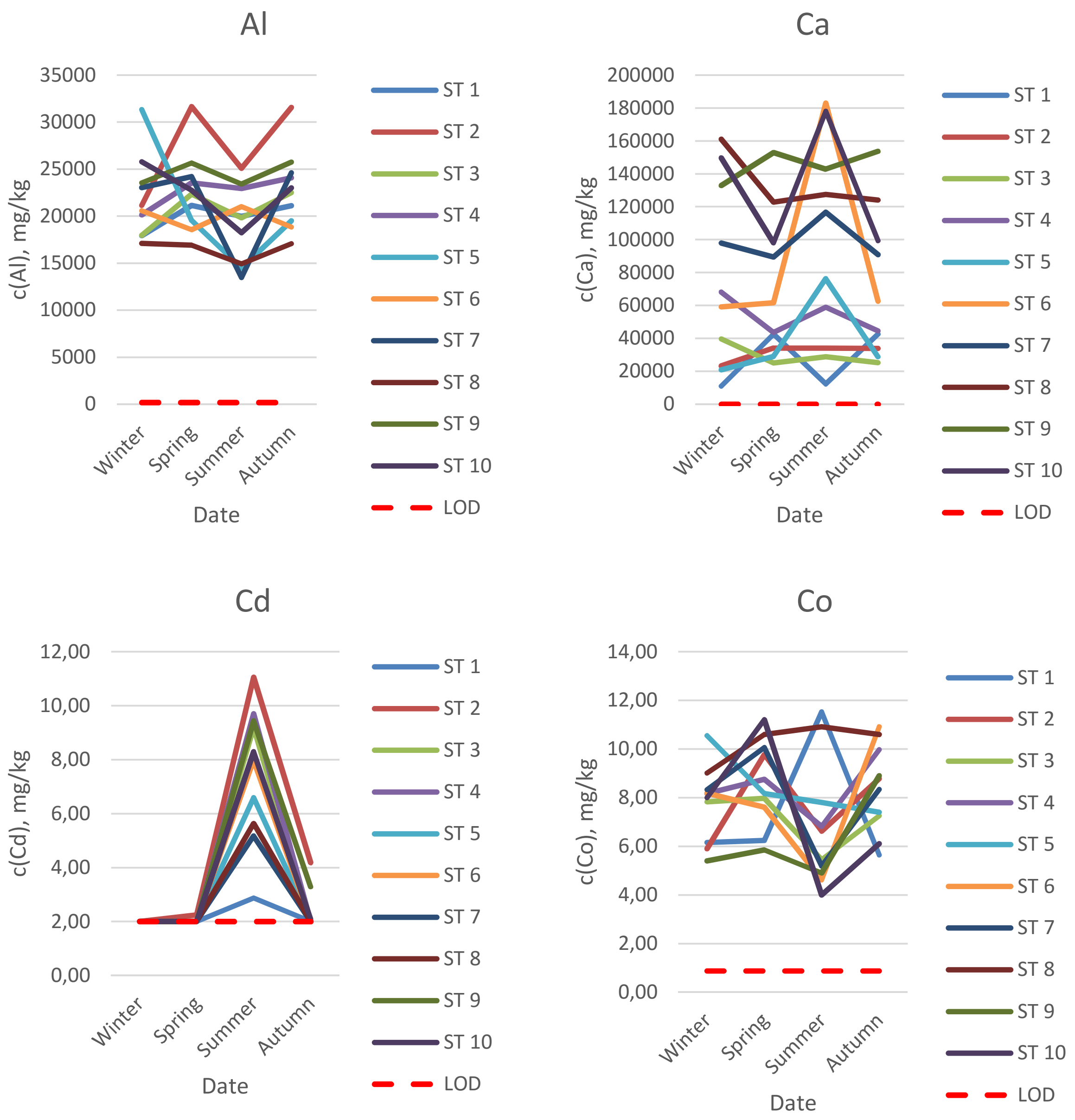
Fig. 4.4.1. Average seasonal amounts of metals in sediments

4.4.3. Average station amounts of metals in sediments

Table 4.4.4. Average station amounts of metals in sediments of The Nestore River basin in mg/kg

		1	2	3	4	5	6	7	8	9	10
Al	AVG	$2,00\cdot10^{4}$	$2,73\cdot10^{4}$	$2,07\cdot10^{4}$	$2,27\cdot10^{4}$	$2,12\cdot10^{4}$	$1,97\cdot10^{4}$	$2,13\cdot10^{3}$	$1,65\cdot10^{4}$	$2,46\cdot10^{4}$	$2,24\cdot10^{4}$
	SD	$1,5\cdot10^{3}$	$5,15\cdot10^{3}$	$2,17\cdot10^{3}$	$1,76\cdot10^{3}$	$7,14\cdot10^{4}$	$1,23\cdot10^{3}$	$5,29\cdot10^{3}$	$1,06\cdot10^{3}$	$1,29\cdot10^{3}$	$3,13\cdot10^{3}$
	RSD	7,52	18,84	10,52	7,76	33,67	6,24	24,79	6,44	5,23	13,94
Ca	AVG	$2,72\cdot10^{4}$	$3,1410^{4}$	$2,98\cdot10^{4}$	$5,39\cdot10^{4}$	$3,88\cdot10^{4}$	$9,16\cdot10^{4}$	$9,87\cdot10^{4}$	$1,34\cdot10^{5}$	$1,46\cdot10^{3}$	$1,31\cdot10^{5}$
	SD	$1,78\cdot10^{4}$	$5,3510^{4}$	$6,83\cdot10^{3}$	$1,19\cdot10^{3}$	$2,53\cdot10^{4}$	$6,09\cdot10^{3}$	$1,25\cdot10^{4}$	$1,82\cdot10^{4}$	$9,80\cdot10^{3}$	$3,93\cdot10^{4}$
	RSD	65,68	17,07	22,96	22,05	65,22	66,48	12,64	13,63	6,73	29,94
Cd	AVG	<2,00	4,37	3,07	3,07	2,25	2,79	2,15	<2,00	3,49	3,08
	SD	--	4,78	4,16	4,47	2,94	3,56	2,17	--	4,20	3,60
	RSD	--	109,22	135,60	145,28	131,01	127,41	101,19	--	120,50	116,83
Co	AVG	7,39	7,77	7,13	8,43	8,48	7,83	7,98	10,28	6,26	7,33
	SD	2,77	1,81	1,16	1,31	1,42	2,58	2,03	0,86	1,80	3,06
	RSD	37,41	23,32	16,26	15,57	16,71	32,97	25,46	8,36	28,82	41,77
Cr	AVG	28,83	38,31	37,14	15,84	12,45	24,11	18,62	18,24	19,79	23,14
	SD	7,18	9,49	16,24	0,96	3,36	6,88	3,05	1,26	0,91	2,60
	RSD	24,91	24,77	43,72	6,06	26,96	28,55	16,40	6,93	4,60	11,25
Cu	AVG	9,87	23,13	17,38	16,80	16,32	33,05	36,17	21,63	20,43	28,60
	SD	2,94	9,53	7,14	7,08	5,15	9,81	14,19	6,48	4,95	8,40
	RSD	29,78	41,23	41,12	42,17	31,53	29,67	39,24	29,98	24,25	29,37
Fe	AVG	$1,92\cdot10^{4}$	$2,60\cdot10^{4}$	$1,99\cdot10^{4}$	$2,14\cdot10^{4}$	$1,92\cdot10^{4}$	$1,98\cdot10^{4}$	$2,09\cdot10^{4}$	$1,57\cdot10^{4}$	$2,37\cdot10^{4}$	$2,26\cdot10^{4}$
	SD	$2,51\cdot10^{3}$	$6,0\cdot10^{3}$	$2,58\cdot10^{3}$	$2,68\cdot10^{3}$	$6,27\cdot10^{3}$	$1,36\cdot10^{3}$	$5,01\cdot10^{3}$	$9,90\cdot10^{3}$	$1,60\cdot10^{3}$	$3,02\cdot10^{3}$
	RSD	13,06	23,24	12,94	12,52	32,58	6,86	23,95	6,31	6,75	13,37
Mn	AVG	616,93	260,39	143,68	465,04	262,52	301,23	482,29	579,24	243,83	275,35
	SD	675,29	218,24	53,57	228,68	153,14	260,71	109,67	278,86	78,94	61,60
	RSD	109,46	83,81	37,28	49,18	58,34	86,55	22,74	48,14	32,37	22,37
Mo	AVG	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95	<1,95
	SD	--	--	--	--	--	--	--	--	--	--
	RSD	--	--	--	--	--	--	--	--	--	--
Pb	AVG	7,22	10,84	11,84	9,91	11,10	14,56	13,16	15,31	6,59	7,16
	SD	2,01	3,85	9,39	1,12	3,78	4,23	5,47	2,81	2,11	2,01
	RSD	27,83	35,51	79,37	11,29	34,10	29,05	41,61	18,34	31,93	28,10
Sb	AVG	1,38	<1,35	<1,35	<1,35	<1,35	<1,35	<1,35	<1,35	<1,35	<1,35
	SD	0,96	--	--	--	--	--	--	--	--	--
	RSD	70,00	--	--	--	--	--	--	--	--	--
Se	AVG	3,11	3,91	2,50	2,12	2,34	3,25	2,98	1,79	3,78	4,66
	SD	1,41	0,36	0,68	1,03	1,41	0,64	0,73	0,65	1,43	1,26
	RSD	45,23	9,22	27,42	48,79	60,26	19,67	24,43	36,50	37,78	27,03
Sr	AVG	28,21	59,61	59,57	117,74	119,92	176,46	271,31	274,03	406,33	338,75
	SD	6,02	23,40	35,91	14,46	48,27	45,49	29,52	35,39	50,79	63,16
	RSD	21,33	39,25	60,28	12,28	40,25	25,78	10,88	12,91	12,50	18,64
V	AVG	33,60	45,46	31,89	31,64	36,66	32,26	34,10	22,23	40,71	42,73
	SD	6,78	10,44	2,69	7,02	18,92	11,37	10,67	3,45	4,95	13,69
	RSD	20,19	22,97	8,45	22,18	51,62	35,25	31,27	15,52	12,15	32,04
Zn	AVG	59,71	14,97	106,74	265,98	44,53	226,97	13,91	13,91	62,48	19,17
	SD	55,26	19,98	148,93	491,88	48,41	447,39	17,90	17,90	118,40	31,78
	RSD	189,01	133,42	139,52	184,93	108,72	197,11	128,72	128,72	189,50	165,78

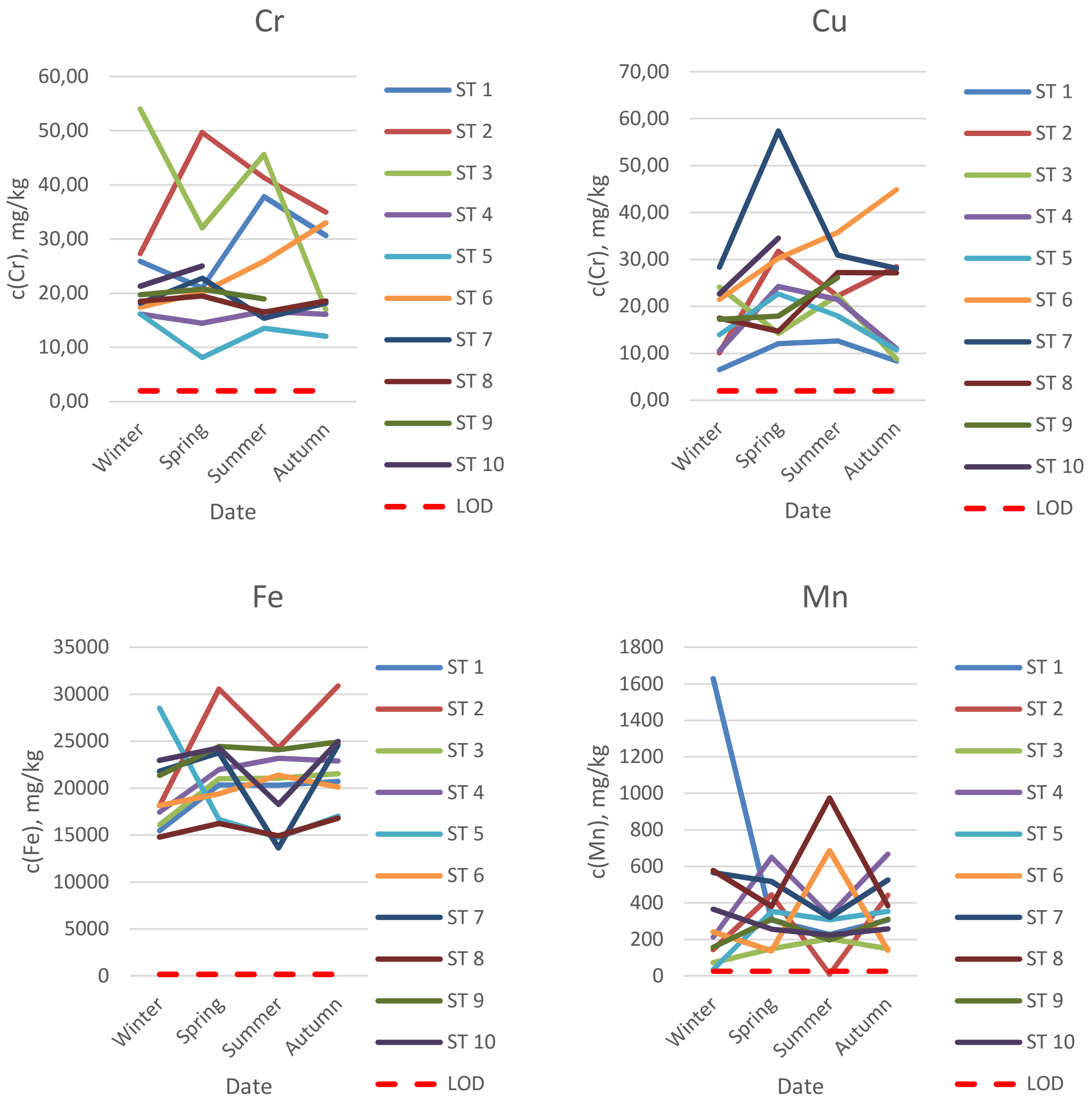
“AVG“, Average value
“SD“, Standard Deviation
“RSD“, Relative Standard Deviation
Highlighted parts represent the biggest value for every single metal.



“LOD“, Limit of Detection

“ST 1-10“, stations 1-10

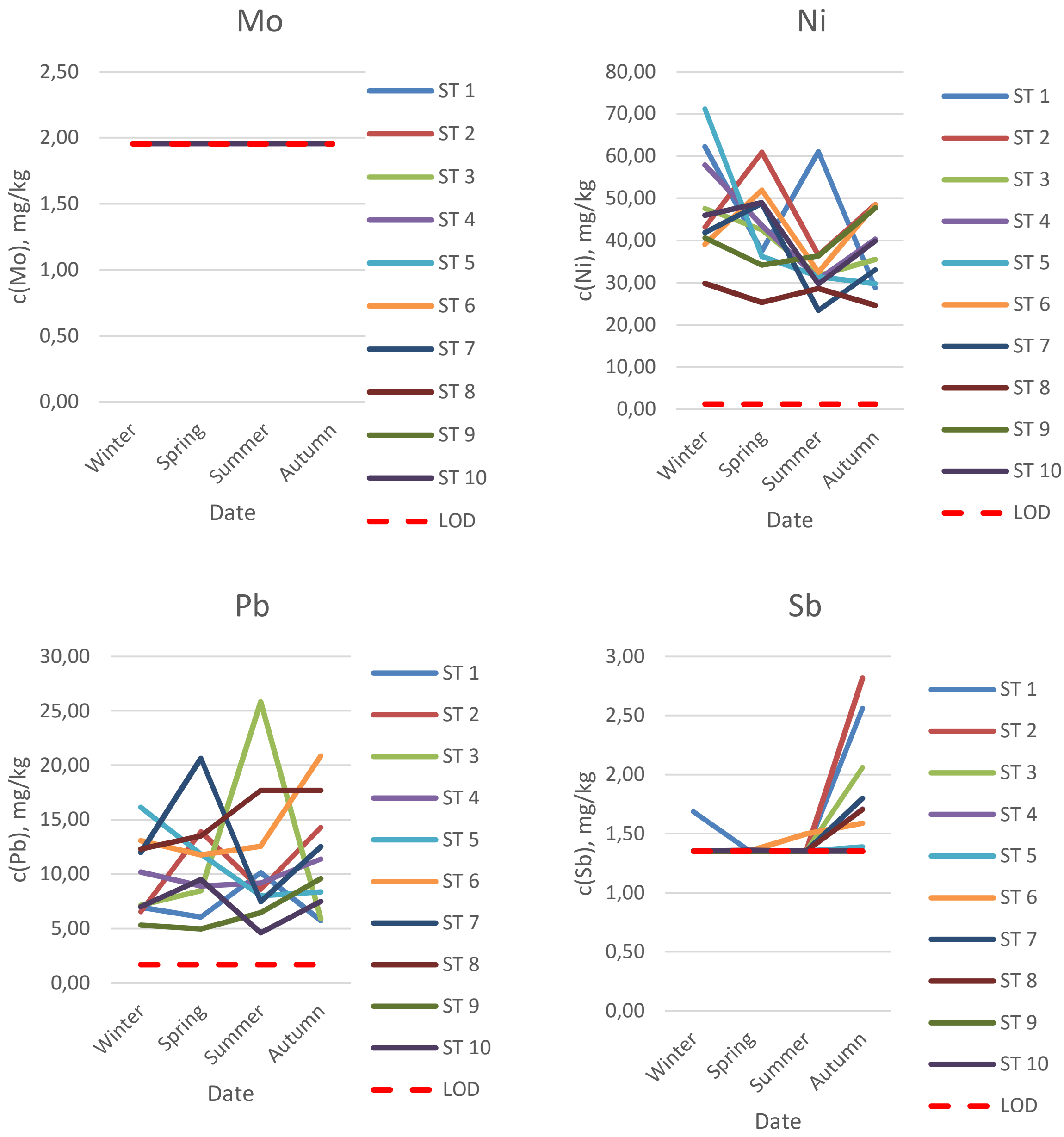
Fig. 4.4.2. is continued on the next page.



“LOD“, Limit of Detection

“ST 1-10“, stations 1-10

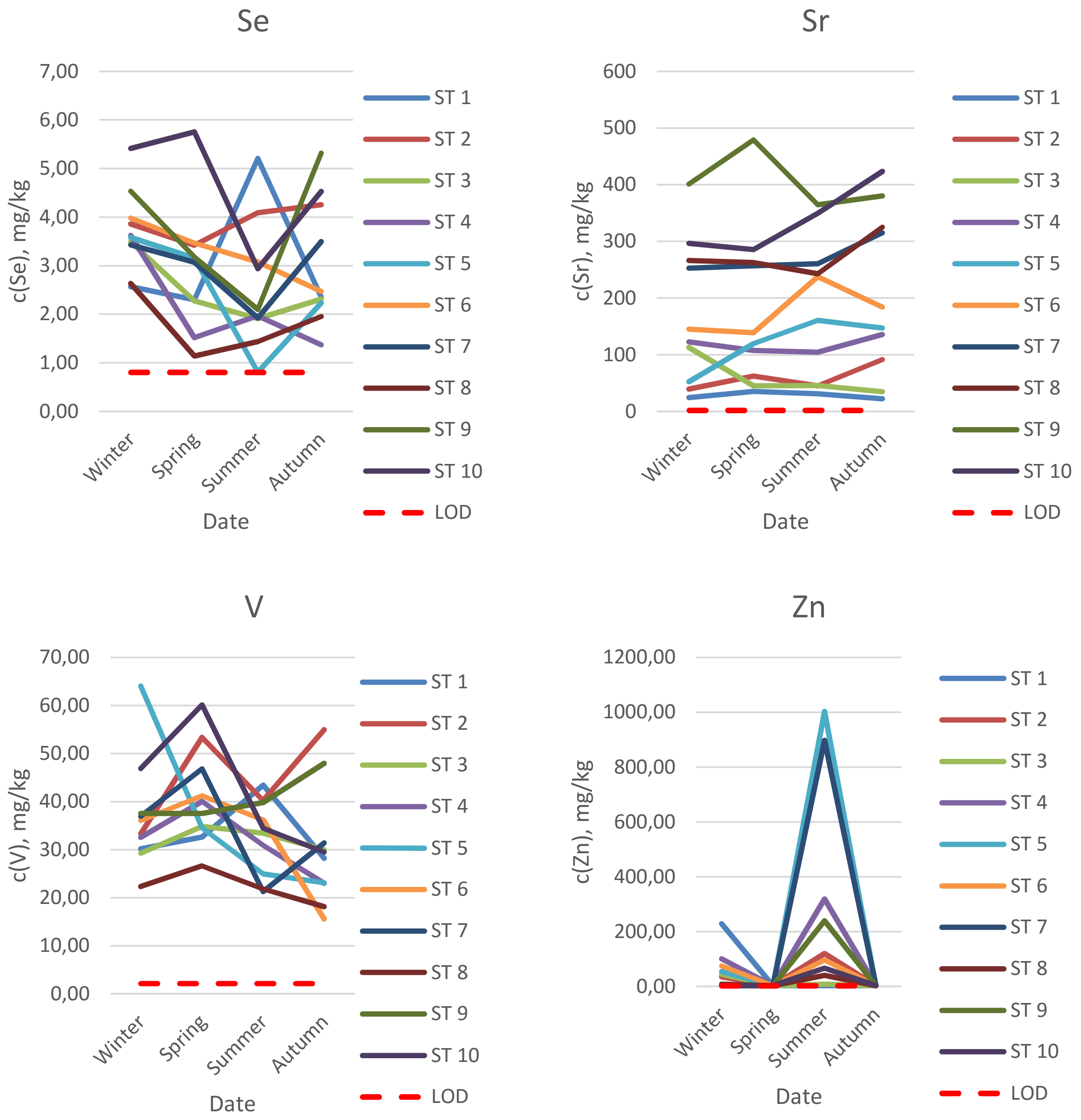
Fig. 4.4.2. is continued on the next page.



“LOD“, Limit of Detection

“ST 1-10“, stations 1-10

Fig. 4.4.2. is continued on the next page.



“LOD“, Limit of Detection

“ST 1-10“, stations 1-10

Fig 4.4.2. Average station amounts of heavy metals in sediments

4.5. ENRICHMENT FACTOR

Table 4.5.1. Enrichment factor according to the station 9 – The Fersinone Stream for The Nestore River basin

	Date/ station	1	2	3	4	5	6	7	8	9	10
Ca	Winter	0,11	0,20	0,39	0,60	0,12	0,51	0,75	1,67	1,00	1,03
	Spring	0,34	0,18	0,19	0,31	0,25	0,56	0,62	1,22	1,00	0,72
	Summer	0,10	0,22	0,24	0,42	0,86	1,43	1,42	1,40	1,00	1,60
	Autumn	0,34	0,18	0,19	0,31	0,25	0,56	0,62	1,22	1,00	0,72
Cd	Winter	--	--	--	--	--	--	--	--	--	--
	Spring	--	--	--	--	--	--	--	--	--	--
	Summer	0,36	1,09	1,15	1,05	1,13	0,94	0,95	0,94	1,00	1,13
	Autumn	--	1,04	--	--	--	--	--	--	1,00	--
Cr	Winter	1,73	1,54	3,59	0,96	0,62	1,01	0,94	1,29	1,00	0,99
	Spring	1,22	1,94	1,77	0,76	0,51	1,34	1,16	1,42	1,00	1,36
	Summer	2,34	2,04	2,84	0,90	1,16	1,52	1,41	1,37	1,00	--
	Autumn	--	--	--	--	--	--	--	--	--	--
Co	Winter	1,50	1,22	1,90	1,77	1,47	1,73	1,58	2,30	1,00	1,35
	Spring	1,29	1,36	1,57	1,63	1,83	1,80	1,82	2,75	1,00	2,16
	Summer	2,76	1,26	1,31	1,42	2,57	1,05	1,84	3,50	1,00	1,05
	Autumn	0,77	0,81	0,93	1,20	1,10	1,68	0,98	1,80	1,00	0,77
Cu	Winter	0,50	0,65	1,83	0,71	0,61	1,43	1,68	1,40	1,00	1,20
	Spring	0,81	1,43	0,91	1,47	1,66	2,33	3,39	1,24	1,00	2,17
	Summer	0,57	0,79	1,01	0,84	1,11	1,52	2,06	1,63	1,00	--
	Autumn	--	--	--	--	--	--	--	--	--	--
Fe	Winter	0,95	0,95	0,99	0,95	1,00	0,97	1,04	0,95	1,00	0,98
	Spring	1,01	1,01	0,99	0,98	0,90	1,10	1,03	1,01	1,00	1,12
	Summer	0,99	0,94	1,03	0,98	0,99	0,99	0,98	0,97	1,00	0,97
	Autumn	1,01	1,01	0,99	0,98	0,90	1,10	1,03	1,02	1,00	1,12
Mn	Winter	13,57	1,02	0,61	1,57	0,17	1,75	3,67	5,04	1,00	2,11
	Spring	1,20	1,16	0,55	2,29	1,50	0,61	1,76	1,86	1,00	0,93
	Summer	1,36	0,05	1,23	1,72	2,54	3,89	2,84	7,80	1,00	1,46
	Autumn	1,20	1,16	0,55	2,29	1,50	0,61	1,76	1,86	1,00	0,93
Mo	Winter	--	--	--	--	--	--	--	--	--	--
	Spring	--	--	--	--	--	--	--	--	--	--
	Summer	--	--	--	--	--	--	--	--	--	--
	Autumn	--	--	--	--	--	--	--	--	--	--

Color becomes darker towards higher values for every single metal.
Table 4.5.1. is continued on the next page.

Ni	Winter	2,01	1,18	1,53	1,66	1,32	1,10	1,05	1,01	1,00	1,03
	Spring	1,33	1,44	1,43	1,39	1,39	2,10	1,51	1,12	1,00	1,62
	Summer	1,97	0,94	1,03	0,87	1,40	1,00	1,12	1,24	1,00	1,05
	Autumn	0,73	0,83	0,85	0,90	0,82	1,39	0,72	0,78	1,00	0,94
Pb	Winter	1,71	1,37	1,76	2,23	2,28	2,81	2,30	3,18	1,00	1,20
	Spring	1,48	2,26	1,96	1,95	3,13	3,27	4,39	4,12	1,00	2,16
	Summer	1,84	1,24	4,71	1,45	2,00	2,16	2,01	4,30	1,00	0,91
	Autumn	0,73	1,22	0,70	1,27	1,15	2,97	1,36	2,78	1,00	0,87
Sb	Winter	--	--	--	--	--	--	--	--	--	--
	Spring	--	--	--	--	--	--	--	--	--	--
	Summer	--	--	--	--	--	--	--	--	--	--
	Autumn	--	--	--	--	--	--	--	--	--	--
Se	Winter	0,74	0,95	1,01	0,93	0,59	1,00	0,77	0,80	1,00	1,09
	Spring	0,88	0,87	0,82	0,52	1,30	1,51	1,02	0,54	1,00	2,04
	Summer	2,91	1,82	1,08	0,96	--	1,63	1,59	1,08	1,00	1,80
	Autumn	0,54	0,65	0,50	0,28	0,55	0,63	0,69	0,55	1,00	0,95
Sr	Winter	0,08	0,11	0,37	0,36	0,10	0,41	0,64	0,91	1,00	0,67
	Spring	0,09	0,11	0,11	0,24	0,33	0,40	0,57	0,83	1,00	0,67
	Summer	0,10	0,12	0,15	0,29	0,71	0,73	1,24	1,04	1,00	1,23
	Autumn	0,07	0,20	0,10	0,38	0,51	0,66	0,87	1,29	1,00	1,25
V	Winter	1,05	0,99	1,02	1,01	1,28	1,10	1,00	0,82	1,00	1,14
	Spring	1,06	1,15	1,07	1,16	1,21	1,52	1,32	1,08	1,00	1,81
	Summer	1,28	0,94	0,99	0,79	1,01	1,01	0,93	0,86	1,00	1,11
	Autumn	0,72	0,94	0,72	0,51	0,64	0,44	0,69	0,57	1,00	0,69
Zn	Winter	--	--	--	--	--	--	--	--	--	--
	Spring	--	--	--	--	--	--	--	--	--	--
	Summer	--	0,47	0,04	1,36	6,75	0,45	6,51	0,26	1,00	0,36
	Autumn	--	--	--	--	--	--	--	--	--	--

Color becomes darker towards higher values for every single metal.

Table 4.5.2. Enrichment factor according to the station 10 - The Calvana Stream

	Date/ station	1	2	3	4	5	6	7	8	9	10
Ca	Winter	0,11	0,19	0,38	0,58	0,12	0,50	0,73	1,62	0,97	1,00
	Spring	0,47	0,25	0,26	0,43	0,34	0,77	0,86	1,68	1,38	1,00
	Summer	0,06	0,14	0,15	0,26	0,54	0,89	0,89	0,88	0,62	1,00
	Autumn	0,47	0,25	0,26	0,43	0,34	0,77	0,86	1,68	1,38	1,00
Cd	Winter	--	--	--	--	--	--	--	--	--	--
	Spring	--	--	--	--	--	--	--	--	--	--
	Summer	0,32	0,97	1,02	0,93	1,00	0,84	0,85	0,83	0,89	1,00
	Autumn	--	--	--	--	--	--	--	--	--	--

Color becomes darker towards higher values for every single metal.
Table 4.5.2. is continued on the next page.

Cr	Winter	1,75	1,56	3,64	0,97	0,62	1,02	0,95	1,31	1,01	1,00
	Spring	0,90	1,43	1,31	0,56	0,38	0,99	0,86	1,05	0,74	1,00
	Summer	--	--	--	--	--	--	--	--	--	--
	Autumn	--	--	--	--	--	--	--	--	--	--
Co	Winter	1,11	0,90	1,40	1,31	1,09	1,28	1,17	1,70	0,74	1,00
	Spring	0,60	0,63	0,72	0,75	0,85	0,83	0,84	1,27	0,46	1,00
	Summer	2,63	1,20	1,25	1,35	2,45	1,00	1,76	3,34	0,95	1,00
	Autumn	1,01	1,05	1,22	1,56	1,43	2,18	1,28	2,34	1,30	1,00
Cu	Winter	0,41	0,54	1,52	0,59	0,51	1,19	1,40	1,16	0,83	1,00
	Spring	0,37	0,66	0,42	0,68	0,76	1,07	1,56	0,57	0,46	1,00
	Summer	--	--	--	--	--	--	--	--	--	--
	Autumn	--	--	--	--	--	--	--	--	--	--
Fe	Winter	0,97	0,96	1,00	0,97	1,02	0,99	1,06	0,97	1,02	1,00
	Spring	0,90	0,90	0,88	0,87	0,80	0,98	0,92	0,90	0,89	1,00
	Summer	1,02	0,97	1,06	1,01	1,01	1,02	1,01	1,00	1,03	1,00
	Autumn	0,90	0,90	0,88	0,88	0,80	0,98	0,92	0,91	0,89	1,00
Mn	Winter	6,42	0,48	0,29	0,75	0,08	0,83	1,74	2,39	0,47	1,00
	Spring	1,29	1,25	0,59	2,46	1,61	0,66	1,90	2,01	1,08	1,00
	Summer	0,93	0,03	0,84	1,18	1,74	2,67	1,95	5,34	0,68	1,00
	Autumn	1,29	1,25	0,59	2,46	1,61	0,66	1,90	2,01	1,08	1,00
Mo	Winter	--	--	--	--	--	--	--	--	--	--
	Spring	--	--	--	--	--	--	--	--	--	--
	Summer	--	--	--	--	--	--	--	--	--	--
	Autumn	--	--	--	--	--	--	--	--	--	--
Ni	Winter	1,95	1,15	1,49	1,61	1,27	1,06	1,02	0,98	0,97	1,00
	Spring	0,82	0,89	0,88	0,86	0,86	1,30	0,94	0,70	0,62	1,00
	Summer	1,87	0,89	0,98	0,82	1,33	0,95	1,07	1,18	0,95	1,00
	Autumn	0,79	0,89	0,91	0,97	0,88	1,48	0,77	0,83	1,07	1,00
Pb	Winter	1,42	1,14	1,46	1,86	1,89	2,33	1,91	2,64	0,83	1,00
	Spring	0,69	1,05	0,91	0,91	1,45	1,52	2,04	1,91	0,46	1,00
	Summer	2,01	1,36	5,15	1,58	2,19	2,36	2,20	4,70	1,09	1,00
	Autumn	0,83	1,39	0,80	1,45	1,32	3,40	1,56	3,18	1,14	1,00
Sb	Winter	--	--	--	--	--	--	--	--	--	--
	Spring	--	--	--	--	--	--	--	--	--	--
	Summer	--	--	--	--	--	--	--	--	--	--
	Autumn	--	--	--	--	--	--	--	--	--	--
Se	Winter	0,68	0,87	0,92	0,86	0,54	0,92	0,71	0,73	0,92	1,00
	Spring	0,43	0,43	0,40	0,25	0,64	0,74	0,50	0,27	0,49	1,00
	Summer	1,62	1,01	0,60	0,53	--	0,91	0,89	0,60	0,56	1,00
	Autumn	0,57	0,69	0,52	0,29	0,58	0,67	0,72	0,58	1,05	1,00

Color becomes darker towards higher values for every single metal.
Table 4.5.2. is continued on the next page.

Sr	Winter	0,12	0,16	0,55	0,53	0,15	0,61	0,95	1,35	1,48	1,00
	Spring	0,13	0,16	0,16	0,36	0,49	0,60	0,85	1,24	1,49	1,00
	Summer	0,08	0,09	0,12	0,24	0,58	0,59	1,01	0,85	0,81	1,00
	Autumn	0,06	0,16	0,08	0,31	0,41	0,53	0,70	1,03	0,80	1,00
V	Winter	0,93	0,87	0,90	0,89	1,13	0,96	0,88	0,72	0,88	1,00
	Spring	0,58	0,64	0,59	0,64	0,67	0,84	0,73	0,60	0,55	1,00
	Summer	1,15	0,85	0,89	0,71	0,91	0,91	0,84	0,77	0,90	1,00
	Autumn	1,04	1,36	1,04	0,74	0,92	0,65	1,00	0,83	1,45	1,00
Zn	Winter	--	--	--	--	--	--	--	--	--	--
	Spring	--	--	--	--	--	--	--	--	--	--
	Summer	--	1,31	0,12	3,79	18,88	1,25	18,19	0,74	2,80	1,00
	Autumn	--	--	--	--	--	--	--	--	--	--
Color becomes darker towards higher values for every single metal.											

4.6. PRINCIPAL COMPONENT ANALYSIS

Principal Component Analysis displays graphic correlation between cases and variables described with certain factors. Also, it calculates the amount of the described data and shows it as a percentage with factors. Cases indicate different seasons (symbols WI,SP, SU, AU) and stations (symbols 1-10). Variables indicate analysed metals. Using positions of data in graph, it is possible to find a connection between certain data, link certain groups of cases and variables and finally draw conclusions.

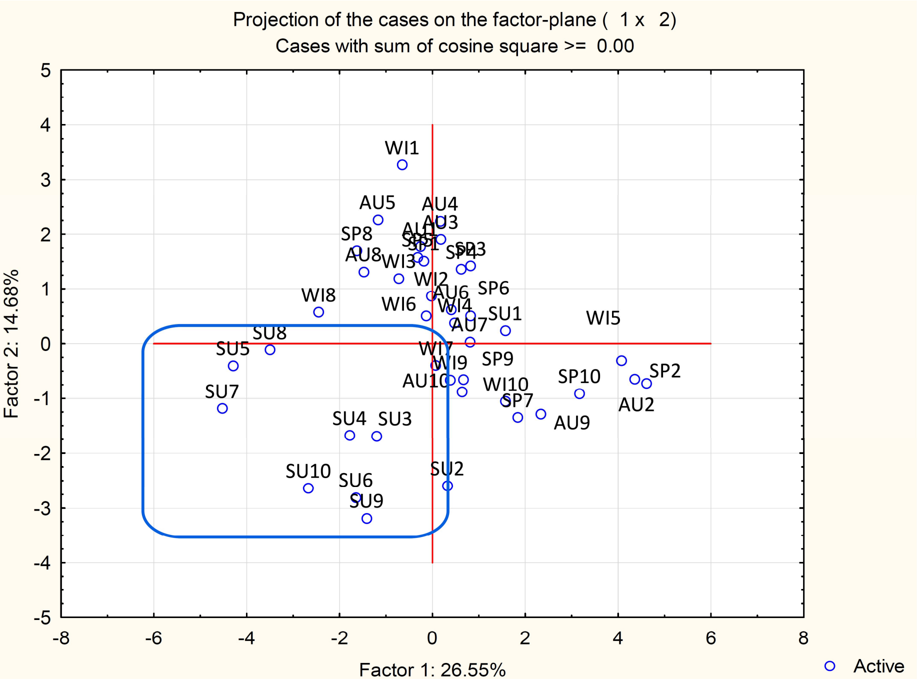


Fig. 4.6.1. Principal Component Analysis projection of the cases for factors 1x2

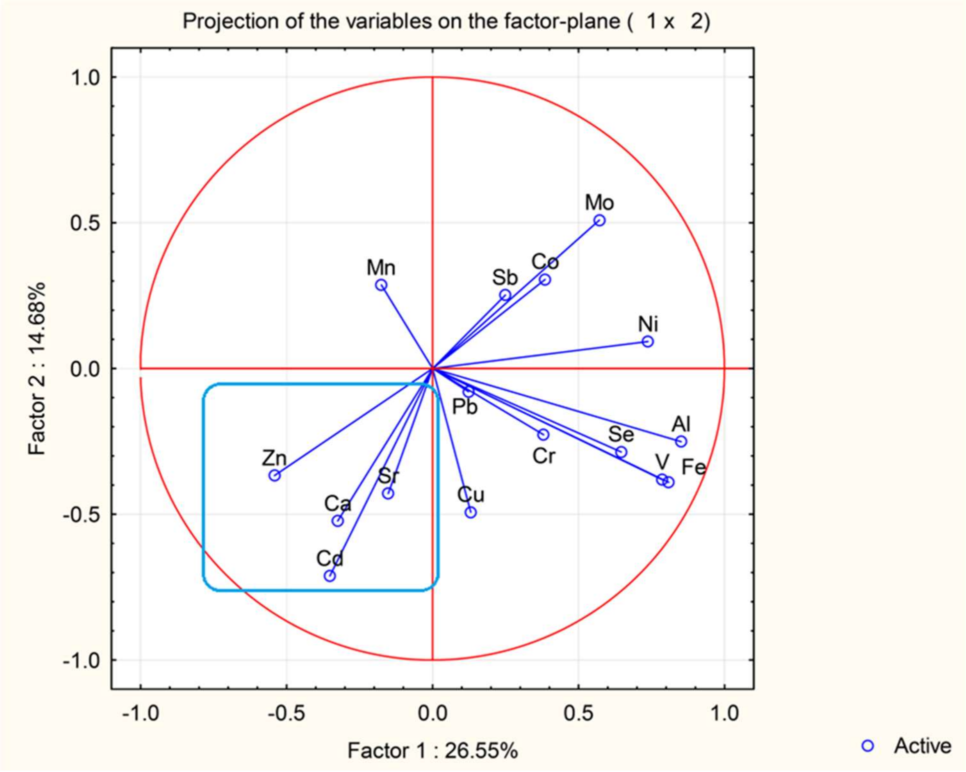


Fig. 4.6.2. Principal Component Analysis projection of the variables for factors 1x2

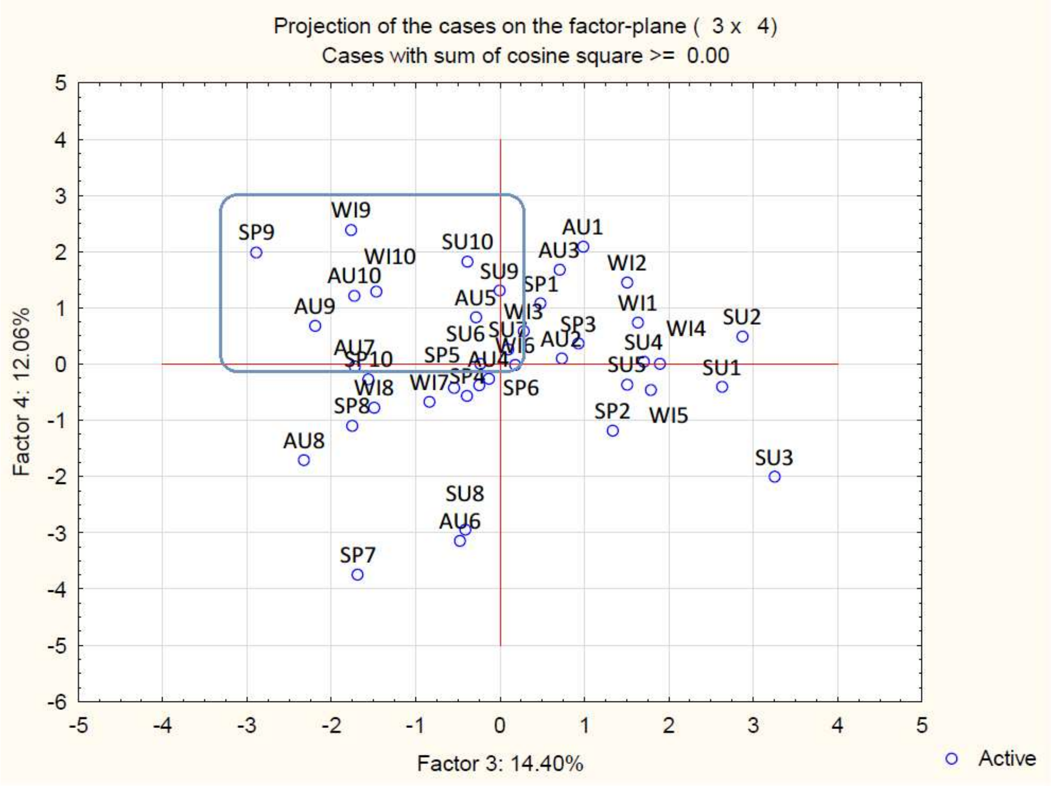


Fig 4.6.3. Principal Component Analysis projection of the cases for factors 3x4

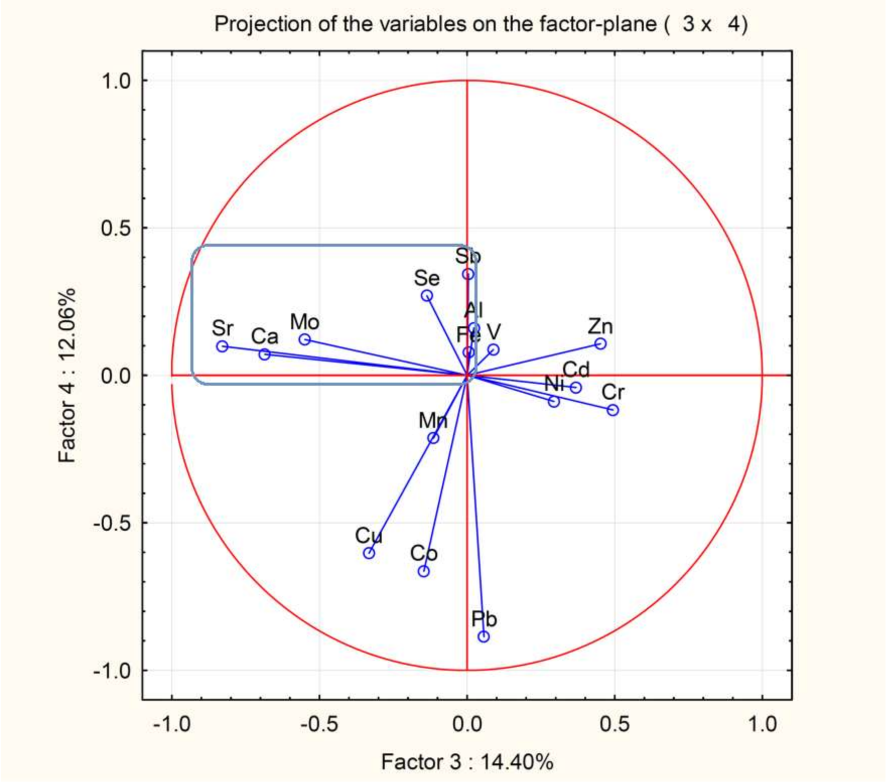


Fig. 4.6.4. Principal Component Analysis projection of the variables for factors 3x4

4.7. BASELINE

4.7.1. Calcium

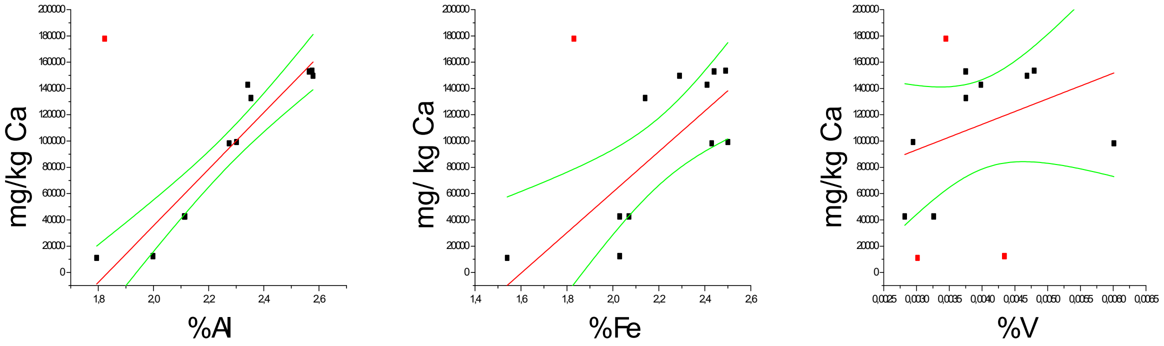
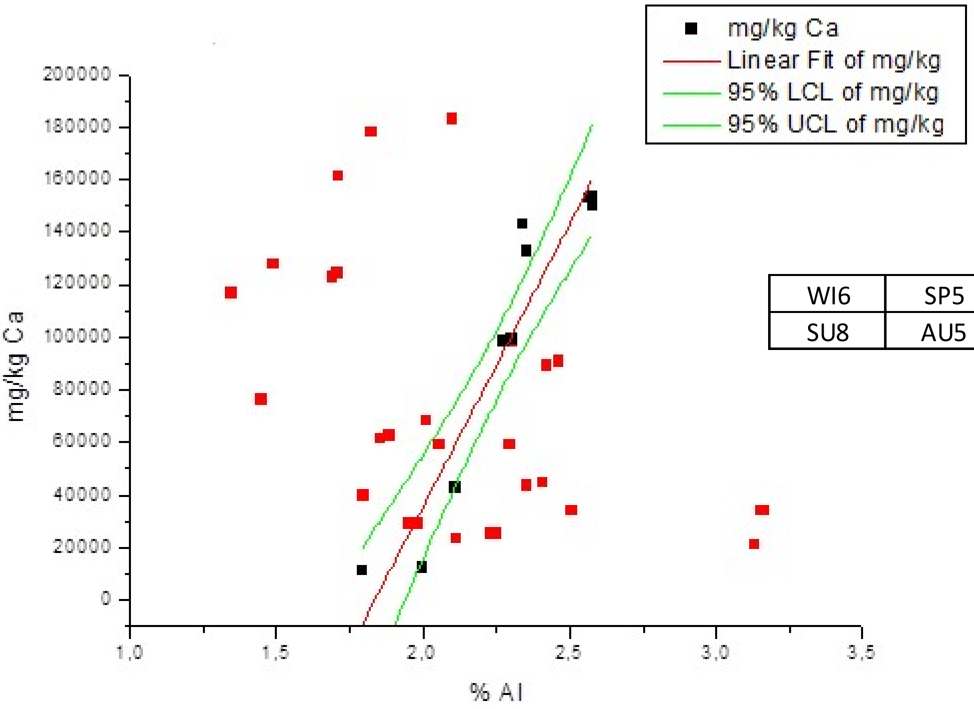


Fig. 4.7.1.1. Normalization of Calcium on the reference elements



WI6	SP5	SU3
SU8	AU5	AU7

“LCL“, lower control limit

“UCL“, upper control limit

“WI,SP, SU, AU”, different seasons (winter, spring, summer, autumn)

“1-10”, number of certain station

Fig. 4.7.1.2. Normalization of Calcium on the Aluminium with data of all stations

4.7.2. Cadmium

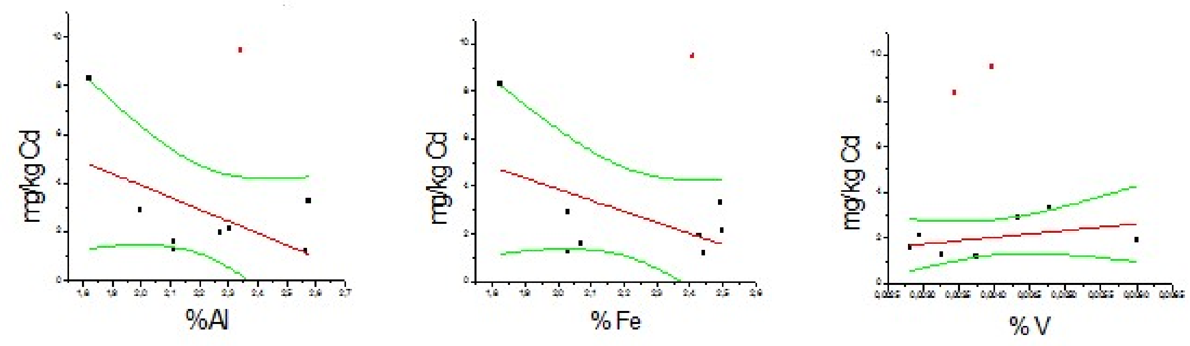
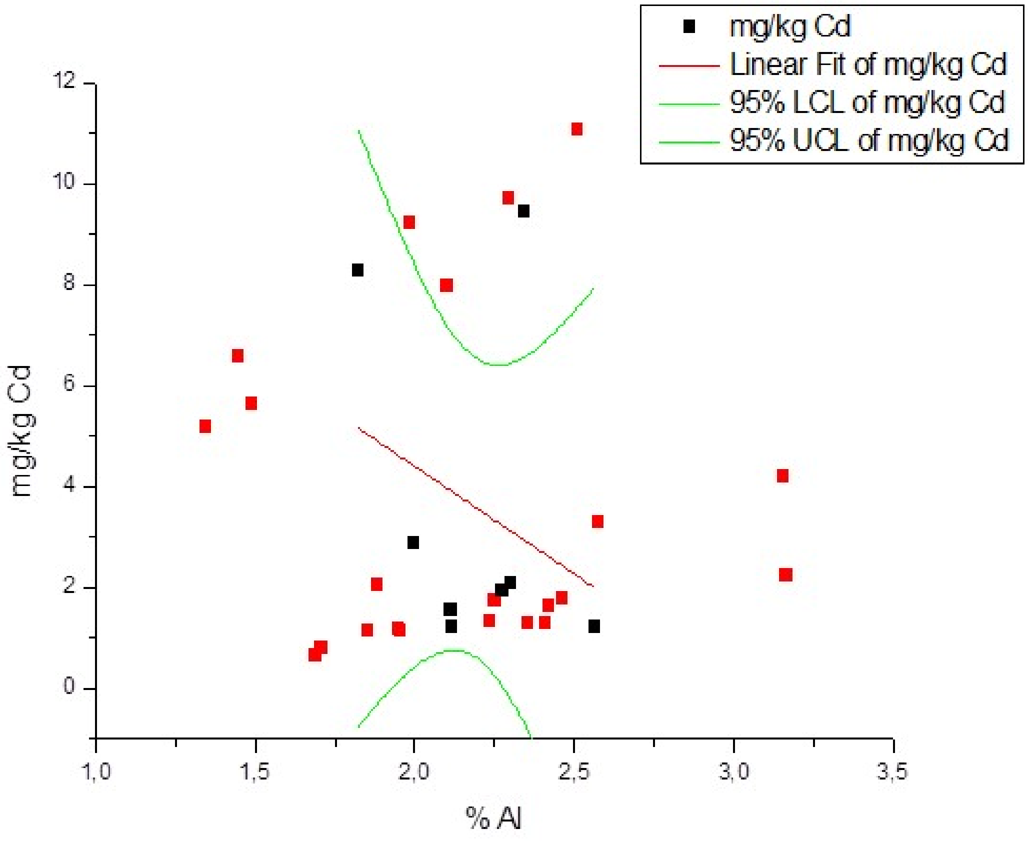


Fig. 4.7.2.1. Normalization of Cadmium on the reference elements



“LCL“, lower control limit

“UCL“, upper control limit

“WI,SP, SU, AU”, different seasons (winter, spring, summer, autumn)

“1-10”, number of certain station

Fig. 4.7.2.2. Normalization of Cadmium on the Aluminium with data of all stations

4.7.3. Cobalt

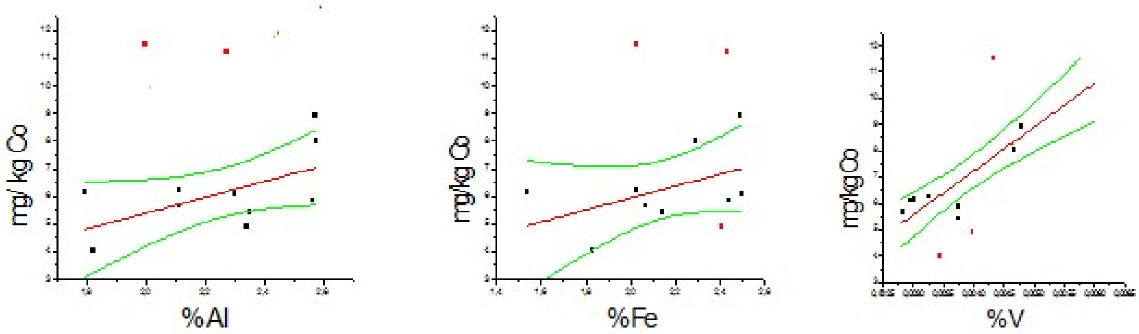
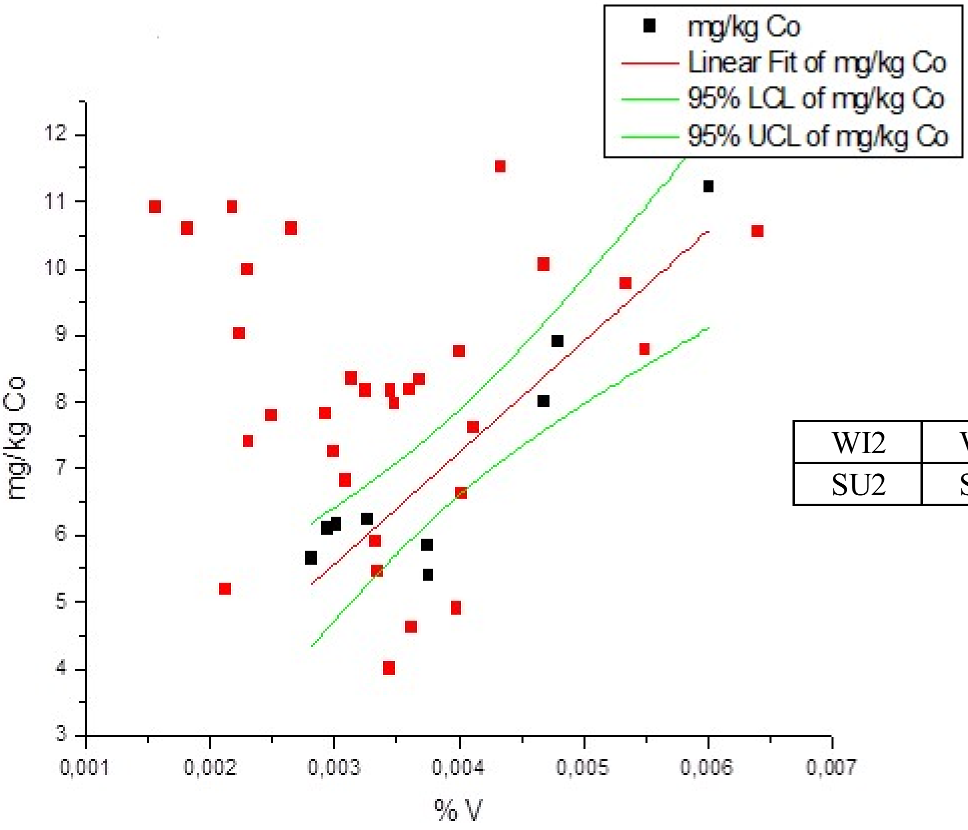


Fig. 4.7.3.1. Normalization of Cobalt on the reference elements



WI2	WI5	SP2
SU2	SU3	AU2

“LCL“, lower control limit

“UCL“, upper control limit

“WI,SP, SU, AU”, different seasons (winter, spring, summer, autumn)

“1-10”, number of certain station

Fig. 4.7.3.2. Normalization of Cobalt on the Vanadium with data of all stations

4.7.4. Chromium

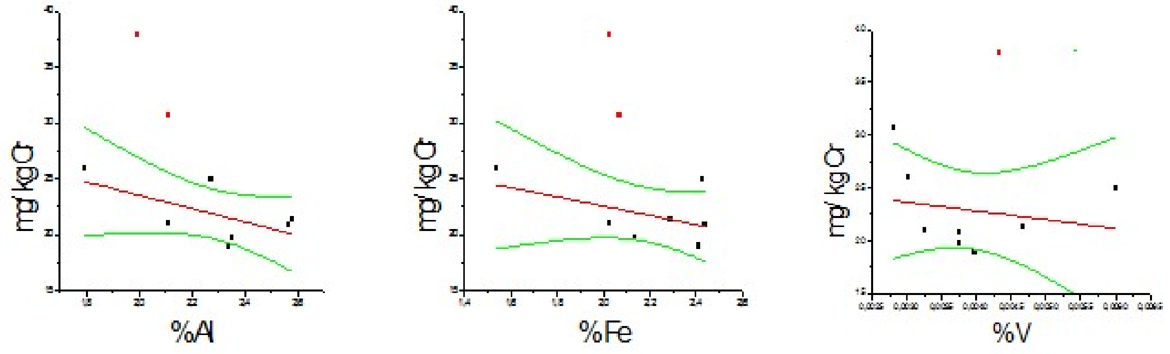
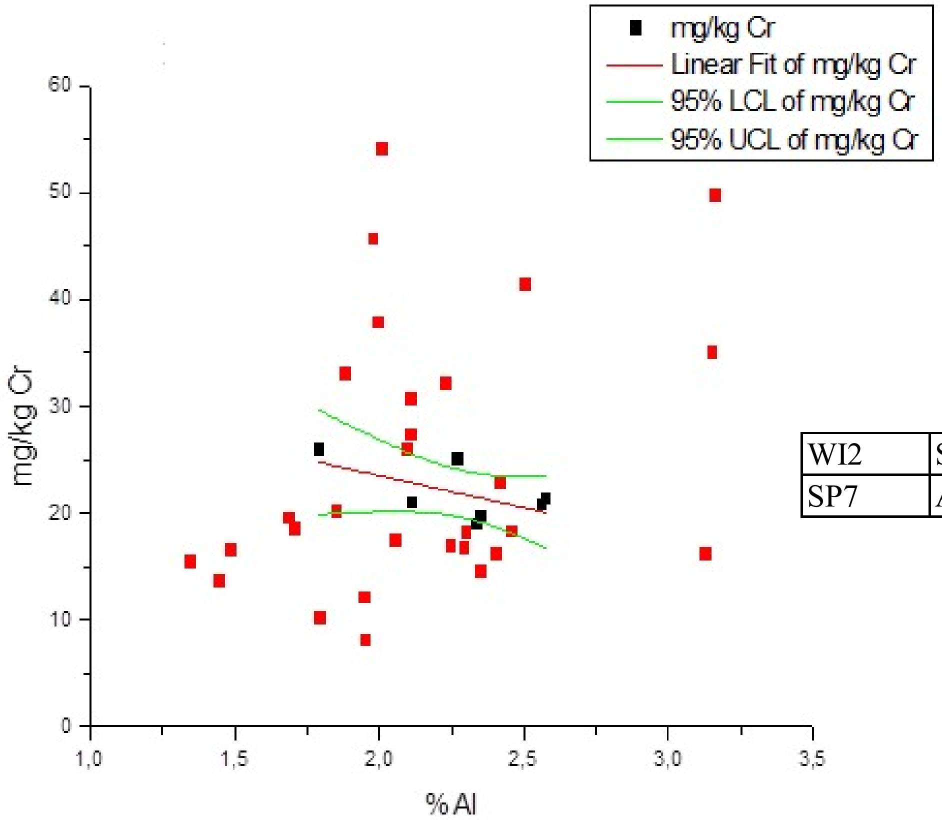


Fig. 4.7.4.1. Normalization of Chromium on the reference elements



WI2	SP6	SU6
SP7	AU7	

“LCL“, lower control limit

“UCL“, upper control limit

“WI,SP, SU, AU”, different seasons (winter, spring, summer, autumn)

“1-10”, number of certain station

Fig. 4.7.4.2. Normalization of Chromium on the Aluminium with data of all stations

4.7.5. Copper

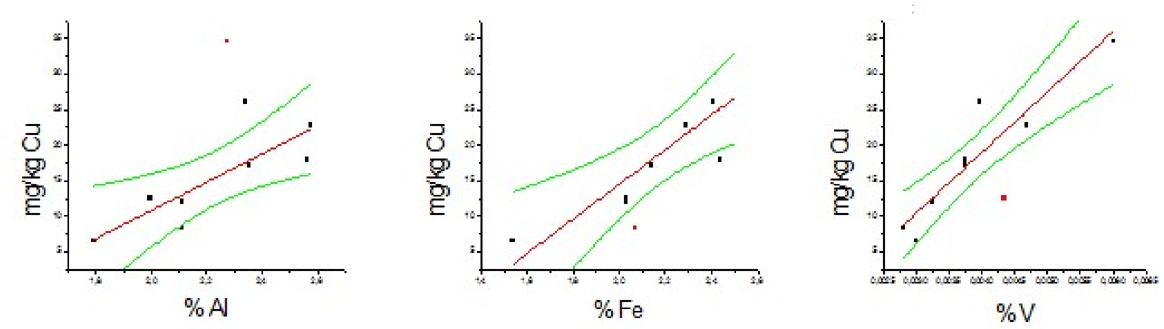
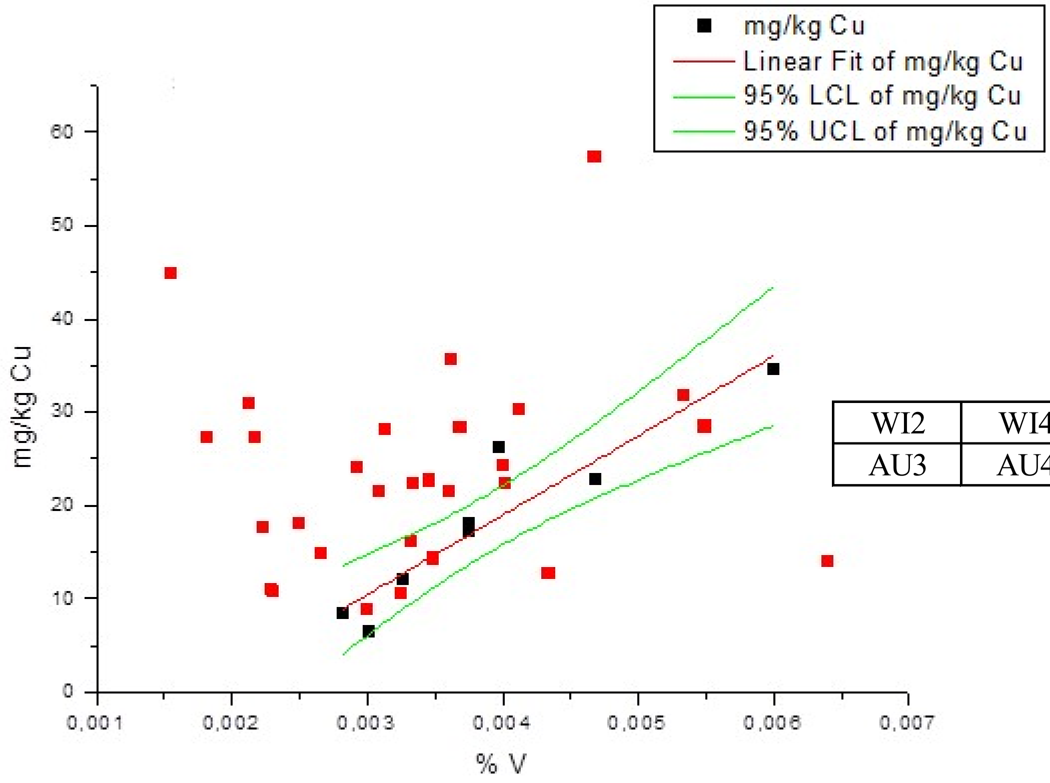


Fig. 4.7.5.1. Normalization of Copper on the reference elements



WI2	WI4	SP3
AU3	AU4	AU8

“LCL“, lower control limit

“UCL“, upper control limit

“WI,SP, SU, AU”, different seasons (winter, spring, summer, autumn)

“1-10”, number of certain station

Fig. 4.7.5.2. Normalization of Copper on the Vanadium with data of all stations

4.7.6. Manganese

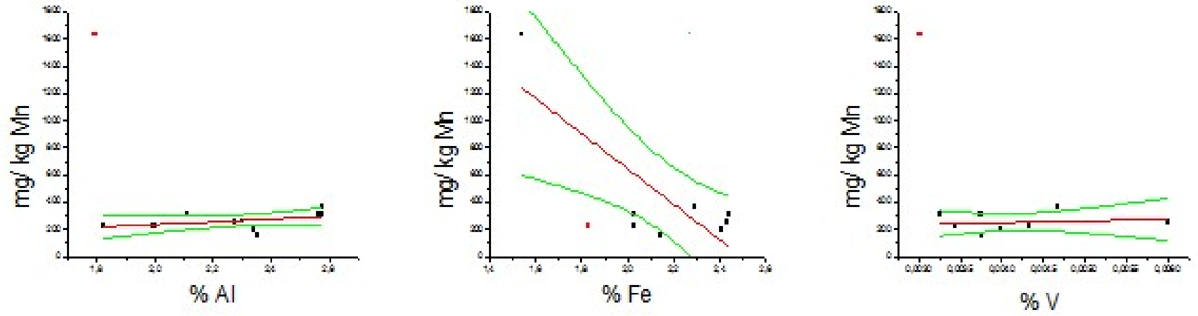
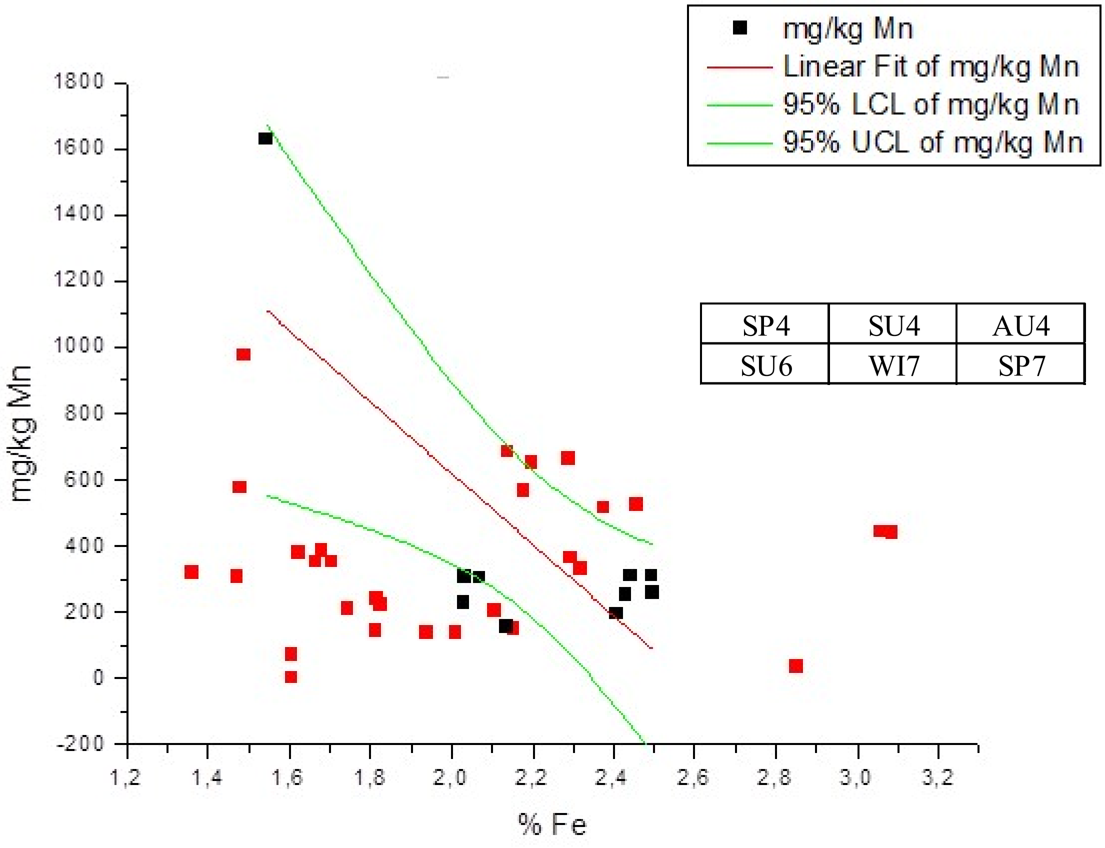


Fig. 4.7.6.1. Normalization of Manganese on the reference elements



SP4	SU4	AU4
SU6	WI7	SP7

“LCL“, lower control limit

“UCL“, upper control limit

“WI,SP, SU, AU”, different seasons (winter, spring, summer, autumn)

“1-10”, number of certain station

Fig. 4.7.6.2. Normalization of Manganese on Iron with data of all stations

4.7.7. Nickel

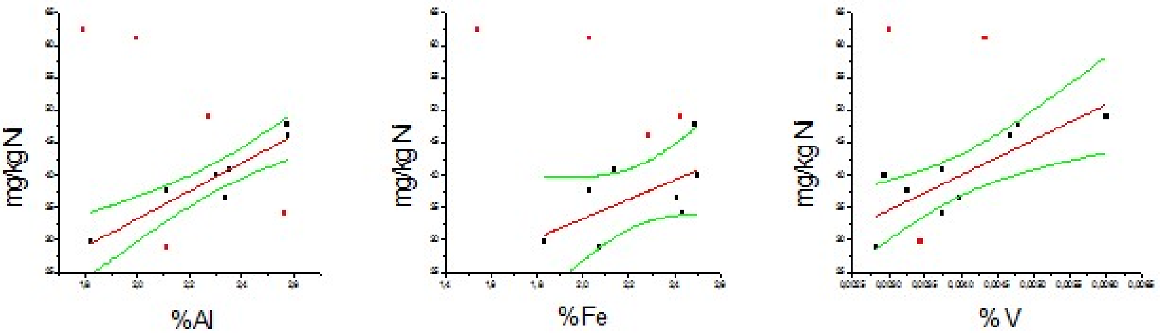
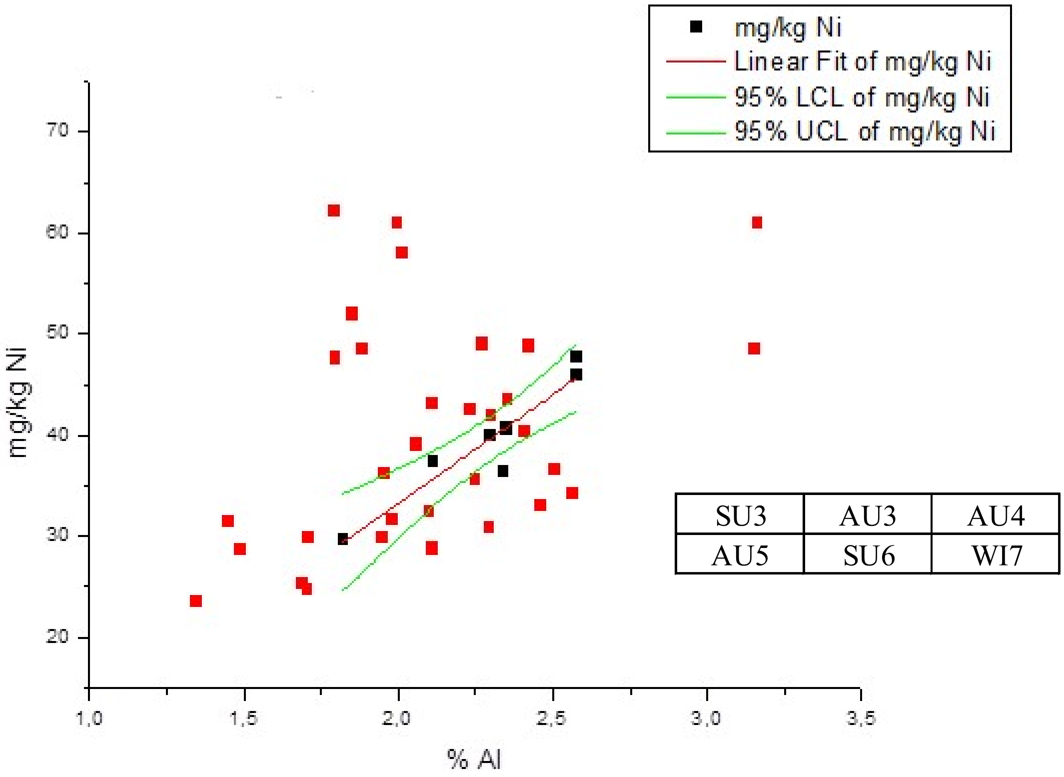


Fig. 4.7.7.1. Normalization of Nickel on the reference elements



SU3	AU3	AU4
AU5	SU6	WI7

“LCL“, lower control limit

“UCL“, upper control limit

“WI,SP, SU, AU”, different seasons (winter, spring, summer, autumn)

“1-10”, number of certain station

Fig. 4.7.7.2. Normalization of Nickel on Aluminium with data of all stations

4.7.8. Lead

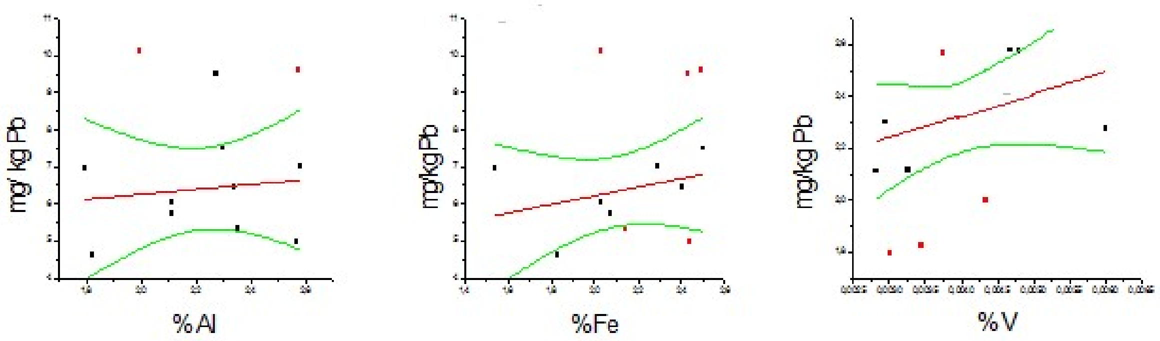
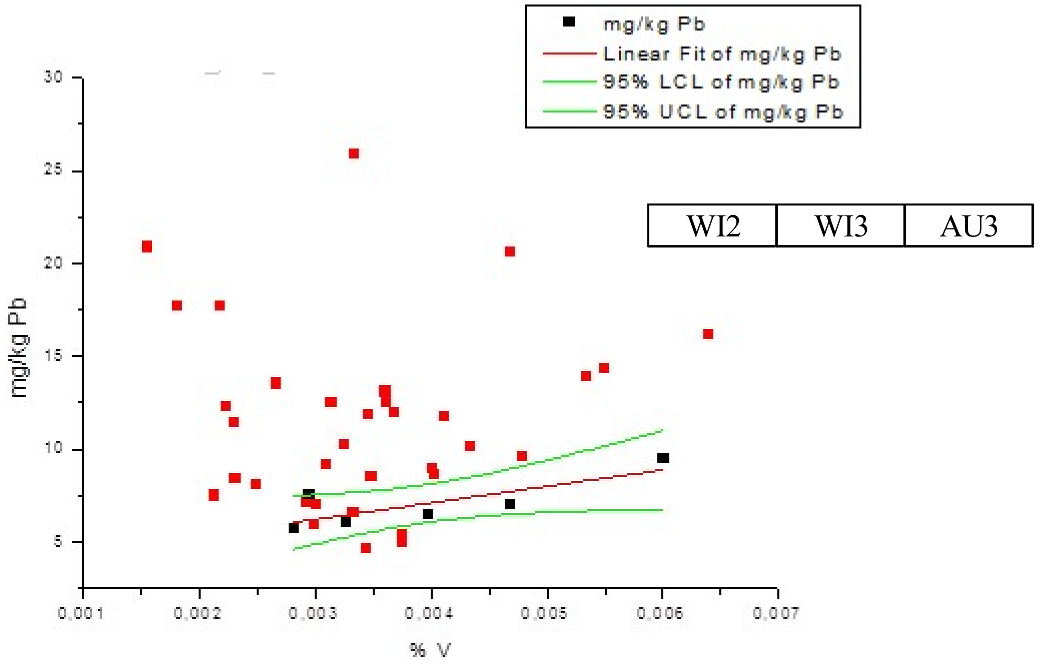


Fig. 4.7.8.1. Normalization of Lead on the reference elements



“LCL“, lower control limit

“UCL“, upper control limit

“WI,SP, SU, AU”, different seasons (winter, spring, summer, autumn)

“1-10”, number of certain station

Fig. 4.7.8.2. Normalization of Lead on Vanadium with data of all stations

4.7.9. Selenium

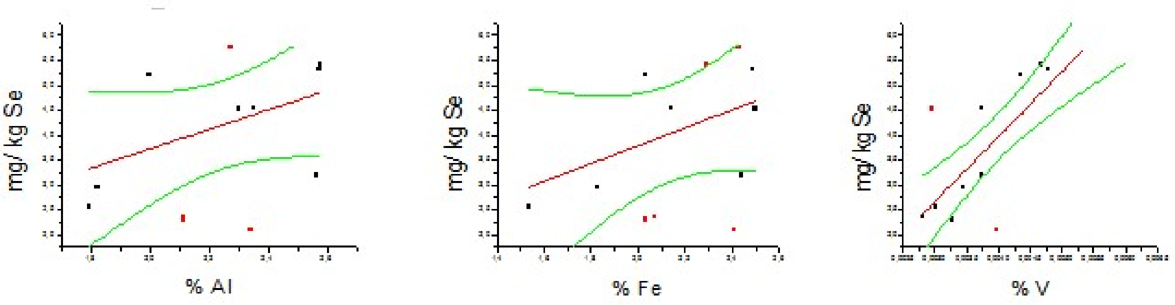
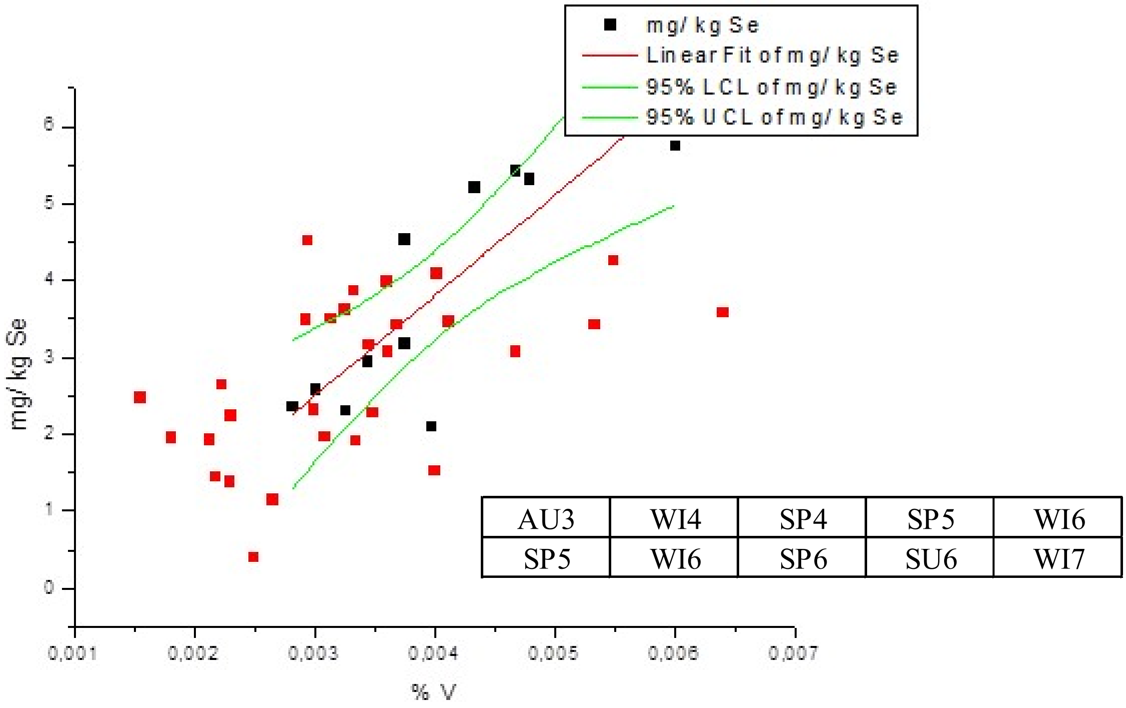


Fig. 4.7.9.1. Normalization of Selenium on the reference elements



AU3	WI4	SP4	SP5	WI6
SP5	WI6	SP6	SU6	WI7

"LCL", lower control limit

"UCL", upper control limit

"WI,SP, SU, AU", different seasons (winter, spring, summer, autumn)

"1-10", number of certain station

Fig. 4.7.9.2. Normalization of Selenium on Vanadium with data of all stations

4.7.10. Strontium

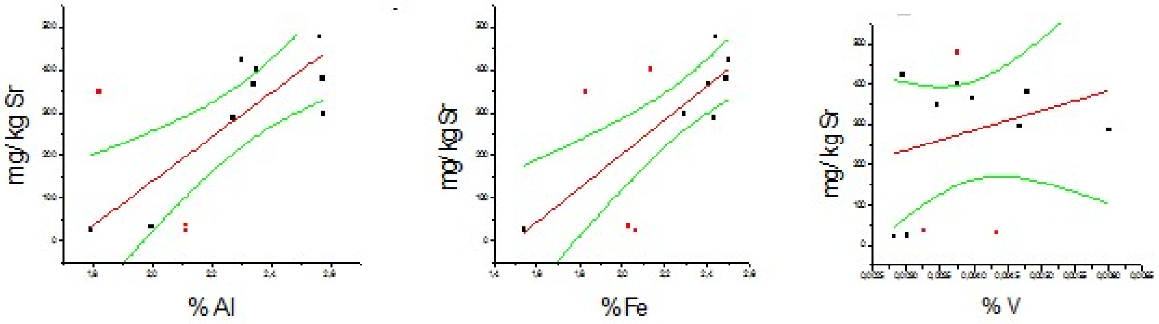
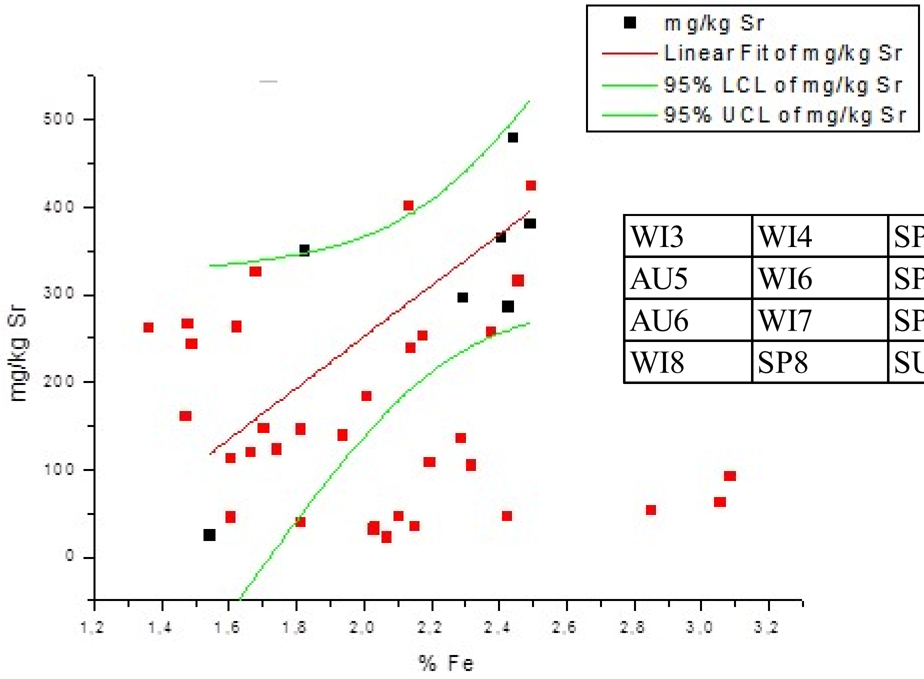


Fig. 4.7.10.1. Normalization of Strontium on the reference elements



WI3	WI4	SP5	SU5
AU5	WI6	SP6	SU6
AU6	WI7	SP7	AU7
WI8	SP8	SU8	AU8

“LCL“, lower control limit

“UCL“, upper control limit

“WI,SP, SU, AU”, different seasons (winter, spring, summer, autumn)

“1-10”, number of certain station

Fig. 4.7.10.2. Normalization of Selenium on Iron with data of all stations

4.7.11. Total baseline results

Table 4.7.11. Linear regression equations for various heavy metals on the reference elements and the corresponding calculated baseline concentrations (mg/kg) in the sediments of the Nestore River basin

Element	Formula	R^2	Baselines			
			MIN	MAX	Range	Average
Ca	$c(Ca)=215341{,}42503\cdot c(Al)-395188{,}46297$	0,8894	$3{,}51\cdot 10^{4}$	$1{,}60\cdot 10^{5}$	$1{,}25\cdot 10^{5}$	$1{,}04\cdot 10^{5}$
Cd	$c(Cd)= -4{,}91356\cdot c(Al)+13{,}72322$	0,1908	1,07	4,77	3,69	2,81
Co	$c(Co)=1669{,}98868V\cdot c(V)+0{,}55457$	0,8282	0,55	10,59	10,04	6,61
Cr	$c(Cr)=-5{,}97124\cdot c(Al)+35{,}45075$	0,2558	20,05	24,74	4,69	21,78
Cu	$c(Cu)=8533{,}02348\cdot c(V)-15{,}19771$	0,8519	8,87	36,09	27,22	18,16
Mn	$c(Mn)=-1073{,}79902\cdot c(Fe)+2766{,}61223$	0,5124	82,11	$1{,}11\cdot 10^{3}$	$1{,}03\cdot 10^{5}$	395,66
Ni	$c(Ni)=21{,}52232\cdot c(Al)-9{,}78852$	0,8608	608,76	$1{,}02\cdot 10^{5}$	408,28	814,65
Pb	$c(Pb)=893{,}91827\cdot c(V)+3{,}51509$	0,5608	6,04	8,89	2,85	7,05
Se	$c(Se)=1303{,}85985\cdot c(V)-1{,}24411$	0,7893	2,43	6,59	4,16	3,95
Sr	$c(Sr)=398{,}46341\cdot c(Fe)-594{,}51727$	0,8224	19,12	401,64	382,52	321,95

Table 4.7.11.2. Values taken for normalization and Q-test values

% Al	mg/kg Ca	Q	% Al	mg/kg Cd	Q	% V	mg/kg Co	Q
1,794	$1{,}11\cdot 10^{4}$		2,114	1,237		$3{,}02\cdot 10^{-3}$	6,16	
2,114	$4{,}26\cdot 10^{4}$		1,998	2,873		$3{,}26\cdot 10^{-3}$	6,24	
1,998	$1{,}24\cdot 10^{4}$		2,112	1,568		$4{,}34\cdot 10^{-3}$	11,52	0,053
2,112	$4{,}26\cdot 10^{4}$		2,565	1,205		$2{,}82\cdot 10^{-3}$	5,65	
2,353	$1{,}33\cdot 10^{5}$		2,342	9,445	0,163	$3{,}75\cdot 10^{-3}$	5,4	
2,565	$1{,}53\cdot 10^{5}$		2,575	3,29		$3{,}75\cdot 10^{-3}$	5,85	
2,342	$1{,}43\cdot 10^{5}$		2,274	1,935		$3{,}98\cdot 10^{-3}$	4,9	0,086
2,575	$1{,}54\cdot 10^{5}$		1,823	8,292		$4{,}79\cdot 10^{-3}$	8,9	
2,579	$1{,}50\cdot 10^{5}$		2,301	2,104		$4{,}68\cdot 10^{-3}$	8	
2,274	$9{,}82\cdot 10^{5}$					$6{,}01\cdot 10^{-3}$	11,21	
1,823	$1{,}78\cdot 10^{5}$	0,172				$3{,}45\cdot 10^{-3}$	4	0,241
2,301	$9{,}94\cdot 10^{4}$					$2{,}95\cdot 10^{-3}$	6,1	

“Q“, Q-test values
Table 4.7.12.2. is continued on the next page.

% Al	mg/ kg Cr	Q	% V	mg/kg Cu	Q	%Fe	mg/ kg Mn	Q
1,794	25,89		$3{,}02\cdot10^{-3}$	6,5		1,54	1628,35	
2,114	20,95		$3{,}26\cdot10^{-3}$	12,03		2,03	306,01	
1,998	37,81	1,715	$4{,}34\cdot10^{-3}$	12,62	0,021	2,03	227,62	
2,112	30,66	0,446	$2{,}82\cdot10^{-3}$	8,34		2,07	305,74	
2,353	19,68		$3{,}75\cdot10^{-3}$	17,2		2,14	157,46	
2,565	20,75		$3{,}75\cdot10^{-3}$	17,95		2,44	310,2	
2,342	18,94		$3{,}98\cdot10^{-3}$	26,13		2,41	196,25	
2,579	21,3		$4{,}68\cdot10^{-3}$	22,66		2,49	311,4	
2,274	24,98		$6{,}01\cdot10^{-3}$	34,54		2,29	364,62	0,037
						2,43	255,29	
						1,83	223,17	0,003
						2,5	258,32	

%Al	mg/kg Ni	Q	% V	mg/kg Pb	Q	% V	mg/ kg Se	Q
1,794	62,21	0,903	$3{,}02\cdot10^{-3}$	6,957	0,129	$3{,}02\cdot10^{-3}$	2,57	
2,114	37,44		$3{,}26\cdot10^{-3}$	6,061		$3{,}26\cdot10^{-3}$	2,3	
1,998	61,02	0,903	$4{,}34\cdot10^{-3}$	10,132	0,166	$4{,}34\cdot10^{-3}$	5,21	
2,112	28,74		$2{,}82\cdot10^{-3}$	5,73		$2{,}82\cdot10^{-3}$	2,35	
2,353	40,65		$3{,}75\cdot10^{-3}$	5,328	0,106	$3{,}75\cdot10^{-3}$	4,54	
2,565	34,16	0,247	$3{,}75\cdot10^{-3}$	4,974	0,2	$3{,}75\cdot10^{-3}$	3,18	
2,342	36,37		$3{,}98\cdot10^{-3}$	6,471		$3{,}98\cdot10^{-3}$	2,1	0,058
2,575	47,71		$4{,}79\cdot10^{-3}$	9,604	0,026	$4{,}79\cdot10^{-3}$	5,31	
2,579	45,95		$4{,}68\cdot10^{-3}$	7,019		$4{,}68\cdot10^{-3}$	5,41	
2,274	48,96	0,069	$6{,}01\cdot10^{-3}$	9,505		$6{,}01\cdot10^{-3}$	5,75	
1,823	29,71		$3{,}45\cdot10^{-3}$	4,609	0,297	$3{,}45\cdot10^{-3}$	2,94	
2,301	39,88		$2{,}95\cdot10^{-3}$	7,498		$2{,}95\cdot10^{-3}$	4,52	0,006

% Fe	mg/ kg Sr	Q
1,54	24,23	
2,03	35,11	0,024
2,03	31,28	0,015
2,07	22,23	0,004
2,14	401,25	0,046
2,44	479,12	
2,41	364,66	
2,49	380,28	
2,29	296,4	
2,43	285,33	
1,83	349,62	0,033
2,5	423,62	

“Q“, Q-test values

5. DISCUSSION

5.1. TOTAL RESULTS

Chemical and physico- chemical parameters of the surface water may be significant factors associated with pollution. Measured values are shown in Table 4.1.1. and colored fileds mark values above average. Temperature influences on biological activity. Every aquatic species has a preferred temperature range. Also, the rate of chemical reactions generally increases at higher temperature. In case of the Nestore River basin, temperature changes are following seasonal changes. Furthermore, the biggest values of temperatures were measured in August on stations 2, 3 and 4 (the Nestore River). With higher temperatures water can dissolve more minerals from the rocks and have a higher electrical conductivity. Moreover, conductivity values in observed stations are the highest in October, when temperature values are above average. Also, a sudden increase or decrease in conductivity in a body of water can indicate pollution. Agricultural run-off, in addition to being high in nutrients, often has a higher concentration of dissolved solids that can influence conductivity. pH rates can affect the solubility and toxicity of chemicals and heavy metals in the water, but in this case are generally constant, mostly alkaline. Dissolved oxygen concentrations are constantly affected by diffusion and aeration, photosynthesis, respiration and decomposition. In freshwater systems such as rivers and streams, dissolved oxygen concentrations vary by season and location, as it is the case with the Nestore River basin. Concentrations of the Chemical Oxygen Demand in measured area are low in comparison to polluted water systems.

Table 4.1.2. contains concentrations of all analized metals in every station and season. Colored fields indicate values above average for every single metal. In cases of Cadmium, Molybdenum, Antimony and Zinc some or all measured concentrations are under the limit of detection.

5.2. CONCENTRATIONS OF METALS IN BLANK SAMPLES

Concentrations of metals in blank samples were subtracted from measured concentrations of metals in sediments samples with *ICP- AES* instrument. In order to make a blank sample, only a mixture between nitric acid and a solution of hydrogen peroxide was digested. During the preparation of the samples, there were used two different types of ultrapure nitric acid. The big values of standard deviations and relative standard deviations shown in Table 4.2.1. suggest that there was a difference in a composition of Carlo Erba and Suprapur® nitric acid for trace analysis. They influence the amounts of further concentration by reducing the accuracy of the next calculations to a small extent.

5.3. CONCENTRATIONS OF YTTRIUM

Concentrations, intensities and intensity factors of Yttrium in diluted solutions are presented in Table 4.3.1. Measured concentrations and intensities values of Yttrium with *ICP-AES* instrument of all diluted samples are mainly similar. Small changes in values are attributable to human error while adding Yttrium external standard. Moreover, calculated intensity factors show minimal deviations, which is notable in value of relative standard deviation of 0,029. Therefore, measurements made for this thesis are consistent and reliable.

5.4. AVERAGE VALUES OF METALS IN SEDIMENTS

Table 4.4.1. demonstrates average values of metals in sediments in The Nestore River basin. High standard deviations and relative standard deviations suggest that composition of sediments varies a lot seasonally and spatially. Aluminuim and Iron contents, metals which are found in biggest quantity, display the lowest change. In order to compare content of sediments, the data of contaminated part of Drava river, Croatia was taken and presented in Table 4.4.2. One the one hand, Copper values are four times and Lead values are three times bigger in Drava river. On the other hand, Cadmium values are ten times bigger in Nestore river which may be an indicator of exessive usage of phosphate fertilizers, presence in the sewage sludge and different industrial uses. However, other values take place in the same order of magnitude.

5.4.1. Average seasonal amounts of metals in sediments

In Table 4.4.3. are presented average seasonal amounts of metals in sediments with belonging standard deviations and relative standard deviations. Maximum values of concentration, standard deviations and relative standard deviations are marked in colored fields. Along with the table, Fig. 4.4.1 illustrates metals seasonal variations on graphs. Watching Aluminium and Iron, two the most abundant metals in Earth’s crust, can be observed almost equal behavior. Their concentrations have the same order of magnitude with similar values of deviations. Both of them increase concentrations in Autumn– station 2 (the Nestore River) and Winter- station 5 (the Nestore River). Because of their spatial and seasonal stability, these two metals are later chosen as reference elements. Average seasonal concentrations of Molybdenum weren’t able to calculate due to small concentrations under the limit of detection. As similar to Molybdenum, most concentrations of Cadmium, Antimony and Zinc are lower than belonging limit of detection. For Cadmium and Zinc, it was possible to detect amount during the summer, when levels of water are decreased and generally concentrations of metals in sediment are higher. In the case of Antimony, values above the limit of detection are spotted in autumn. There is a general trend observed that Calcium and Strontium accumulate with the flow of the Nestore

River, in fact increase their concentration from station 1 to station 10. Concentrations of Cobalt, Copper, Manganese and Selenium are relatively stable during all seasons and tracing all locations with some exeptions. Cooper concentrations raise in the station 7 which could be the consequence of near purifiers. The high Manganese level in station 1 is prescripted to the experimental error and that is the reason why average Manganese values increase in winter season. Vanadium and Nickel concentrations were the highest during the winter in the station 5. It is located in Nestore River after entering the Genna, a contributary that catches waters from the Stone Bridge purifier and Olmeto purifier. Compared with other metals, with Lead and Chromium is notable growth in stations 2 and 3 due to the influence of the near glass factory.

5.4.2. Average station amounts of metals in sediments

In Table 4.4.4. are presented average station amounts of metals in sediments with belonging standard deviations and relative standard deviations. Furthermore, graphs for every analyzed metal and station are demonstrated in Fig. 4.4.2. Location review confirms average seasonal results. Generally, the station with the biggest average amounts of metals (Aluminuim, Cadmium, Chromium, Iron and Vanadium) is station 2, what is explainable with its vicinity to the plant of glass processing.

5.5. ENRICHMENT FACTOR

The calculation of an enrichment makes it possible to discriminate anthropogenic metals and gives a simple quantitative criterion for characterizing the sediment according to the degree of metal pollution and the results are visible in Table 4.5.1. and Table 4.5.2. The calculation of enrichment factors showed that Manganese, Lead and Zinc in summer had the highest enrichment factor values among the elements studied. According to the station 9, enrichment factor of Manganese reaches a value of 7,80 in the station 8 (when the station 1 does not count due to experimental error), Lead a value of 4,71 in station 3 and 4,30 in station 8 and Zinc a value of 6,75 and 6,51 in stations 5 and 7. When concentrations are compared with station 10, Manganese reaches a value of 5,34 in the station 8 and Lead a value of 5,15 in station 3 and 4,70 in station 8. In cases of Manganese, Lead and Zinc, enrichment is moderate and moderately severe. Chromium, Cobalt and Copper had minor enrichment, all at one different location. For Chromium it is station 3, for Cobalt station 8 and for Copper station 7. Calcium, Cadmium, Iron, Nickel, Selenium, Strontium and Vanadium had mostly minor enrichment, somewhere there was no enrichment. According to the calculated enrichment factor, the degree of pollution is highest during the summer as a result of lower water levels. Also, the degree of metal pollution is most visible in station 3 after the Nestore river passes near glass factory and in station 8 where stream Genna receives water from purifiers.

5.6. PRINCIPAL COMPONENT ANALYSIS

According to Principle Component Analysis results, heavy metals concentrations in sediment of 10 sample sites of 4 seasons could be grouped into a two two-component models, which accounted for 67% of all the data variation.

The first two factors accounted for about the 41% of the total variance, which presents a problem. The first factor (F1) explains about 27%, the second (F2) almost 15%. For factors 1 and 2, the PCA projection of cases for heavy metal contents is listed in Fig. 4.6.1. All summer data is grouped in the third quadrant. Other stations and seasons showed no significant correlation. According to the PCA projection of variables in Fig. 4.6.2., the reason for grouping summer data are quantities of Calcium, Cadmium, Strontium, and Zinc. Presence of Calcium, Cadmium and Strontium is caused by geogenic sources. Moreover, earlier is defined their no or minor enrichment. As for Zinc, its amount was possible to detect only during the summer season. Its enrichment is previously described as moderately severe. Therefore, Zinc originates from anthropogenic activities and presents a threat as a pollutant in the Nestore River basin.

The second two factors explained about the 27% of the total variance. The third factor (F3) describes about 14%, the fourth (F4) around 12%. For factors 3 and 4, the PCA projection of cases for heavy metal contents is listed in Fig. 4.6.3. It is visible that all data from stations 9 and 10 is located in second quadrant. Observing Fig. 4.6.4., where the PCA projection of cases is displayed, it is visible the correlation between stations mentioned and metals: Strontium, Calcium, Molybdenum, Selenium, Antimony, Aluminium and Vanadium. All of the listed metals are classified as metals with no or minor enrichment. Judging by the given result, it is confirmed conclusion from biological research that stations 9 and 10 are environmentally the purest ones and uncontaminated.

5.7. BASELINE

The baselines calculated using the normalization method were dependent on the reference elements selected. Objective of baseline calculations was to determine if elemental enrichment exists, as a matter of fact to determine concentrations of metals originating from natural geogenic sources or from anthropogenic activities. Figures 4.7.1.1.- 4.7.10.2. display linear regression with reference elements for uncontaminated stations 1, 9 and 10 together with the best data from all stations for the reference element with the highest value of Coefficient of determination. Also, in tables near the graphs are written names of data that enters the confidence interval. For Cadmium, reference elements used in this thesis were not applicable.

Stations entering the confidence interval are counted and locations with the highest number of times entering are stations 6 (Nestore River) and station 7 (Caina Stream). In other words, metals of these two stations originate from natural geogenic sources. Strontium is metal in which case the largest number of data inputs the confidence interval (16). This information confirms results obtained from Enrichment factor and Principal Component Analysis. The bigger part of data didn't enter confidence interval which means that metals origin is mostly from anthropogenic activities. For data that came out of confidence interval in linear regression Q-test was made. Values of Q-test are shown in table 4.7.12.2. along with linear regression values of the best reference element for every metal. All suspicious data is significantly abnormal at the 95% confidence level, exept for cases of Chromium where one pair of data (Q=1,715) and for Nickel where two pairs of data (Q=0,903) are not significantly abnormal at the 95% confidence level. From conducted regression analysis the equation that can be used to calculate concentration of certain metal in baseline range was obtained and presentedin Table 4.7.11.2. Besides that, minimum, maximum, range and average concentration in baseline range for every metal were determined.

6. CONCLUSIONS

Heavy metal pollution is an important problem for the Nestore River basin. They are considered as serious pollutants in river sediments and nowadays present problem because of their toxicity, bioaccumulation, persistence and the impact on the ecosystem and the human body. The Nestore River basin in Umbria region, Central Italy is chosen due to changes by pollution sources made by urbanization, industry, agriculture and extensive livestock production. The aim of this thesis was to study the regional impacts of heavy metals (Cadmium, Cobalt, Chromium, Copper, Iron, Molybdenum, Manganese, Lead, Antimony, Selenium, Vanadium and Zinc) and other metals (Aluminium, Calcium, Strontium) on pollution sources.

Calcuations of average metals concentrations suggest that composition of sediments varies a lot seasonally and spatially. Metals that exhibit moderate and moderately severe enrichment are Manganese, Lead and Zinc followed by Chromium, Cobalt and Copper that showed minor enrichment. Presence of Calcium, Cadmium and Strontium is caused by geogenic sources. Also, according to the Principal Component Analysis, all data from stations 9 (The Fersinone Stream) and 10 (The Calvana Stream) is grouped due to correlation between metals: Strontium, Calcium, Molybdenum, Selenium, Antimony, Aluminium and Vanadium. All of the listed metals are classified as metals with no or minor enrichment and these results confirm conclusion from biological research that stations 9 and 10 are environmentally the purest ones and uncontaminated.

The degree of pollution is highest during the summer as a result of lower water levels. Also, the degree of metal pollution is most visible in station 3 after the Nestore river passes near glass factory and in station 8 where stream Genna receives water from purifiers. Baseline concentrations give conclusion that metals from station 6 (Nestore River) and station 7 (Caina Stream) originate from natural geogenic sources. The bigger part of data (stations 2,3,4,5 – The Nestore River, station 8- The Genna Stream) didn’t enter confidence interval which means that metals origin is mostly from anthropogenic activities. This thesis suggested that point sources of heavy metals in freshwater sediments should be closely monitored.

7. LIST OF SYMBOLS

a - the slope of the line

b - the y-intercept/ the slope of the calibration curve

C_M - the baseline concentration of one of the analized metals (mg/kg)

C_N - the concentration of the reference element (mg/kg)

COD – chemical oxygen demand (mg $\cdot L^{-1}$)

c – concentration (mg/L, mg/kg)

DO – dissolved oxygen (mg $\cdot L^{-1}$)

EF – enrichment factor

ICP – AES – Inductively Coupled Plasma Atomic Emission Spectroscopy

ICP-OES - inductively coupled plasma optical emission spectroscopy

LCL – lower control limit (mg/kg)

LOD – limit of detection (mg/L, mg/kg)

m – mass (g)

PCA - Principal Component Analysis

Q – outlier values verified by Q-test

RSD – relative standard deviation

S_a - standard deviation of the response *b* is the slope of the calibration curve

SD – standard deviation

ST –station

t- temperature

UCL – upper control limit

x – dependent variable

y- independent variable

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9. BIOGRAPHY

Bernarda Damianić was born on 5th December 1992 in Pula, Croatia, where she finished Elementary school „Veruda“in 2007. The same year she enrolled in high school „Gimnazija Pula“and finished it in 2011 with an excellent success. In September of 2011, she started to attend Faculty of Chemical Engineering and Technology, University of Zagreb, course chemical engineering. She graduated in September of 2014.with the bachelor thesis titled: „Technologies of energy efficient windows“. For the Master degree she chose Chemical engineering in the Environmental protection. During the Master Degree she participated in making of Chemical engineering laboratory with title: „ The use of fatty acids in the protection of corrosion“and was a student assistant (demonstrator) in Electrochemistry laboratory. For the last semester, she got a scholarship for the Erasmus+ program and went to Perugia, Italy where she performed the experimental part of her Master thesis.